FABRICATION AND ASSEMBLY OF ONE-DIMENSIONAL SEMICONDUCTOR NANOSTRUCTURES AND THEIR APPLICATION TO MULTI-FUNCTIONAL DEVICES

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ABSTRACT

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One-dimensional (1D) semiconducting nanostructures have been extensively studied in the past few decades due to their excellent electrical, chemical and optical properties, which enable remarkable performance in various applications such as electronic/optoelectronic devices, chemical/biological sensors and energy harvesting. Since water pollution becomes as one of the most challenging global issues, photocatalytic degradation has received considerable attentions as an efficient water treatment technology with regard to removing organic contaminants. Upon receiving UV or sunlight irradiation with energy higher than their bandgap, semiconducting materials generate charge carriers such as electrons and holes that react with water and produce reactive species for decomposition. TiO₂ and ZnO are the most widely used photocatalysts because of their higher degradability and lower production cost. Especially, TiO₂ and ZnO nanostructures exhibit better degradability thanks to their low recombination of charge carriers and large active surface areas. However, the challenges like low utilization of sunlight (mainly responsive to UV light) and non-recyclability limit their large-scale use as photocatalysts. In this work, we tackle these limitations by developing a new immobilized photocatalytic system to improve their recyclability and investigating a novel semiconductor-semiconductor heterogeneous material to enhance their optical response in the visible region. First, ZnO nanowires (NWs) have been synthesized using a hydrothermal process and hybridized with silicon nanocrystals (SiNCs). This heterojunction lowers the ZnO bandgap (more active under visible light) and exhibits superior photodegradation performance under the visible and white light conditions compared to original

ZnO NW photocatalysts. Second, we have developed a novel fabrication technique to create a vertically-aligned ZnO NW array on a polymer substrate with strong adhesion. The proposed twostep fabrication process allows the part of NWs to be embedded into the polymer matrix, securing the nanomaterials for harsh operating environments. A ZnO-NW/Polydimethylsiloxane (PDMS) film presents the unique immobilized photocatalytic system that can float on the water surface, targeting buoyant pollutants. In particular, crude oil has been used a model pollutant for degradation experiment. A strong adhesion of ZnO NWs to the polymer substrate also enables two new implementations of the photocatalytic system including the application with high shear stresses and piezoelectrocalysis. The latter application is particularly interesting as organic pollutants were degraded via mechanical vibration without resorting to light energy. Finally, this two-step synthesis technique combined with strain engineering allows us to create multifunctional soft micromotors, i.e., the ZnO-NWs/PDMS submillimeter 3D structures integrated with various nanomaterials (metal nanoparticle catalysts, magnetic nanoparticles, etc.). The micromotors possess multiple functionalities such as photocatalysis, piezoelectrocatalysis, locomotion/selfpropulsion, and magnetic response. This level of multifunctionality integration on a single platform can be rarely found in the literature. In the end, an immobilized photocatalytic system with high surface areas, improved mass transfer, and easy recyclability has been developed, which can find its uses in biomedical and environmental applications. Apart from the photocatalytic applications, the research has also been oriented to address some technical challenges in deterministic assembly of the solution-processed 1D nanostructures for device integration.

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CHAPTER 1

INTRODUCTION

1.1 Synthesis and frication of one-dimensional semiconductor nanostructures

In the past decades, one-dimensional (1D) semiconductor nanostructures have attracted considerable attention due to their promising applications in electrochemistry [1], gas sensing [2], photocatalysis $[^3]$, and optoelectronics $[^4]$. Various devices enabled by 1D semiconductor nanostructures, such as light emitting diodes, solar cells, and chemical sensors, have demonstrated remarkable enhancements in their performance thanks to their unique physical properties that are not available in the bulk counterparts. Devices made out of individual 1D nanostructures typically exhibit these nascent electrical, mechanical, and optical properties and are suitable for the proofof-the-concept devices. But the fabrication of such devices relies on the "pick and place" method to position individual 1D nanomaterials and is painstakingly time consuming and ineffective. Moreover, these individual nanodevices are prone to device-to-device variation and low signal-tonoise ratio due to charge fluctuation, material inhomogeneity and defects [5]. It is therefore not suitable for many device applications or production on a large scale, at low cost and high throughput. Instead, the use of networks or ensembles of 1D nanostructures presents a highly promising route to addressing these issues. The objective of the dissertation is to present novel nanomanufacturing approaches to 1D nanostructure assembly. The notion of nanomanufacturing encompasses both top-down and bottom-up processes that deal with the production of nanomaterials (e.g. nanoparticles, nanowires, nanotubes, etc.), the integration or assembly of these nanoscale building blocks, and the interconnection techniques to link nanoscale features to the macroscopic world.

The 1D nanostructure networks or ensembles take various assembled forms including vertically-aligned 1D nanostructure array and aligned or random 2D networks of 1D nanostructures. The former assembly approach is advantageous because it offers high surface-area-to-volume ratio with minimal interface with the substrate and the variation of individual nanostructures becomes averaged and less susceptible to noise. The latter assembly approach is most common especially with random orientations of 1D nanostructures laying on the substrate. In this dissertation, each assembled structure (vertically-aligned and 2D random network) will be investigated with an emphasis on development of novel fabrication methods tailored for target applications. For vertically-aligned, semiconductor 1D nanostructures, we pay our attention to the growth of zinc oxide (ZnO) and titanium dioxide (TiO2) nanowires (NWs) on various substrates. Likewise, for developments of a random network of 1D nanostructures, single-walled carbon nanotubes will be considered as a model 1D structure for 2D assembly.

A number of techniques have been developed to create vertically-aligned NWs on different substrates, which can be roughly classified in two primary strategies: directly growth vs. post-processing. Direct growth indicated the generation of desired nanostructures through chemical synthesis. For TiO2 and ZnO NWs, gas-phase and solution-phase methods are widely employed to create vertically-aligned NW array structures [^{6,7}]. In general, gas phase methods such as chemical vapor deposition (CVD) [^{8,9}], metal organic chemical vapor deposition (MOCVD) [^{10,11}] and vapor-liquid-solid (VLS) [^{12,13}] processes provide well-aligned, polycrystalline semiconductor directing grown onto the substrates. However, the synthesis temperature is rather high (typically over 500°C), limit the type of substrates that nanomaterials can grow on. In contrast, solution-based approaches such as the hydrothermal method [^{14,15}] and solvothermal synthesis [^{16,17}] can be used to grow NWs at relatively low temperature (< 200°C), expanding the options for growth

substrates [^{6,18}]. For example, ZnO NWs can be directly synthesized on polymeric substrates using the hydrothermal method [¹⁹]. Polymer substrates cannot be used in a high-temperature, gas-phase reaction approach. Specifically, this dissertation will address the issues associated with the adhesion of hydrothermally-grown NWs to polymeric substrates.

Another aspect of nanomanufacturing is to assemble the solution-processed nanomaterials, in particular 1D nanostructures. Due to ease of handling, transporting, and patterning, 1D nanostructures are typically suspended in solutions before further manipulation. Post-processing of the solution-processed 1D nanostructures refers to assembling NWs (or nanotubes, NTs) onto different substrates after synthesis, by which external stimuli and the assistance of templates are usually employed. The attempts on using external stimuli, such as electrical and magnetic fields, enabled precise placement of NWs but worked inefficient in a large area [^{20,21}]. Although template-based assembly method worked better in a wafer scale, it has drawbacks in difficulty control of NW density and uniformity [^{22,23}]. Here we will address these issues by proposing a new assembly approach based on soft-lithographic patterning of porous nanomembranes and vacuum filtration of 1D nanostructures through the patterned membrane. The fabrication and assembly methods for NWs/NTs in this dissertation will be investigated for two main applications, photocatalytic degradation and electronic devices.

1.2 Fabrication challenges of NW assemblies for environmental remediation

Since water pollution has been considered as one of the major global challenges, photocatalytic degradation, as one of the prospective approaches, has been extensively studied with the semiconductor nanostructures that harness photons to produce reactive species for degradation. As one of the most studied semiconductor materials, ZnO has been suggested as an efficient catalyst for the photocatalytic degradation [^{24–27}] due to its high UV light absorption as well as compatible band structure, offering excellent photocatalytic activities in decomposing organic compounds. Although promising photocatalysis performance has been observed, ZnO has limitations due to the high rate recombination of photogenerated electron-hole pairs and low utilization of solar spectrum [²⁸]. Numerous methods have been developed to extend the absorbance spectrum to the visible region and circumvent surface charge recombination of the photogenerated electronhole pairs within ZnO. Amongst, hybriding ZnO with other materials is regarded as one potential way to counter those defects in ZnO photocatalysis.

In Chapter 2, recent progresses regarding ZnO-based hybrid photocatalysts are summarized including various foreign materials and different kinds of photocatlayst systems. On the basis of this extensive literature review, we extract some important factors that can elevate the photocatalytic performance of ZnO (and TiO₂) photocatalysts. A novel hybrid photocatalayst systems consisting of ZnO NWs and Si nanocrystals is than introduced, whose improvements in charge transportation and spectral response were explored and the degradabilities with respect to different light-irradiation condition were analyzed. Aside from the abovementioned challenges, there are particular demands in fabrication of ZnO photocatalysts for different working conditions. Usually, solution-based hydrothermal synthesis has a merit of low synthesis temperature, which allows the ZnO NWs to be created on a flexible polymeric substrate with highly ordered array. However, one main challenge of this process is weak adhesion between the ZnO NW array and the substrate. It was often observed that the NWs after growth were detached from the polymer surface and re-suspended in the solution. With this respects, an immobilized-platform of ZnO photocatalysts is discussed in the following chapter, describing a novel method to partially embed

ZnO NWs in flexible polymeric films for better adhesion. The capability and versatility of the novel immobilized photocatalysts were investigated afterwards.

1.3 Fabrication challenges of NW assemblies for electronic and optoelectronic devices

Many nanoelectronic devices utilize the uniformly patterned film (or network) of nanomaterials because the device performance depends on uniformity of conductivity as well as transparency across the patterned substrates. The previous methods to assemble networks of nanomaterials, including magnetic-field guided assembly, electric-chemical guided assembly, and flow-field-based approach, provide some successes in obtaining patterned random network structures^{[29}]. However, it is still difficult to produce predictable patterns distributed over a large area, and even more challenging is to create a uniformly patterned film of hybrid nanostructures. In a later chapter, we describe a solution-based filtration process for the scalable production of patterned single-walled carbon nanotubes (SWCNTs) networks. A vacuum filtration process has been originally developed for the separation of solutes from solvents and has been extensively used in chemistry laboratories. This filtration technique has been used to produce a large-area sheet of various nanomaterials including carbon nanotubes $[^{30}]$ and graphene/graphene oxide $[^{31}]$. In order to create desired devices, a sheet of nanomaterial obtained from filtration needs to be further patterned typically via photolithography, liftoff or etching, unavoidably generating nanomaterial wastes. Here, the filter membrane is pre-patterned using the soft-lithography-based technique, called blanket transfer, previously reported by our group $[^{32}]$, permitting directed assembly of the nanomaterials and patterning. By means of filtrating suspended SWCNTs solutions over the prepatterned filter membrane and the subsequent transfer technique, we demonstrate an array of SWCNT patterns with uniform distribution into predetermined windows on the filter membrane.

This integration creates a larger number of standard SWCNT transistors across a 2" wafer with reasonable performance.

1.4 Research objectives and scopes of the dissertation

Heterogeneous photocatalytic degradation working as an effective treatment towards toxic organic pollutants in industrial wastewaters, has attracted increasing attention in the past 40 years. Photocatalysts are typically semiconductor materials whose bandgap can absorb the light energy (i.e. photons) and separate charge carriers such as electrons and holes. Among a number of semiconductor materials, TiO₂ and ZnO have been well investigated and widely used due to their environmental benign nature, nontoxicity, low cost and remarkable photocatalytic activity. Their typical low dimensional nanostructures, including nanoparticles and nanowires, have been experimentally verified to serve as efficient photocatalysts, whereas the issues still remain. First, for the majority of photocatalysis study, nanosized TiO₂ or ZnO materials are used in suspension during degradation experiments, and therefore, they need to be separated from the cleaned water. Various immobilized photocatalytic platforms have been studied extensively as well, but their performance is far below that of the suspension systems due to the decreased surface areas and mass transfer rate. Second, for both TiO_2 and ZnO, their spectral response to sunlight is limited to the UV region. Therefore, a separate UV source has been implemented for photodegradation, significantly hampering a widespread adoption in wastewater treatment facilities or other units. In addition, low degradability against pollutants with high hydrophobicity is also a main limitation [³³]. Unlike TiO₂, ZnO suffers from photocorrosion (is particularly weak under acids and bases ^{[34}]) and thus hindering recyclability and long-term use.

In Chapter 3 we will present the synthesis strategies of TiO₂ and ZnO nanostructures including nanowires andnanotubes. Series of experiments including SEM, TEM, EDS, XRD, Raman and photoluminescence were carried out to characterize the as-synthesized TiO2 and ZnO nanostructures. The photocatalytic degradation and other applications are studied basing on their various shapes.

Among the variety of ZnO nanostructures, one-dimensional (1D) ZnO NWs has been proposed as a promising material system owing to its compatibility to various substrates, large surface area to volume ratio, and rich materials chemistry developed for forming ZnO-based heterogenous nanostructures [^{35,36}]. In Chapter 4, we report for the first time that the hybrid structure of Si nanocrystal/ZnO Nanowires (Si NCs/ZnO NWs) is synthesized through the hydrothermal method and low pressure plasma process, consecutively. The Si NCs boost the ZnO's spectral response to more visible light, thus absorbing more solar radiation. In addition, heterojunction formed by ZnO NWs and Si NCs facilitate the charge carrier separation by proper band alignment. The Si NCs-decorated ZnO NWs exhibit the better degradability in comparison to pure ZnO NWs under all lighting conditionos (UV, visible and white-light irradiations). The characterizations of the morphology and crystal structures are presented. The loading effect of Si NCs on the optical response of ZnO NWs is systematically studied using UV/Vis absorption spectra and photoluminescence. Possible mechanism of the charge carriers transport and enhanced photo-degradability will be proposed and discussed.

Chapter 5 illustrates a novel method to fabricate vertically-aligned ZnO NW array on the ultra-thin flexible polymeric film as an immobilized photocatalytic system. The NW array has reliable adhesion to the substrate as well as excellent photo catalytic degradation capability. The key strategy is that instead of directly growing ZnO NW array from the seed layer on the polymeric

substrate, a two-step growth process is utilized to encapsulate hydrothermally-grown ZnO NWs in a thin polymer layer and use the exposed region of the NWs as a seed layer to regrow them in the same solution to a desired length. As-grown ZnO NW arrays exhibit the wurtzite crystallites which are found possessing excellent photocatalytic activities and structural stability. Investigation on a decomposition rate in four cycles demonstrates not only the stability of the catalytic activity but also the minimal loss of the as-grown ZnO NW array from the flexible substrate. A strong adhesion of ZnO NWs to the flexible substrate allows us to mount the film onto a circular rod. The NWs can survive from harsh operation conditions with high shear stresses such as overhead mixing and sonication. This also allows us to test the piezocatalytic effect of ZnO, demonstrating that pollutants are degraded under mechanical vibration without any light energy. This system provides a pathway to further improve photocatalytic performance of ZnO-based hybrid photocatalysts. Finally, this immobilized system is lighter than water and thus floating on the surface of water, targeting hydrophobic or lightweight pollutants such as oil droplets. It has been shown that the ZnO-NW-based floating catalysts can degrade crude oil on the water surface.

In Chapter 6 we reports a novel photocatalytic platform of micromotors with multiple functionalities. The proposed micromotor consists of ZnO NWs as photocatalysts and Polydimethylsiloxane (PDMS) as a base substratefor catalyst immobilization. A ZnO NWsembedded PDMS layer and another pre-stretched PDMS layer are bonded together with an oxygen plasma surface treatment, which induces an out-of-plane deformation to form 3D shaped microstructures. The immobilization technique for ZnO NWs has been introduced in Chapter 5. The micromotors with the predetermined shape, especially tubular shape, can be created by the interfacial stresses associated with the initial strain mismatch. Self-propelling micromotors created by the rolled-up technique are composed of the multiple layers where the bubble-generating catalysts (e.g. Pt, Ag) are located at inner wall. Bubbles are generated when H₂O₂ is catalytically decomposed into O₂ and propel micromotors along the axis. Another functionality, which is remote navigation, was conferred to micromotors by incorporating Fe-based materials for themagnetic control [³⁷]. We also show that this modified ZnO catalytic micromotors (ISMs) created by means of the stretched PDMS bonding method (SPB) have remarkable photocatalytic degradability owing to its significant increment of active surface area and reduction in mass transfer resistance. Moreover, the SPB supports to fabricate diverse shapes of ISMs, which may open a door for creating multifunctional micromotors towards other applications.

The Filtration-Guided Assembly (FGA) method is described in Chapter 7, describing the fabrication of SWCNT films with specified patterns. By using both the modified soft lithographyic technique, called blanket transfer (BT) method, and standard photolithography, an array of microscale patterns is fabricated onto a mixed cellulose ether (MCE) filter membrane. A solution containing the SWCNTs is filtered through the patterned filter membrane, and the SWCNTs are deposited onto the open region in the filter subsequently, resulting in an array pattern of SWCNT networks. Soft lithographic (using PDMS) or other processes have been developed to pick up the majority of patterned SWCNTs from the membrane and transfer print to a target substrate with an alignment to an electrode-array. An array pattern of homogeneous SWCNT network films is created over an area of 20 cm² within 10 min. Herein, a 2"×2" size array of SWCNT transistors is fabricated with the critical pattern size of 5 µm and the pattern transfer yield is more than 80%. The electrical performance of the back-gated transistors made from the FGA and transfer method of 95% pure SWCNTs is then demonstrated. It is believed that the combination of BT and FGA is compatible to a variety of low-dimensional nanostructures and is an effective way to build an array of numerous electronic devices on a wafer-scale area.

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CHAPTER 2

LITERATURE REVIEW

2.1 Approaches of ZnO-based hybrid photocatalysts

In the past few decades, water pollution has been becoming a serious global issue due to the rapid development of the industry and the widespread use of chemical and biological synthetic materials. Therefore, the research on the aspect of pollutants removal for the natural water system is highly urgent and essential. Among numerous strategies photocatalysis is one promising technology of disinfection and detoxification and has been demonstrated to be effective to various types of organic pollutants originated from the industrial and agricultural wastes. This process mainly involves two reactions, oxidation and reduction. With the assistance of solar energy photocatalysis is economic and applicable to versatile environmental conditions so that it has attracted considerable interest in recent years. Up to now a number of photocatalysts, including TiO₂, ZnO, WO₃ and Fe₂O₃, have been synthesized and modified by various micro/nano fabrication techniques.

ZnO serving as a prospective photocatalyst has been applied to a variety of organic pollutants [^{1–4}]. Comparing to other candidates, ZnO as a metal oxide semiconductor has a lot of advantages, such as well-band-alignment to redox, tunable band gap by doping, high quantum yield in the near-UV spectral region and diverse nanostructures whereby its photocatalytic performance is easier elevated by incorporation with other nanomaterials. Besides, the particular properties like biocompatible, environmental benign, biodegradable and low cost fabrication make ZnO industrial available to address large-scale wastewater problem.

ZnO is a wide band gap (3.2-3.5 eV) semiconductor and has three major crystal structures, including rocksalt, wurtzite and zinc blende [⁵]. Amongst, wurtzite ZnO in hexagonal crystal

geometry is the most common structure at ambient temperature which possesses better thermodynamic stability. As of now a number of works with respect to the characterization and test of wurtzite ZnO have been reported. Although excellent photocatalytic activity of wurtzite ZnO has been observed in comparison with other photocatalysts, the drawbacks such as narrow spectral response at visible region and high recombination rate of charge carriers impede the range of application. In these years considerable efforts have been dedicated to diverse ZnO nanostructures in order to counter these defects as working for photocatalyst. It is already known that one effective way to modify ZnO is the formation of hybrid structures using appropriate nanostructures and foreign materials so that the photocatalysis process can be facilitated.

2.1.1 The mechanism of photocatalytic degradation using ZnO

ZnO is capable of decomposing a variety of organic pollutants by use of the heterogeneous photocatalysis process ascribe to the sufficient build-in potential in comparison to the reduction potential of the H^+/H_2 redox pair as well as the oxidation potential of the O_2/H_2O redox pair under normal hydrogen electrode (NHE) [⁶⁻⁸]. This process generally takes place when photogenerated electron-hole pairs are excited under sunlight irradiation and subsequently transported to the surface of ZnO nanostructures, where the surrounded organic pollutants are gradually mineralized into water, CO_2 and other inorganic molecules in the presence of reactive oxidants, such as hydroxyl radicals (·OH). The process detail can be represented by a series of chemical equations (see Figure 2.1), which consists of a number of oxidation and reduction reactions occurring at the interface of ZnO nanostructures and water. As seen in Figure 2.1, upon the irradiation of sunlight, the photons energy greater than the bandgap of ZnO can stimulate electrons (e-) escaping from valence band (VB) to conduction band (CB), resulting holes (h+) generated at the corresponding

original positions. When transporting to the active sites on the surface of ZnO nanostructures, these electron-hole pairs are highly probable to convert hydroxyl anions in water and oxygen into active superoxide radicals and hydroxyl radicals, respectively, and other oxidants in subsequent redox reactions. Eventually, the organic pollutants surrounding these oxidants are mineralized into water, carbon dioxide and some inorganic molecules. It is worthwhile noticing that a considerable quantity of photogenerated electron-hole pairs recombines and dissipates in the form of heat prior to the participation of reaction. Therefore one potential way to improve the photocatalytic activity of ZnO is to suppress the recombination rate of electron-hole pairs.



Figure 2.1. Schematic of photocatalysis process on single-component ZnO photocatalysts, where chemical equations represent detail photocatalysis process

2.1.2 The mechanism of charge separation using hybrid ZnO

The rapid recombination of photogenerated electron-hole pairs is one primary issue impeding the quantum yield of ZnO that has attracted much attention in recent years. Apart from the solutions such as thermal treatment and element doping, hybridization with foreign nanomaterials (e.g. metal, semiconductor, carbon, and polymer) has been demonstrated as an effective methodology in this regard. As shown in Figure 2.2, the constituent such as TiO₂ in ZnO-based hybrid structure is employed to prolong the lifetime of charge carriers [⁹]. A heterojunction

bridging ZnO and TiO₂ enables photogenerated electrons and holes to transport in accordance with the direction in band diagram (Figure 2.2). In detail, the electrons generated at the CB of TiO₂ is likely to flow towards the CB of ZnO due to the potential difference. Likewise, the holes at the VB of ZnO moves to that of TiO₂ under the sunlight irradiation. It can be seen that the transportation of photogenerated electron-hole pairs is able to work continuously as long as the heterojunction is valid. As a result, the electrons and holes accumulated at the CB and VB can respectively react with oxygen and water for reactive oxidants. Furthermore, the formation of heterojunction decreases the bandgap of ZnO as well as TiO₂, resulting an increment yield of charge carriers on both components. In this manner, the photogenerated electron-hole pairs are effectively separated prior to the possible recombination whereby improves the photocatalytic activity of ZnO.



Figure 2.2. Band diagram of ZnO/TiO2 hybrid nanostructures, where the heterojunction formed between ZnO and TiO2 promotes charge separation. (Adapted from Reference 9)

Figure 2.3 illustrates three types of band alignments in the field of semiconductor hybrid structures, including straddling gap (type-I), staggered gap (type-II) and broken gap (type-III) [¹⁰]. As seen, all three scenarios possess the capability to separate photogenerated electron-hole pairs derived from one (or both) photocatalyst through the heterojunction. However, the photogenerated electrons and holes in type-I heterostructures are separated from wider bandgap component and

directed to the same side of the heterojunction, resulting charge accumulation at the narrower bandgap component thus has the higher probability of recombination. In other words, type-I heterostructures promote the charge recombination instead of separation which is unlikely to be pursued by researchers in photocatalysis. In contrast, type-II and type-III heterostructures are the desired band alignments for charge separation. In type-III the CB potential of one component is even lower than the VB potential of the other component, which is capable of separating photogenerated electron-hole pairs. Type-II heterostructures render a pathway to confine the photogenerated electrons and holes on different sides of the heterojuntion after separation that reduces the recombination rate efficiently. Such the band alignment as ZnO/TiO₂ hybrid structures is belonged to type-II heterostructures, which is favored to elevate the photocatalysis performance. In addition, comparing to n-n heterojuntion (e.g. TiO₂/ZnO), p-n heterojunction base on type-II and type-III heterostructures enable further enhancement in charge separation due to the opposite build-in potential in components.



Figure 2.3. Three types of band alignments. (a) type I, (b) type II and (c) type III. (Adapted from Reference 10)

As displayed in Figure 2.4, p-CuO/n-ZnO formed in p-n heterojuntion has particular advantages in charge separation and free carriers promotion [¹¹]. For instance, an internal build-in electrical field established at the interface of the p-n heterojunction promotes the separation of photoinduced electrons and holes. In addition, the resultant bandgap by the formation of

heterojunction can yield more free electrons and holes respective to p-type and n-type semiconductors under sunlight irradiation, directly increasing the reactive oxidants.



Figure 2.4. Band diagram of n-ZnO/p-CuO hybrid nanostructures, where the heterojunction formed between ZnO and CuO promotes charge separation. (Adapted from Reference 11)

2.1.3 The factors influence the performance of ZnO photocatalyst

On the basis of relevant studies in the field of photocatalytic degradation, some primary factors are worthwhile noticed that can significantly affect the performance of photocatalysts, which includes the aspects of material, solution and light source [¹²]. In detail, material involves mass loading, surface area, and morphology, defect and so on. Solution refers to PH value and temperature. Light source contains light intensity and wavelength. For slurry system, optimal loading and uniform distribution of photocatalysts are always desired. The problems such as light scattering and absorption, agglomeration and sedimentation derived from too much loaded photocatalysts may cause the serious reduction of photocatalytic activity. Moreover, it can be imagined that excessive loading in practical application will increase the cost of applied photocatalysts as well as post-treatment process. In contrast, proper photocatalyst loading allows sufficient photons and spaces accommodating them, thus resulting best performance in water cleanliness. With a given loading, photocatalysts in larger surface area is able to generate larger quantity of reactive oxidants under sunlight irradiation and increase adsorption of pollutants as

well. The relevant works have indicated that larger specific surface area of photocatalyst can elevate the degradation rate of pollutant $[^{13-15}]$. Therefore, surface area is another essential factor regarding slurry system as well as immobilized system. The detailed comparison of slurry system and immobilized system will be discussed in next chapter, where catalytic surface area is one critical factor. In the aspect of solution, PH value and temperature are two key factors influencing the type of dominate oxidants and degradation rate. It has been found that photogenerated holes (h+) are the major oxidants in acidic solution (low PH value) while hydroxyl radicals (·OH) are responsible for the oxidation for the rest conditions $[^{16}]$. The appropriate PH value can reduce the effect of charge carrier scavenger in pollutants thus elevate the degradability. On the other hand, the increment of temperature can lead to an improvement of degradation rate which obeys Van't Hoff-Arrhenius law [¹⁷]. In general, ZnO as photocatalyst works best under UV light irradiation because the photons possess sufficient energy to activate the formation of photogenerated electronhole pairs, meanwhile its photocatalytic activity in visible spectrum has also been confirmed thanks to the surface defects and oxygen vacancy $[1^{18}]$. And the irradiation light in higher intensity promotes the yield of oxidants whereby accelerates the degradation process. However, in some cases, such as the excitation light with wavelength matching with the absorption spectrum of pollutant, may cause the evaluation difficulty due to the unexpected byproducts via the natural decomposition of pollutant. Additionally, high intensity light requires extra power which is not economic in large-scale application. Taking the research analysis and cost-effectiveness into consideration, suiTable light source is necessary in the process of photocatalytic degradation. Apart from the abovementioned aspects, the proper utilization of photocatalysts is another option to improve photocatalysis performance. The suspension and immobilization are two major methods widespread utilized for evaluation of photocatalysts, which however have intrinsic

defects in particular working conditions. The recent progress regarding their modification and the development of potential method will be discussed in the following chapter.

2.1.4 ZnO/metal oxide hybrid

ZnO has become one of the most attractive materials over the past few decades and its unique properties in photoelectronics and electrochemicals has been applied to various devices. In the field of environmental remediation, ZnO is also prospective thanks to non-toxicity, biodegradability and biocompatiblity. ZnO has remarkable performance as a photocatalyst in decomposing a wide range of organic pollutants, which however exhibits a long-standing issue, the limited photocatalytic activity. Hybrid structure is effective to elevate the photocatalytic activity of ZnO through enhancement of charge separation and extension of response spectrum. As mentioned above, type-II and type-III heterostructures are desired band alignments with respect to the modification of ZnO. In this section some major metal oxide semiconductors serving as foreign materials formed these special band alignments when coupling with ZnO, which are reviewed in terms of the performance and capability.

2.1.4.1 ZnO/TiO₂ hybrid structure

TiO₂ is a well-documented material [¹⁹] which has been widely used in solar cells, batteries, supercapacitors and biomedical devices. Other than these applications, so far, considerable efforts have been devoted to water purification [⁸]. TiO₂ has three crystal structures, including anatase (3.2 eV), rutile (3.0 eV) and brookite (3.4 eV). The first two structures are prior photocatalyst candidates since they are sTable in ambient condition and are capable of working under both UV and visible light [²⁰]. Comparing to ZnO, TiO₂ is more sTable in the use of potocatalysis in harsh
conditions. However some fundamental challenges such as fast recombination and slow transportation of charge carriers still remain. Like ZnO, the major strategies including thermal treatment and element doping have been proposed to counter these problems, in which the hybridization is identified as a very promising method to facilitate the photocatalytic activity of TiO₂. In ZnO-based hybrid photocatalyst system, TiO₂ is employed as a foreign material mostly in view of two specialties, the similarity of its properties to ZnO and the appropriate band configuration in a good agreement with the redox potential under NHE. Moreover, the heterojunction of ZnO/TiO₂ performs type-II band alignment that is favored in photocatalysis optimization.

<i>Table 2.1.</i>	General summary	of ZnO/TiO2	hybrid phot	tocatalysts
			<i>v</i> .	•

Structure	Component	Pollutant	Light source	Reference
ZnO/TiO ₂ nanoparticles	ZnO/TiO ₂	Acridine Orange (AO)	Solar	21
	ZnO/TiO ₂	Acid Red 14 (AR 14)	UV	22
	ZnO/TiO ₂	Sodium Methyl Red (SMR)	UV	23
	Mn/ZnO/TiO ₂	Methylene Blue	UV	24
	ZnO/TiO ₂	4-chlorophenol	UV	25
	ZnO/TiO ₂	Diazinon	UV	26
	ZnO/TiO ₂	Methyl Orange Methyl Blue	UV	27
	ZnO/TiO ₂ /Clay	Methyl Green	UV	28
	ZnO/TiO ₂ /SiO ₂	Methyl Blue	UV, Visible	29
	7.0/T:0	Rhodamine B (RhB)	1137 37:-11-	30
	$ZnO/11O_2$	Norbornadiene (NBD)	UV, VISIBle	50
	ZnO/TiO ₂	Methyl Blue	UV, Visible	31
	ZnO/TiO ₂ /Ag ₂ O	Methyl Blue	UV	32
	ZnO/TiO ₂ /CNT	Methyl Orange	UV	33

ZnO/TiO ₂	Azo dye sunset yellow Heterocyclic dye methyl blue Xanthene dye rhodamine B	UV	34
ZnO/TiO ₂	Azo dye Remazol Red Brilliant F3B (RR180) Pesticide 2,4- dichlorophenoxya cetic acid (2,4-D)	UV	35
ZnO/TiO ₂	Methyl Orange	UV	36
ZnO/TiO ₂ /Er ₂ O ₃ / Y ₂ O ₃ /Fe	Acid Red B	Sunlight	37
S/ZnO/TiO ₂	Rhodamine B	Visible	38
ZnO/TiO ₂ /Fe ₃ O/P ANI	Methyl Orange	Visible	39
ZnO/TiO ₂	Methyl Orange	UV	40
Ag/ZnO/TiO ₂	Rhodamine B Crystal Violet (CV) Methyl Blue Methyl Orange	UV, Visible, Solar	41
ZnO/TiO ₂	4-chlorophenol (4-CP)	UV	42
ZnO/TiO ₂ /Er ³⁺ /Y AIO ₃	Acid Red B Methyl Orange Rhodamine B Azo fuchsine (AF)	Solar	43
ZnO/TiO ₂	Methyl Orange	UV	44
ZnO/TiO ₂	Brilliant golden yellow (BGY) (azo dye widespread for textile/dyeing industries)	Sunlight	45
ZnO/TiO ₂	Rhodamine B Malachite green	Visible	46
ZnO/TiO ₂ /graphe ne	Rhodamine B Texbrite BAC-L Texbrite NFW-L	Visible	47

Table 2.1. (cont'd)

ZnO/TiO ₂ nanowires/nanoro ds/nanotubes	I/ZnO/TiO ₂	Rhodamine B	Visible	48
	ZnO/TiO ₂	Bromo-Pyrogallol Red (Br-PGR)	UV, Visible	49
	ZnO/TiO ₂	Rhodamine B	UV	50
	ZnO/TiO ₂ /CdS	Rhodamine B Atrazine Textile wastewater	UV, Visible	51
	ZnO/TiO ₂ /CNT	Acid Orange 7 (AO7)	UV	52
	ZnO/TiO ₂	Methyl Red Rhodamine B	UV	53
	ZnO/TiO ₂	Methyl blue	UV	54
	ZnO/TiO ₂	Methyl orange	UV	55
ZnO/TiO ₂ film	ZnO/TiO ₂	4-nitrophenol (4- NP)	UV, Visible	56

As shown in Table 2.1, up to now, ZnO/TiO_2 hybrid photocatalysts have exhibited remarkable performance towards the decomposition of numerous organic pollutants with the assistance of the enhanced phototcatalysis. Owing to the various conditions researchers applied to their works, the quantitative comparison is difficult. Herein we will discuss the potential development of ZnO/TiO_2 by summarizing some recent progress reported in terms of various pollutants and degradation under varied working conditions.

Azo dyes are commonly used as probe pollutants to evaluate the photocatalytic activity of ZnO-based hybrid photocatalysts. And optical measurement of pollutant is the primary method to analyze capability of photocatalysts. During degradation process, the characteristic absorbance peak of pollutant was observed diminishing by using UV/Vis spectrometer, which reflected the decrement concentration of polluntants in the presence of photocatalysts. Note that Bouguer–Lambert–Beer law reveals the relationship of attenuation of spectrum to pollutant concentration,

with which the degradation rate can be eventually obtained from the diagram of the spectrum intensity change at characteristic absorbance peak as a function of the length of light irradiation. In this manner, single-component ZnO photocatalyst and ZnO/TiO₂ hybrid photocatalysts were studied, from which ZnO/TiO₂ hybrid photocatlysts performed higher degradation rate than singlecomponent ones in the case of valid heterojunction $[^{36,54}]$. In recent years, many attempts have been made to practically utilize ZnO/TiO₂ hybrid photocatalysts. As a way, a lot of pollutants that contained complex chemical components have been employed as probe pollutants. Consequently, the results regarding the removal of majority pollutants are promising under UV light irradiation $[^{26,42,50}]$. On the other hand, the studies associated with the ZnO/TiO₂ hybrid photocatalysts under the irradiation of visible light demonstrated the functional synergy effect in promoting the degradation of pollutants $[^{30,31,56}]$. Especially, the research towards the textile/dying pollutant of using the sunlight paves a way for ZnO/TiO_2 hybrid photocatalyst in practical application [⁴⁵]. Notably, as of now, a number of strategies with respect to the improvement of ZnO/TiO₂ hybrid photocatalyst have been implemented successfully. For instance, core-shell structure was exploited to counter the drawbacks of ZnO, such as photocorrosion and slow charge mobility, which showed prospective results in chemical stability and photocatalytic activity [21-23]. Moreover, the facilitation of the band-band charge separation using piezotronic effect was proved in ZnO/TiO_2 nanoplates as a potential way to further improve the photocatalysis [²⁷].

Except for the structural/morphologic modification, the combination of numerous methods, including doping, phase mixing and foreign materials coupling were also introduced to further modify ZnO/TiO₂ hybrid photocatalysts in regard of the spectral response and charge separation. For example, ZnO/TiO₂ hybrid photocatalysts doped by particular species would change the electronic band configuration which caused promotion of electron-hole pair generation

and transportation [^{24,38,57}]. Meanwhile it has been proved that the mixed multiple crystalline phases of TiO₂ could broaden the range of light absorption owing to the change of band structures [⁴⁶]. When additional foreign materials were introduced to ZnO/TiO₂ to form ternary composites, it would not only reinforce the hybrid photocatalysis but also bring advantages such as better chemical stability, larger surface adsorption and Fenton reaction compatibility [^{39,41,51}]. It worthwhile notices that the recent trend about modifying ZnO/TiO₂ hybrid photocatalyts is to add extra components, which can effectively address some drawbacks emerged in two-component hybrid photocatalysts.

2.1.4.2 ZnO/WO₃ hybrid structure

Over the past few years WO₃ nanostructures have displayed great capabilities in the application of gas sensors, super capacitors, solar cells, electrochromic devices and photocatalysis [58,59]. When using as photocatalysts, TiO₂ and ZnO with wide bandgap electrical property have drawbacks in regard of spectral response, which can only utilize a small fraction of solar spectrum (3-5%). At this point WO₃ is a valuable photocatalyst since it has remarkable photocatalytic activity under the presence of sunlight irradiation thanks to its proper bandgap [60] in spite of its flaws in rapid charge recombination and inappropriate CB level. As yet, various WO₃ crystal structures have been discovered (monoclinic, orthorhombic, tetragonal, triclinic, hexagonal and cubic) with band gaps varied from 2.5 eV to 2.8 eV, which are correspond to UV region and blue-region of solar spectrum [60,61]. Notably, among these phases, monoclinic-WO₃ has displayed the best photocatalytic activity and chemical stability whereby attracts a lot of attention in the research of water treatment. The recent research associated with the ZnO/WO₃ hybridization implies that monoclinic-WO₃ is a suiTable foreign material due to the appropriate bandgap alignment (type-

II), which made significant contributions in broadening the spectral response and facilitating charge separation in hybrid photocatalysts.

Structure	Component	Pollutant	Light source	Reference
ZnO/WO ₃ nanoparticles	ZnO/WO ₃	Methyl Orange	UV, Visible	62
	ZnO/WO ₃	Methyl blue Anionic Orange G (OG)	Visible	63
	ZnO/WO ₃ /ZnWO ₄	Methyl Orange	UV	64
	ZnO/WO ₃	Methyl Orange	UV, Visible	65
	Ag/ZnO/WO ₃	Reactive Red 120 (RR120) Reactive Orange 4 (RO4)	UV	66
	Ag/ZnO/WO ₃	Naphthol Blue Black (NBB)	Sunlight	67
	ZnO/WO ₃	Acid orange II	UV	68
	Ag/ ZnO/WO ₃	Reactive red 120 (RR120)	Sunlight	69
	Ag/ZnO/WO ₃	Acid black 1 (AB 1)	UV	70
ZnO/WO ₃		2,4-		
nanowires/nanoro ds/nanotubes	ZnO/WO ₃	dichlorophenoxya cetic acid (2,4-D)	Sunlight	71
	ZnO/WO ₃	resorcinol (ReOH)	UV	72
	ZnO/WO ₃	phenol	UV	73

Table 2.2. General summary of ZnO/WO3 hybrid photocatalysts

So far, a number of attempts have been made towards finding the optimal combinations of ZnO and WO3 in terms of their morphology and proportion. And numerous works regarding the evaluation of their degradation efficiency against a verity of pollutants have been reported. Table 2.2 summarized some updates about the ZnO/WO₃ hybrid photocatalysts in view of pollutants and light conditions.

Upon sunlight irradiation, when photons in a wide range of energy were converted into the photogenerated carriers by hybrid photocatalysts, electrons and holes were able to be respectively

transported to ZnO and WO₃ due to difference potential of their band structures. In this manner, the enhanced charge separation derived from ZnO/WO₃ heterojunctions promoted the photocatalytic activity of photocatalysts. As reported, the enhancement of degradation efficiency contributed by WO₃ was usually above 25% [⁷⁴]. More specifically, ZnO/WO₃ heterojunctions could boost the degradation rate to some pollutants which is resistive to single-component ZnO photocatalysts [^{70,72}]. In these years, one kind of ternary composites, Ag/ZnO/ WO₃, was intensively investigated to remove particular pollutants under sunlight irradiation. The perspective result indicated that the noble metal in hybridization can further facilitate the charge separation [⁶⁷]. Besides, the study on hybridization of extra foreign materials, ZnWO₄, confirmed double heterojunctions between ZnO and WO₃ phases, which revealed a potential mechanism to suppress the charge recombination [⁶⁴]. In view of the above, strategies in multiple composites and multiple heterojunctions will bring more promising results in modifying ZnO/WO₃ hybrid photocatalysts in the near future.

2.1.4.3 ZnO/Fe₂O₃ hybrid structure

Motivated by the electronic recording devices for data storage, iron oxide were extensively investigated in the past decades because of the distinguishable chemical stability and magnetic property. Nowadays, with the development of iron oxide nanostructures, the application has been widely extended to biomedicine and environmental remediation. The typical crystal structures of iron oxide include wustite (FeO), hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄) [^{75,76}]. In photocatalysis study, hematite and maghemite belonging to iron(III) oxide are two main classes of iron oxide which are of interest to researchers due to their natural magnetic behavior as well as diverse geometries. One primary obstacle that hinders photocatalysts in practical application is the recyclability (or recovery). Most of techniques regarding the separation of micro-/nano- scale particles currently used in research and industrial would significantly increase the cost in large-scale water treatment. In the light of magnetic property, the fabrication of iron(III) oxide for photocatalysts could be one potential solution to counter this challenge [$^{77-79}$]. In addition, the bandgap energy of iron(III) oxide varies from 1.9 eV to 2.2 eV, which is capable of absorbing a wide range of sunlight, approximately from deep UV region to visible yellow region. Therefore, iron(III) oxide serving as foreign materials are getting an increased attention. However, there are some drawbacks of iron(III) oxide, such as in-direct bandgap and high charge recombination rate, that have been noticed when using as photocatalysts independently. Due to this reason, the hybridization of iron(III) oxide to other photocatalysts is being explored. The recent progress of ZnO/Fe₂O₃ is tabulated (Table 3).

Recently both ZnO/ α -Fe₂O₃ and ZnO/ γ -Fe₂O₃ hybrid photocatalysts have been demonstrated to be effective to degrade various pollutants. In particular, the enhancement of photocatalysis has been elaborated that the photogenerated charge carriers were separated through the ZnO/Fe₂O₃ heterojunction, resulting a larger number of active ·OH and O₂⁻· [⁸⁰]. On the other hand, the investigations towards the dye degradation in the presence of visible light irradiation confirmed the extension of spectral response of ZnO photocatalysts as incorporating with Fe₂O₃. As a result, with the assistance of facilitated charge separation and light absorption, the degradation efficiency of ZnO/Fe₂O₃ photocatalysts was evidently improved in case of sunlight irradiation. Aside the abovementioned studies, the assessment of Ag/ZnO/ Fe₂O₃ ternary photocatalysts has be confirmed to address some issues existed in ZnO/Fe₂O₃ hybrid photocatlysts [⁸¹]. To our best knowledge, not many ZnO/Fe₂O₃ ternary photocatalysts have been reported. ZnO/Fe₂O₃-based hybrid photocatalysts has a high potential in large-scale application as considering the commercialization.

Structure	Component	Pollutant	Light source	Reference
ZnO/Fe ₂ O ₃ nanoparticles	ZnO/y-Fe ₂ O ₃	2,4- dichloropenoxyace tic acid (2,4-D)	UV	82
	ZnO/Fe ₂ O ₃	2,4- dichlorophenoxya cetic acid (2,4-D)	Sunlight	83
	ZnO/Fe ₂ O ₃	Salicylic acid (SA)	UV	80
	ZnO/a-Fe ₂ O ₃	Methyl orange	UV	84
	ZnO/α -Fe ₂ O ₃	Rhodamine B	UV, Visible	85
	ZnO/y-Fe ₂ O ₃	Methylene blue Rhodamine B Methyl orange	Visible	79
	ZnO/Fe ₂ O ₃	3,6- dichlorophenoxya cetic acid (Dicamba) 2,4- dichlorophenoxya cetic acid (2,4-D)	Solar	86
	ZnO/a-Fe ₂ O ₃	Pentachlorophenol (PCP)	UV, Visible	87
	ZnO/y-Fe ₂ O ₃	Chlorophenoxyace tic acid	UV	88
	ZnO/a-Fe ₂ O ₃	Pentachlorophenol (PCP)	UV, Visible	89
	ZnO/γ-Fe ₂ O ₃	2,4- dichlorophenoxya cetic acid (2,4-D)	UV	90
	ZnO/γ -Fe ₂ O ₃	chlorophenol	Sunlight	91
ZnO/Fe ₂ O ₃ nanowires/nanoro ds/nanotubes	ZnO/Fe ₂ O ₃	Methylene blue	visible	92
	Ag/ZnO/Fe ₂ O ₃	Methyl orange Iodoform (CHI ₃)	UV, Visible	81

Table 2.3. General summary of ZnO/Fe₂O₃ hybrid photocatalysts

2.1.5 ZnO/carbon-based hybrid

Although carbon-based nanomaterials have been investigated for many decades, the excellent capabilities originated from their unique properties are keep emerging in every relevant field. As representative nanomaterials, each breakthrough regarding diamond, fullerene, carbon nanotubes (CNTs), graphene and so on, has brought numerous opportunities for fabricating high-performance devices and further raised research interest in widespread applications. Comparing to metal oxide nanomaterials, carbon-based nanomaterials are usually known as stronger (covalent bond) and lighter (atomic weight) thanks to their structures and constituents. Furthermore, some special properties, such as superconductivity [⁹³], charge carrier mobility [⁹⁴], nonlinear/linear optical property [⁹⁵] and biocompatibility [⁹⁶] have been widely used to various applications. In the field of photcatalysis, the combination of ZnO and carbon-based nanomaterials has achieved many objectives involving overcome some intrinsic defects and improved photocatalytic activity of single-component ZnO photocatalysts. In this section we will briefly summarize the ZnO-based photocatalysts hybridizing with some typical carbon-based nanomaterials and discuss their up-to-date challenges and potentials.

When working as photocatalysts, CNTs were found to be advantageous in chemical stability, electron scavenger and diffusion of reacting species boosted by mesoporous character $[^{97-99}]$. In last few decades a number of photocatalysis approaches have implied the remarkable degradation performance of various photocatalysts in the presence of hybridization with CNTs (see Table 2.4) $[^{100}]$. As known, the heterostructures formed by CNTs have enhancements not only in efficient charge separation but also the extension of spectral response especially to wide bandgap materials like TiO₂ and ZnO, which makes them functional upon broaden solar spectrum $[^{101}]$. Moreover, studies associated with synergetic effect of ternary composite photocatalysts indicated

that CNTs could further suppress the recombination of charge carriers with the assistance of metal/nonmetal ions, through which the degradation rate of numerous pollutants were significantly increased [^{102,103}].

As a result of the excellent electronic and optical properties, graphene has also successfully been employed to wastewater treatment [¹⁰⁴]. The recent research towards hybrid photocatalysts revealed that photogenerated electrons favor to transfer through π bonds in the presence of graphene, which is effective to suppress the charge recombination [¹⁰⁵]. Furthermore, the superior optical transparency and large surface area of graphene in comparison with CNTs allowed more reactive sites forming hence accelerated the degradation process [^{106–108}]. Table 2.5 summarizes the recent works about the ZnO/graphene hybrid photocatalysts. Like ZnO/CNTs hybrid photocatalysts, ZnO/graphene hybrid photocatalysts are also capable of utilizing the majority of solar spectrum and degrading a verity of textile pollutants. To date, ZnO/graphene ternary composites have attracted considerable attention because of their degradation efficiency in various pollutants. It has been demonstrated that significant improvements in charge separation and spectral response have been obtained by using the formation of ternary composites. Basing on relevant works, both metals and semiconductors are suiTable to form ZnO/graphene-based ternary photocatalysts [^{109,110}].

Except for carbon nanotubes and graphene, some other carbon-based nanomaterials, such as carbon fibers and carbon quantum dots, also displayed attractive degradability [^{111–114}]. Overall, carbon-based nanomaterials are promising as foreign materials in coupling with ZnO for hybrid photocatalysts. More specifically, ZnO/carbon-based hybrid photocatalysts with the combination of extra metal/metal oxide materials are of interest to researcher in order for higher photocatalytic activity.

Structure	Component	Pollutant	Light source	Reference
ZnO/CNT nanoparticles	ZnO/CNT	Rhodamine B	Sunlight	115
	ZnO/MWCNT	Cyanide (CN)	UV	116
	ZnO/MWCNT	Rhodamine (RhB)	UV	117
	Ag/ZnO/CNT/PI	Methyl orange	UV	103
	Cu/ZnO/MWCNT	Methyl orange	Visible	118
	ZnO/MWCNT	Methylene blue Rhodamine 6G (Rh6G)	UV	119
	Mg/ZnO/MWCN T Co/ZnO/MWCNT	Methyl orange	UV	102
	ZnO/MWCNT	Methyl blue	UV	120
	ZnO/MWCNT	acetaldehyde	UV	
	ZnO/CNT/rGO	Methyl blue	UV	121
	ZnO/CNT	MB	UV Visible	122
	ZnO/CNT	phenol	Solar	123
ZnO/CNT nanowires/nanoro ds/nanotubes	ZnO- carbon nanofiber	Rhodamine B	UV	125

Table 2.4. General summary of ZnO/CNT hybrid photocatalysts

Table 2.5. General summary of ZnO/G and ZnO/rGO hybrid photocatalysts

Structure	Component	Pollutant	Light source	Reference
ZnO/G, ZnO/GO,				
ZnO/rGO	ZnO/rGO	Methyl blue	UV	121
nanoparticles				
	ZnO/rGO	Orange II	Solar	124
	ZnO/G	Methyl blue	UV	126
	ZnO/G	Methyl blue	UV	127
	7nO/C	Methyl blue	Visible	128
	ZIIO/G	Methyl orange	VISIOIE	
	Ag/ZnO/G	Methyl Orange	UV	109
	ZnO/GO	Methyl blue	UV	129
	ZnO/rGO	Methyl blue	UV	130
	ZnO/G	Methyl orange	UV	131
	ZnO/rGO	MB,MO	UV	132
	ZnO/G	MB	Visible	133
	ZnO/GO	MO	UV, Visible	134
	ZnO/GO	4-nitrophenol (4- NP)	UV	135

Table 2.5. (cont'd)

 ZnO/G	MB	UV, Visible	136
ZnO/GO	Rhodamine(RhB)	UV	137
ZnO/rGO	MB	UV, Visible	108
ZnO/GO/g-C ₃ N ₄	MB	Visible	110
ZnO/GO	МО	Solar	138
ZnO/G	RhB	UV	139
ZnO/GO	MB	UV	140
ZnO/GO/TiO ₂	MB Texbrite BAC-L Texbrite BBU-L Texbrite NFW-L	Ultrasonic	141
ZnO/rGO	RhB	Solar	142
ZnO/rGO/RuO ₂	MB	Solar	143
 ZnO/rGO	MB	UV, Sunlight	144
ZnO/G	MO Pyrogl Red(PR)	Visible	145
ZnO/rGO/TiO ₂	MB	UV	146
Ag/ZnO/GO	MB	UV, Visible	147
ZnO/GO/CuAu	MO MB Indigotin (IN) Sunset (SY) Tartrazine (TT)	Solar	148
ZnO/GO	Brilliant Red X- 3B (X3B)	UV	149
ZnO/rGO	CH3CHO	UV, Visible	150
ZnO/rGO	MB MO RhB	Visible	105
ZnO/GO/nanocell ulose	Ciprofloxacin (CF)	Solar	151
ZnO/rGO	MB	UV	152
ZnO/rGO	MB	UV	153
ZnO/GO	MB	UV	154
Ag/ZnO/rGO	RhB	Visible	155
ZnO/GO	Deoxynivalenol (DON)	UV	156

2.1.6 ZnO/metal hybrid

Up to date works associated with the ZnO/metal hybrid nanostructures have attracted considerable attention owing to their outstanding properties in electronics and optics that can well

fit for various optoelectronic applications. In the research of environment remediation, taking the advantages of this hybrid nanostructures, such as effective charge separation and extended light absorption, ZnO/metal hybridization have also become one pathway for fabricating highperformance photocatalysts. As can been in Table 6, the recent studies imply that ZnO/metal photocatalysts are able to treat a variety of pollutants in water under the presence of suiTable light irradiation, which have comparable degradation performance like other ZnO-based heterostructures. Differ from ZnO/metal oxide hybrid photocatalysts, the major promotion of ZnO/metal hybrid photocatalysts are derived from the special functionalities, mostly electron scavenger and surface plasmonic resonance (SPR), of decorated metal particles. In detail, upon light irradiation, the electrons in metal particles excited by SPR effect allow an increased possibility to generate reactive oxidants such as .OH. Meanwhile the misaligned band structure enables a positive transportation of photogenerated electrons from ZnO to metal, suppressing the recombination of charge carriers. Except for the improvement of the photocatalytic activity, these effects caused by metal particles are also effective to overcome the photocorrosion of ZnO, offering a pathway for further enhancement of degradation [157]. Thus, hybridization with metal is a promising route to modify ZnO-based photocatalysts.

So far many kinds of metal particles, including Au, Ag and Pt have been employed to assistant ZnO photocatalysts in order for desired performance. On the basis of these works, two primary modification strategies are suggested to further optimize ZnO/metal hybrid photocatalysts. One way is to build binary composites by taking account the effects of the dimension, morphology and synthesis method of metal particles. Such work as ZnO/Au hybrid photocatalysts revealed a possible restriction about the particle size with respect to photocatalysis promotion from charge separation and SPR, from which optimal degradation performance could

be realized under the proper combination [¹⁵⁸]. Moreover, it is reported that the solution-based process is favored since it provides a slow growth rate for metal particles to uniformly decorate ZnO nanostructures [¹⁵⁹]. Another way, same as other abovementioned hybrid photocatalyts, is to fabricate ternary (or quaternary) composites to approach multiple synergetic effects. According to relevant reports, the extra metal particles serving as electron sinks could further suppress charge recombination as well as produce more oxidants [¹⁶⁰], while the extra metal oxide/carbon-based materials with narrow bandgap allowed the hybrid photocatalysts working under a broader range of light [¹⁶¹]. In this manner, since the charge separation, the spectral response and the chemical stability were facilitated simultaneously and effectively, ternary (or quaternary) composites exhibited excellent photocatalytic activity as desired (see Table 2.6).

Structure	Component	Pollutant	Light source	Reference
ZnO/Au nanoparticles	ZnO/Au	RhB	UV, Visible	162
	ZnO/Au	RhB	UV	163
	ZnO/Au	RhB, MO, MB	Visible	164
	ZnO/Au	MB	Sunlight	165
	ZnO/Au	MB	Solar, UV	166
	ZnO/Au	Effluent treatment plant (CETP)	Sunlight	167
	ZnO/Au/rGO	RhB	Solar	168
	ZnO/Au	RhB	Visible	169
	ZnO/Au	phenol	UV, Visible	170
	ZnO/Au	MO	UV	171
	ZnO/Au/NiO	RhB	UV	172
	ZnO/Au	RhB	UV	173
	ZnO/Au	RhB	Solar	158
ZnO/Ag nanoparticles	ZnO/Ag	PF	UV, Visible	174
	ZnO/Ag	RhB	UV	175
	ZnO/Ag	Metamitron, metribuzin	Solar	176
	ZnO/Ag	MB	UV	177

Table 2.6. General summary of ZnO/metal hybrid photocatalysts

Table 2.6. (cont'd)

		4 1 1	T T T	160
	ZnO/Ag/Ba	4-nitrophenol	UV	100
	ZnO/Ag	RhB	UV, visible	178
	ZnO/Ag	MB	Visible	179
	ZnO/Ag	RhB	Solar, UV, Visible	180
	ZnO/Ag/Ag ₂ WO ₄	RhB, MB,MO, fuchsine	visible	161
	ZnO/Ag	Ketorolac tromethamine (KTC)	Solar	181
	ZnO/Ag/GO	MB	Visible	182
	ZnO/Ag	MB, Cr(VI)	Visible	183
	ZnO/Ag/In ₂ O ₃	MO,4-NP	Visible	184
	ZnO/Ag	MO,phenol	UV	185
	ZnO/Ag	MO	UV	186
	ZnO/Ag	RhB,MB,MO	Solar	187
	ZnO/Ag /rGO/TiO2	RhB	Visible	188
	ZnO/Ag	MB	UV	157
	ZnO/Ag/CNT	Acid orange 7 (AO7)	Visible	189
ZnO/Pt nanoparticles	ZnO/Pt/C	MB	UV	190
	ZnO/Pt	RhB	UV, Visible	191
	ZnO/Pt	MB	UV	159
	ZnO/Pt	R6G	UV	192
	ZnO/Pt	MB	UV	193
	ZnO/Pt	Malachite green	Visible	194

2.1.7 Summary

In summary, multi-component hybridization is effective to improve the photocatalytic performance of ZnO. The valid heterojunctions between ZnO and foreign materials are able to reduce the charge recombination whereby promote generation of reactive oxidants. In addition, the modifications in nanostructure morphology, such as core-shell structures and hollow structures, have solved many problems of single-component ZnO in using as photocatalysts. Apart from the abovementioned hybrid photocatalysts, many other efficient ZnO-based hybrid photocatalysts, such as ZnO/CuO, ZnO/CdS, ZnO/ZnS and etc, have also been developed and examined under

various working conditions. Owing to the coupling of foreign materials, a lot of ZnO-based hybrid photocatalysts possessed superb optical, electronical, chemical and physical properties and extra functionality that have been working in other fields. As examples, foreign materials such as NiO, Ag₂O and SiO₂ have shown attractive capabilities in magnetic response, bacterial control and electron tunneling, which are extremely desired not only in wastewater treatment but also in biosensors and electronic devices. In current situation, considering the complex environment conditions, compatibility and versatility are primary demands to photocatalysts. An increased number of attempts towards selecting and modifying appropriate photocatalysts for special cases, involving particular pollutants, wide spectrum of light irradiation and varied light intensity and working temperatures have been devoting in these years.

2.2 The improvement of photocatalysts in various systems

Over the past decades photocatalysis has been widely introduced in the fields of watersplitting hydrogen evolution, self-cleaning surface and wastewater treatment thanks to its advantages like infinite energy source, environmental-friendship, and cost-effectiveness. To achieve high efficiency in wastewater cleanliness, numerous types of photocatalysts are being developed while their photocatalytic activities with respect to different organic pollutants are being explored. On the basis of the previous research regarding photocatalysts, some factors have been recognized playing important roles in affecting photocatalytic degradation performance, including mass loading and defect content, thermal and chemical stability, surface contaminants and area, particle adsorption and photon conversion efficiency. Besides, there are two more important points to evaluate the photocatalysts in practical application, which are degradation efficiency with respect to particular pollutants and cost originated from the fabrication and recycling process of photocatalysts. Taking account all these conditions some efforts are devoted to study efficient photocatalysts, such as TiO₂, ZnO and Fe₂O₃, and their corresponding large-scale fabrication methods. Meanwhile, investigations are also carried out on proper manners for utilizing photocatalysts. Presently, there are two primary photocatalyst systems, slurry system and immobilized system, which are widely adopted in photocatalyst research [¹⁹⁵]. Briefly, slurry system has the photocatalysts uniformly dispersed into the solution, which usually gives a fast degradation process but suffers from the potential agglomeration and difficult recovery of photocatalysts. In contrast, immobilized system stands for photocatalysts fixed on some sTable substrates, partially losing catalytic surface area but making the photocatalysts basing on these two systems and discuss some modifications and other potential utilization methods.

2.2.1 Slurry system

Upon reviewing progress on photocatalysis, various pollutants are found to be rapidly decomposed by photocatalyst suspension under the presence of light irradiation in lab-scale experiment. With the assistant of post-treatments like sedimentation and filtration, these suspended photocatalyst particles are able to be completely removed, leaving purified and cleaned water eventually. As known from the relevant studies, slurry system is an efficient methodology for organic dye decomposition. In order for desired performance and reproducibility, photocatalytic degradation are usually carried out in special reactors which has homogenous particle dispersion and controllable working environment. Those special reactors, namely photoreactor, is a device that can effectively utilize photocatalysts during the entire photodegradation process. In general, for slurry photoreactor the polluted solution should always have photocatalysts uniform suspended

after injected to the reaction chamber. In addition, there are many other factors that helps to improve the photocatalysis. For instance, the filled chamber should be transparent and thin enough for the maximal penetration depth of light irradiation. Benefiting from effective light utilization, high photocatalytic area to reactor volume ratio and low mass transfer limitation, photocatalysts in slurries usually exhibit remarkable photocatalytic activity than that of immobilized ones under the same working conditions [^{196–199}]. Furthermore, owing to the advantages of photoreactors, photocatalytic degradation performance deriving from slurry system are established as benchmarks for the evaluation of photocatalysts [²⁰⁰]. One typical example is Degussa P25 powder, which in certain weight percentage with respect to particular concentration of pollutants is usually used to assess other developed photocatalysts [^{201–203}]. To date the most of photocatalysts has been tested in slurry photoreactor in research, among which ZnO and its hybrid structures have been intensively studied. Table 2.7 shows the recent progress of ZnO-based photocatalysts in view of slurry systems, which includes a wide range of pollutants and various working conditions.

Although the superb compatibility and capability have been demonstrated, some limitations hinder the slurry system from large-scale application. As an example, the separation of photocatalysts is always challenging when the system is scaled up, causing unexpected residues and increased cost. For small-size photocatalyst particles the problems as agglomeration significantly influence their photocatalytic activity [²⁰⁴]. The shadow effect penetration depth of the irradiation light raised by the absorption and light scattering of suspended photocatalysts and pollutants can result non-homogeneous and poor photocatalytic reaction. As one potential solution, there are a lot of modified slurry photoreactors that contain functionalities such as continuous stirring and ultrafiltration, by which some drawbacks faced in slurry system can be overcome [^{205,206}]. And many attempts are focused on improving particle uniform distribution and recovery

functionalities in slurry system. At the same time, the investigation on the immobilized photocatalysts is being carried out as an alternative solution.

Туре	Morphology	Pollutant	Light	Reference
ZnO	Particle plus membrane	Reactive black 5 (RB5) and etc.	UV	207
ZnO	particle	Real refinery wastewater with pretreatment	UV	208
Ag/ZnO	particle	MB	Visible	209
Ag/ZnO/CdO	particle	MO and MB	Visible	210
N-ZnO	particle	formaldehyde	Visible	202
Y (yttrium)-ZnO	particle	MB	UV	211
ZnO/Fe ₃ O ₄	particle	phenol	UV+visible	212
ZnO	particle	Malachite green (MG)	UV	213
CuO/ZnO	particle	Arsenite (As III, As V)	UV	214
Dy (dysprosium)- ZnO	particle	Acid red (AR17)	Visible	215
CuO/ZnO	NWs	Hexavalent chromium (Cr VI)	Visible	216
ZnO/Ag ₃ VO ₄ /AgI	particle	RhB and MB	Visible	217
ZnO	particle	Textile effluent	UV	203
ZnO/Fe ₃ O ₄ /AgBr	particle	RhB	Visible	218
ZnO/TiO ₂	particle	MB	UV	219
La/ZnO, Se/ZnO	particle	Acid yellow 29, coomasie brilliant blue G250, acid green 25	Visible	220
ZnO/NiFe ₂ O ₄	particle	Congo red (CR)	Solar	221
ZnO	particle	MB	UV	12
ZnO/AgBr/Fe ₃ O ₄ / Ag ₃ VO ₄	particle	RhB	Visible	222
ZnO/kaolin clay	NWs	Hexavalent chromium	UV	223
ZnO/g-C ₃ N ₄	particle	MO and humic acid(HA)	Visible	224
ZnO/GO	NWs	MB	UV	225
ZnO	particle	MO	UV	226
ZnO/nanoclinoptil olite zeolite (NCP)	particle	4-nitrophenol	UV	227

Table 2.7. Summary of ZnO-based photocatalysts in slurries

2.2.2 Immobilized system

In these years the research associated with photocatalysts has oriented towards the immobilized system, which refers to the photocatalysts in form of film or nanowire array structures are fixed onto substrates before applying to photo degradation. The immobilized ZnO nanostructures on various substrates possess remarkable degradation capabilities thanks to their diverse morphologies such as particle-gathered films, vertical-grown nanowire arrays, multi-brunches tree array and so on [²²⁸]. Comparing to slurry system, the immobilized photocatalysts are more advantageous in fewer post-treatment for separation and recycling meanwhile retaining the comparable photocatalytic capability in photocatalytic degradation, satisfying the demands of practical application. Nevertheless, the ordinary immobilized system which simply grow photocatalysts on substrates without any further setup assistance usually displayed the decrement of photocatalytic activity attributed to limited catalytic surface area and mass transfer. In this regards, two modified immobilized systems including immobilized photocatalysts in various aspects.

2.2.2.1 Immobilized photoreactors

Immobilized photoreactor has been proven to be effective to solve the emerged problems of slurry system and immobilized photocatalysts. Differ from slurry photoreactor, immobilized photoreactor doesn't require complicated recovery process for photocatalysts after photocatalytic degradation. As for the design of the majority of these works, the photocatalysts were used to be immobilized onto the reactor wall where the incident light had concentrated irradiation to elevate the photocatalytic activity. The probe pollutants were injected along with a continuous flow system which established a circulated flow to enhance mass transfer to surroundings. Consequently, the polluted solution was thoroughly cleaned after flown across the immobilized photocatalysts multiple times. It worthwhile notices that the immobilized photoreactors has no post-treatment demand in comparison to the slurry one whereby suiTable to large-scale application. It has been found that there are many factors such as surface-to-volume ratio of photocatalysts, connection between photocatlayst and reactor, depth of light penetration and flow rate of polluted solution that potentially affect the device performance. For instance, approaches on using high aspect ratio capillary with the combination of porous- or nanowire-structural photocatalysts have accomplished faster degradation rate because of large active catalyst surface area [^{229–231}]. On the other hand, the fabricated thin layer of immobilized photocatalysts in combining transparent substrate has greatly reduced the depletion of photocatalyst from the incident light hence boost the reaction rate [^{229–231}].

With an increased interest in this field, the modification of photoreactors in terms of photocatalysts with multiple composites are being conducted in order for reduced charge recombination and enhanced chemical stability [^{232–234}]. Table 2.8 is the summary of immobilized ZnO-based photocatalysts in these years, which indicated that the research are focusing on ZnO-based hybrid structures as targeting low cost, high photocatalytic activity and diverse morphology. More specifically, considerable attention is given to the exceptional degradability towards various pollutants under the presence of solar light to confirm potential performance in practical application [^{235,236}]. In chapter 4 we will discuss a novel prototype of an immobilized photoreactor, which in superb photocatalytic performance is believed as a pathway to overcome some limitations currently faced by immobilized photocatalysts.

Туре	Morphology	Pollutant	Light	Reference
ZnO/PMMA	Nanorods	МО	UV	229
ZnO/TiO ₂ /Glass	composites	phenol	UV	232
ZnO/TiO ₂ /Glass	Coat on nanorods	MO	UV	233
N-ZnO/Polyester Fabric (PF)	Particle film	Amaranth (AM)	Solar light	235
ZnO, TiO ₂	membrane	Textile wastewater	UV	230
ZnO	Particles coat on disk	Reactive Yellow 81 (RY81)	UV	237
ZnO	particles	Humic substances (HS)	UV	238
ZnO/Polyvinyl Pyrrolidone (PVP)	particles	Congo red (CR)	UV	239
ZnO	nanorods	МО	UV	231
ZnO	Particle formed film	МО	UV	240
ZnO/glass spiral	Particle formed film	Reactive red 120 (RR-120)	Solar light	236
Ag/ZnO/Metal Mesh	NWs	Food black 2 (FB2) and MO	visible	234
ZnO	Particle formed film	carbamazepine	UV	241

Table 2.8. Summary of immobilized ZnO-based photocatalysts

2.2.2.2 Buoyant photocatalysts

Although the approaches associated with photoreactors have proven the continuality and reusability of immobilized photocatalysts in degrading various pollutants, photoreactors still face challenges in some practical cases. In order for best performance the artificial light with high output power energy is usually employed to supply intense and concentrate light irradiation. However this scenario is hardly realized by solar light in natural environment ascribe to the limited light receiving area of the reactor and low light density that fails to achieve expected light absorption. Besides, the scalable utilization of reactors brings more technical problems such as external power supplies for the circulated water flow system and post-treatment process. Aside from the aforementioned disadvantages, there are some severe restrictions in slurry system and immobilized photoreactor. For instance, the rapid attenuation of incident light in water, especially that of UV light, would significantly affect the activity of photocatalysts distanced from the water surface [²⁴²], which confines the scale of slurry system. In addition, both slurry system and immobilized photoreactor are ineffective to deal with insoluble pollutants (e.g. oil splits) floating at water surface. In recent years buoyant photocatalysts has been demonstrated as an ideal model to serve to large-scale application owing to the excellent recyclability, optimal sunlight utilization and effectiveness to oil pollutants.

Buoyant photocatalysts refer to the photocatalysts immobilized on floatable substrates which can maximally utilize incident light during the entire degradation process. This system is designed to prevent incident light from scattering and absorption before arriving to the surface of photocatalysts. As known, for immobilized photocatalysts a good support possesses the features include reliable substrate-to-photocatalyst contact, stable property against generated oxidants, long lifetime in water and environmental benign. As a modified immobilized system one more feature that need to take account in fabrication buoyant photocatalysts is the lightweight. So far, except for many kinds of polymers [^{243–245}], other types of materials have also been used as floatable substrates [^{246–250}]. However some defects such as low surface-area morphology of photocatalysts and complex fabrication for substrate-to-photocatalysts attachment are still remain. Moreover, to our knowledge, ZnO working as one type of buoyant photocatalyst is rarely explored. Comparing to TiO₂ and other photocatalysts, ZnO has obvious advantages in cost-effectiveness, substrate compatibility and superior degradability. As seen the recent approaches with respect to ZnO buoyant photocatalysts (Table 2.9), although a variety of organic dyes have been successfully decomposed using ZnO-based photocatalysts, few of them have been tested by ZnO in form of buoyant photocatalysts. In Chapter 5 we propose a novel ZnO-based photocatalytic film which

possesses long life-time as well as large surface area. The performance and advantages of the film in serving as the buoyant photocatalysts will be discussed.

Туре	Morphology	Pollutant	Light	Reference
Zno/Polystyrene	particle	MB	UV	251
n-Zno/p-Ag ₂ O/Nylon Film	Film+particle	MB	Visible	252
Ni/ZnO/Glass	Film+particle	Methyl green (MG)	Visible	253
Ir/ZnO/Zn	film	MO	UV	254
Polypyrrole (ppy)/ZnO/Flyash Cenosphere (Fac)	particle	МО	Visible	255
Redot/Zno/Fac	particle	MO	Visible	256
Zno/Oak Charcoal	particle	ammonia	UV	257

Table 2.9. Recent approaches with respect to ZnO buoyant photocatalysts

2.2.3 Micromotor system

Micromotor is a device whose dimension is in micro/nano scale. In general, micromotors have capability to swim in solution (e.g. water) with or without the presence of external stimuli and sometimes own specific functionality. Recently, upon the combination of various fabrication techniques and diverse geometry, micromotors have realized multiple functions such as photocatalysis, cargo delivery, antibacteria, objective capture and so on, which could perform complex tasks in biomedicines and environmental remediation [^{258–260}]. The recent studies in photocatalytic degradation have implied the capability of micromotors in rapidly degrading a variety of pollutants thanks to their advantages such as particular functionalities, suspension working ways and build-in hybrid nanostructures [²⁶¹]. Table 10 shows the comparison of three immobilized systems in terms of some key factors. In detail, when working as photocatalysts, owing to uniform suspension and large quantity in wastewater, micromotors are sometimes regarded as a slurry system. But differ from typical photocatalysts in slurry, some of micromotors have photocatalysts immobilized on surface meanwhile have other functional materials as body. In this manner, in comparison to abovementioned immobilized systems micromotors possess

higher photocatalytic surface area to reactor volume ratio and desired mass transfer thereby elevates degradation rate [^{262–265}]. Moreover, the integrated functionality on micromotors also renders milder situation in agglomeration and recovery to the suspended micromotors in solution as comparing to the similar size of the suspended photocatalysts. More specifically, both the selfpropulsion based on physical and chemical cues and the remote motion-control realized by external stimuli have been proven to counter the gravitation as well as mass transfer limitation between micromotors, relaxing drawbacks in slurry system. Additionally the remote motion-control are able to promote the separation of micromotors after the degradation hence become costcompetitive. Furthermore, the attempts on the hybrid composites and diverse morphology give a way to further improve the photocatalytic performance of micromotors. Up to date a large number of approaches regarding water remediation have been reported, in which TiO₂ and its hybrid structures were commonly employed in the construction of micromotors due to outstanding stability and desired synergy effect in charge transportation $[^{266-268}]$. It worthwhile notices that TiO₂-based micromotors are built on solid and rigid substrates. These approaches successfully integrated various materials onto small-size micromotors whereas increased the probability of corrosion and damage in wastewater environment, which would also have potential to become extra pollutants as failed recovery. As an alternative, soft micromotors fabricated by biocompatible and flexible materials could retain shape for a long time span. Nevertheless, some flaws such as larger dimension and fewer building block candidates impede widespread applications [²⁶⁹]. Thus, combining advantages of different types of micromotors is one pathway to pursue practical-used micromotors.

Our literature research indicated that progress of ZnO-based micromotors were mostly on the manageable movement [^{270,271}] instead of the function of water cleaning was scarcely reported.

Taking account the comparable photocatalytic performance, mild fabrication condition and other advantages, we believe that ZnO-based micromotors for photocatalytic degradation will interest more researchers in the future. In Chapter 6 we introduce a novel micromotor design which has embedded ZnO NW array on flexible substrate [²⁷²]. The impacts of particular motion and functionality with respect to degradation of organic dye will be discussed.

Table 2.10. Comparison of three immobilized systems

	Immobilized	Buoyant	Micromotor System
	Photoreactors	Photocatalysts	
Light utilization	Good	Excellent	Good
Mass transfer	Good	Good	Excellent
Lifetime	Good	Good	Excellent
Active surface area	Good	Good	Excellent
Recovery/separation	Excellent	Excellent	Good

Table 2.11. Comparison of slurry and immobilized systems

Slurry System		Immobilized System	
Advantages	High catalyst surface area to reactor volume	Continuous degradation process	
	Low mass transfer limitation	Easy catalyst separation	
Disadvantages	Serious agglomeration at high catalyst loading	Potential high mass transfer limitation	
	Difficult catalyst separation	Potential contamination from residue catalyst	

2.2.4 Summary and outlook

ZnO nanostructures have been proven as one efficient photocatalyst in the past studies. In this paper we have tried to list the recent progresses regarding ZnO-based photocatalysts since ZnO has been demonstrated possessing a number of particular advantages that are superior to other photocatalysts in practical application. For instance, the production cost of ZnO is approximately one quarter of TiO₂ which is much favored by industrial for saving total cost in wastewater treatment. Furthermore, the milder synthesis environment and diverse geometry allow ZnO photocatalysts having compatibility in coupling with many other materials than that of TiO_2 whereby possessing high capability in countering complicated environmental conditions. In addition, the remarkable performances of detoxification and antimicrobial activity of ZnO have been investigated, whose applications in biology and biomedical fields implies the potential multifunctionality of ZnO when using as photocatalysts.

As non-toxic photocatalysts, the improvement of ZnO in terms of degradability have been extensively explored, where the form of multiple-composites has exhibited outstanding performance. With the assistance of foreign materials, many aspects of ZnO, including defect level, energy potential, stability and charge transportation, could be significantly modified. At meantime, some special properties of foreign materials brought additional functionality which enhanced the capability of ZnO as photocatalysts. On the other hand, as a well-documented semiconductor, the fundamental study of the elevated performance towards ZnO and coupled foreign materials could result a win-win situation as introduced to other applications.

From the literature research we found that considerable efforts in last few years were devoted to develop novel ZnO-based photocatalysts while the methodology in using them was rarely improved. Table 2.11 summarizes the advantages and disadvantages of slurry and immobilized systems in photocatalytic degradation process [^{273,274}]. Recently a number of weak points that associated with the performance of photocatalysts, such as low-efficiency and non-recovery, have been overcome by using specific photocatalyst system. However, the flaws are still existing in those developed systems. More progresses are desired in this field as considering the challenges in large-scale application. For instance, the slurry system is efficient but there is no economic way to scale up. The majority of the slurry photoreactors focused more on the highest

degradation rate but neglected the post-process for recovery. As the promising alternative, immobilized system has some practical issues such as demands of external power sources and rapid reduction of photocatalytic activity, which shorted the lifetime hence increased the entire cost. It is worth to pay more attention to the ways of properly using photocatalysts in future research.

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CHAPTER 3

SYNTHESIS AND APPLICATION OF SINGLE 1D SEMICONDUCTOR NANOSTRUCTURES

3.1 Synthesis and application of 1D TiO₂ nanostructures

3.1.1 Hydrothermal synthesis of TiO₂ nanowires

The TiO₂ NWs in anatase-phase and rutile-phase have been demonstrated possessing remarkable performance including photocatalysis [^{1–4}], water-splitting [^{5–8}], solar cells [^{9–11}], and lithium-ion batteries [^{12–14}]. As an efficient synthesis way, the hydrothermal method is usually conducted in a sealed chamber with high pressure and temperature. It is known that the morphology and quality of TiO₂ NWs are subject to temperature, reaction duration and solute concentration [¹⁵]. For the TiO₂ NWs of a large aspect ratio, an optimized condition is required. Figure 3.1 illustrated the correlation of factors we obtained from the TiO₂ NWs is more related to the concentration of the solute, more specifically, the molarity of NaOH. In out experiment the thicker NWs was obtained under the high concentrated NaOH solution. On the other hand, the NWs in large length could be obtained after longer reaction time.



Figure 3.1. The correlation parameter towards TiO2 NW growth, (a) wire dimension as a function of molarity of the solute, (b) wire length as a function of growth time. Scale bar: $1 \mu m$.

The as-prepared TiO₂ NWs in high aspect ratio is shown in Figure 3.2a. All reagents used in this experiment were commercially available without further purification. The detail process was as follows: 0.6 g TiO₂ nanopowder (32 nm, Dow Co.) was dispersed in 50 mL 10 M NaOH solution, which was prepared by NaOH particles (Fisher Scientific) and deionized (DI) water. After stirred for 5mins at room temperature, the mixed solution was sonicated for another 10 mins for the further uniform distribution. Then the mixed solution moved to a 200 mL Teflon-lined autoclave was heated 30 hrs at 180 °C, and centrifuged for the separation of the sediments at 10000 rpm with multiple times after it cooled down at room temperature. Subsequently, the sediments were rinsed with DI water thoroughly and dried with N₂. Figure 3.2b exhibits the XRD pattern of the as-prepared TiO₂ NWs, where the anatase and rutile characteristic peaks of TiO₂ could be identified and marked.



Figure 3.2. (a) A SEM image of the TiO2 NWs via the hydrothermal method. (b) XRD pattern of the as-prepared TiO₂ NWs. Scale bar: $1 \mu m$.

As reported, the anatase- TiO_2 is a high efficient catalyst in comparison with other crystalline phases. In order to investigate the performance of the as-prepared TiO₂ NWs, the photocatalysis was carried out in the aqueous solution with Methyl Blue (MB) as the model pollutant (Figure 3.3a). 10 mg TiO₂ NWs was uniformly dispersed in 40 mL of a 10 mM MB aqueous solution, which was initially kept in dark for 30 mins to reach an equilibrium status. After

starting the UV light irradiation, a certain volume of the solution was extracted at a constant interval, which then centrifuged at 10000 rpm for the catalyst removal. The purified solution were characterized via a UV-Vis spectrometer (see Figure 3.3b). The normalized optical absorbance recorded at 667 nm from the decontaminated solution and the stock solution as a control was shown as a function of degradation time. It is seen that the MB dye was decomposed rapidly in the presence of TiO_2 NWs. It is worth noting that the agitated stirrer was employed during the reaction to improve the mass transfer, which also prevented the sedimentation of the TiO_2 NWs.



Figure 3.3. Photocatalytic degradation of MB dye at room temperature. (a) the UV-Visible absorbance spectra of a MB dye with dispersed TiO_2 NWs. (b) normalized MB dye concentration measured at 665nm from (a) with and without TiO_2 NWs as a function of time.

As discussed in Chapter 2, the fixed NWs may be a proper catalyst due to the obvious advantages in recyclability. In this regard, it is essential to introduce a method to grow TiO_2 NWs on the substrate. So far there are many methods against the direct growth of rutile- TiO_2 NWs on the glass and anatase- TiO_2 on the Ti film [^{1,3,15}], whereas only a small number of groups reported the appropriate method for the anatase- TiO_2 NW growth on the glass or flexible substrate [¹⁶]. In this chapter a novel fabrication process was developed regarding the TiO_2 NWs growth. Generally, a colloidal solution combined with the TiO_2 -coated film was used for the direct growth of the NWs on the substrate [^{16–18}], which rendered the uniform NWs with the superior electrical property. Large-scale production remains an issue, however. Here we scaled up this technique by replacing

the TiO_2 film by the anatase- TiO_2 nanopowders and successfully obtained the high quality TiO_2 NWs on both glass and polymer substrates.



Figure 3.4. The schematic of the fabrication of the TiO_2 NWs on the glass substrate.

As depicted in Figure 3.4, the TiO₂ nanoparticles dispersed in ethanol were initially sprayed on the substrate. A uniformly thin TiO₂ layer was formed after the few-hour annealing at the temperature varying from 150°C to 300°C (which is the substrate temperature). The density of the TiO₂ layer was subject to the concentration of the TiO₂ nanoparticles while the adhesion force between TiO₂ and the substrate was mainly derived from the annealing. Before transferred to a Teflon-lined autoclave for the NWs growth, a solution consisting of 0.002 mol K₂TiO(C₂O₄)₂, 30 mL diethylene glycol (DEG) and 10 mL DI water was sonicated for 30 mins. Subsequently the TiO₂-coated substrate was entirely immersed into the solution and followed by the consistent heating at 180 °C for 6 hrs. When the solution was cooled down to the room temperature, the asprepared sample was rinsed by DI water and dried at 150°C for 1 hour in ambient air. Consequently, the TiO₂ NWs were grown on the substrate.



Figure 3.5. SEM images of the TiO_2 NWs via the hydrothermal method grown. (a) on a glass substrate, (b) on a polyimide film. Scale bar: (a) 100 μ m on a large view and 10 μ m in the inset, (b) 20 μ m on alarge view and 5 μ m in the inset.

The TiO_2 NWs on the two different substrates are displayed in Figure 3.5. For the glass substrate (Figure 3.5a), TiO_2 NWs have the uniform distribution, where the random cracks can be attributed to the volume expansion of the NWs during the growth. Compared to the free NWs (Figure 3.2a), the fixed NWs on the glass have a smaller aspect ratio due to the different growth mechanism and the mass-transport limitation, which requires the further optimization. Figure 3.5b reveals TiO₂ in hierarchical structures on a polyimide (PI) film. The hierarchical structures are composed of hemispherical structures of approximately $\sim 2 \mu m$ in diameter and the numerous short NWs spiking out from the dome surface, which is larger than the size of the initial TiO₂ powder (~ 32 nm in diameter). One possibility of this unique structure may ascribe to the agglomeration of the powder during the reaction, preventing the inner nanoparticles from contacting the solution and thus limiting the further growth. Besides, the numerous gaps and defects observed on the entire substrate may be caused by the bending of the substrate and its weak adhesion to the nanoparticles, leading the numbers of structures falling off the surface. The glass possesses the higher adhesion force to the TiO₂ NWs than that of the PI film, which is mainly due to the discrepancy of the surface energy. A proper surface treatment against the polyimide film is necessary to increase the surface energy glass.



Figure 3.6. Photocatalytic degradation of TiO_2 NWs grown on the glass substrate at room temperature. (a) the UV-Visible absorbance spectra change of MB dye with dispersed TiO_2 NWs. (b) degradation of the MB dye with and without TiO_2 NWs catalysts measured by the normalized peak height of (a) at 665 nm as a function of time.

The photocatalytic degradation of the TiO_2 NWs fixed on the glass substrate was implemented at the room temperature (Figure 3.6). A 1 in. by 1 in. glass substrate was immersed into 20 mL of a MB aqueous solution without stirring. Evidently, the MB dye was decomposed in the presence of the TiO_2 substrate. Compared to the suspended NWs, the degradation rate of the TiO_2 NWs fixed on the glass substrate is twice times slower for the first hour, Lower photocatalytic performance of the immobilized catalysts can be attributed to the smaller contact area of the catalyst to the pollutant and the severe mass transport limitation. However the consistent degradability of the immobilized NW catalyst implies its stability in a long-term usage, which is important for developing reliable and highly efficient photocatalysts in the future work.

3.1.2 Electrochemical synthesis of TiO₂ nanotubes

Aside from the TiO₂ NWs, vertically-aligned TiO₂ nanotubes (NTs) are another candidate for immobilized photocatalysts. TiO₂ NTs has been synthesized from the Ti foil or Ti-coated layer and their high surface area render outstanding photocatalytic activity in the aqueous solution [¹⁹], significant improvement in solar cells [²⁰] and high performance in gas sensors [²¹]. In general, those particular NT structures are grown differ from TiO₂ NWs, which are achieved by top-down anisotropic etching rather than bottom-up oriented deposition. Most commonly, the electrochemical anodization method is used to fabricate the tubular structures, where an electrolyte concentration and an anodic voltage are the key parameters to affect its geometry.

Here we used the two-step anodization process at room temperature to produce high quality TiO₂ NT arrays. The electrolyte for the anodization was composed of 0.3 wt% NH₄F, 99.7% wt% ethylene glycol and 2 vol% H₂O. After 15 mins vigorous stirring, the electrolyte was kept in dark for an hour to achieve the equilibrium status. A piece of Ti foil cleaned by acetone, isopropanol and DI water was immersed in the electrolyte serving as a working electrode while a Pt plate as the counter electrode was placed in the same container around ~8 cm away from the Ti foil. The Ti foil was firstly anodized for 30 mins at 20V and sonicated in 1M HCl to remove the produced irregular TiO₂ NTs, leaving the hexagonally arranged grooves on the Ti surface. The Ti foil was subsequently anodized for another 20-30 hours with the anodic voltage varied from 5 V to 30 V. After rinsed by DI water and dehydrated at 60°C, the vertically-aligned TiO₂ NT array could be obtained on the Ti foil surface.



Figure 3.7. SEM images of the TiO_2 NTs via the electrochemical anodization method. (a) one-step anodization, (b) two-step anodization. Scale bar: (a) 1 μ m on the large view and 100 nm in the inset, (b) 5 μ m on the large view and 500 nm in the inset.

As displayed in Figure 3.7, the irregular TiO_2 NTs are observed from the one-step anodization, which may be caused by the defects on the original surface, hindering or accelerating

the local reaction. When this layer was removed, a uniform surface was exposed for the second anodization, leading to a more regular TiO_2 NT array. Furthermore, it is clearly seen that the NT arrays in both cases are free of cracks, implying their superior mechanical stability. According to our experiment, the NT length increases with a higher anodic voltage and/or a longer reaction time, which has good agreement with the previous reports[^{17,22,23}], although the increasing rate of the TiO₂ NTs varies in different electrolytes.



Figure 3.8. SEM images of the TiO_2 NT array. (a) cross-sectional view, (b) bottom view. Scale bar: 200 nm in (a) and 100 nm in (b).

On the basis of the anodization mechanism [¹⁷], the TiO₂ NTs should exhibit a uniform radical dimension along its tubular axis till ended with a round convex structure. This characteristic TiO₂ NT structure can be confirmed in Figure 2.8, where a small flake was scratched off from the anodized substrate (anodized for 34 hrs at 20 V). As depicted in Figure 2.8a, the majority of NTs stand parallel with the similar length, demonstrating that the NTs have high uniformity in anodization. The convex structures of the NTs (Figure 2.8b) further indicate that the NTs possess the similar lengths and dimensions. Moreover, the intact convex ends were obtained thanks to their weaker adhesion to the substrate, which have thicker tube walls than that of the body [¹⁷].

Recently the free-standing TiO₂ NT array films have raised more attention as a transparent photochemical electrode [²⁴]. Therefore significant efforts have been devoted to fabricate a membrane with an array of through-hole TiO₂ NTs. To our knowledge, there are three common

ways associated with the electrochemical anodization method to fabricate the through-hole NT array films: (i) thermally-induced self-detachment [25], (ii) electrically-induced in-situ separation [26] and (iii) vapor-induced etching [19]. We evaluated these techniques and tried to find a reliable and reproducible method to fabricate large-scale free-standing films with opened TiO₂ NT array. To account for our method, we first tabulated the key step of the three techniques (Table 3.1).

	First step	Second step	Third step
Thermally-induced self-detachment	Anodization at 60 V to remove irregular layer	Anodization at 60 V followed by the thermal treatment	Anodization at 60 V to obtain the free- standing film
Electrically-induced in-situ separation	Anodization at 60 V to remove irregular layer	Anodization at 60 V followed by a short- term larger anodic voltage at the end	N/A
Vapor-induced etching	Anodization at 60 V	Dissolve the Ti substrate to obtain the free-standing semi- open tubular film	Apply HF vapor to dissolve the closed bottoms of the free- standing film

Table 3.1. A brief comparison of the three techniques with respect to the through-out free-standing TiO_2 NT array films.

Apparently, the free-standing film of the TiO_2 NT usually demands a higher anodic voltage and a proper self-detaching method. In our work, we also noticed that an anodic voltage higher than 60 V is required to obtain a desired free-standing NT film. In addition, two-step anodization was employed again to acquire the ordered NT array on the substrate. The key step different from the above mentioned techniques is the ultra-sonication in DI water after the secondary anodization, forcing the NT array film to separate from the substrate. As shown in Figure 3.9, the NT film restrains its free-standing form even after sonication. The opaque yellowish color stems from the closed bottom of the film. Moreover, the natural bending occurring on the free-standing film can be attributed to the expansion of the TiO_2 NTs during the experiment. Herein, by using the vacuum filtration and the PDMS-assisted transfer printing [27], the flakes of the TiO₂ NT films could be collected as well. These flakes of the TiO₂ NTs will be applied to the photocatalytic degradation test in the future works. The as-prepared TiO₂ NT array films detached from the substrate will be exposed to vaporized HF to open up the closed end for the electrode and nanofluidic applications.



*Figure 3.9. Optical images of the as-prepared free-standing film of TiO*₂ *NT array.*



Figure 3.10. SEM images of the as-prepared free-standing TiO₂ NT film. (a) a Ti substrate after detachment, (b) the detached TiO₂ NT film. Scale bar: (a) 10 μ m on the large view and 1 μ m in the inset, (b) 10 μ m on the large view and 2 μ m in the inset.

The detached side of the TiO_2 NT film has the convex nanostructures, which should create the corresponding concave nanostructures on the remaining Ti substrate. In Figure 3.10a, the periodical concave nanostructure is observed as the NT film gets peeled off, and shows the smaller dimension, which is in agreement with the growth mechanism [¹⁷]. The angled view in Figure 3.10b displays the uniform NT array fabricated after detached from the substrate, where the parallel tubular structures with a large length is observed.



Figure 3.11. SEM images of the as-prepared free-standing TiO_2 NT film and its corresponding. Scale bar: $1\mu m$.

The crystallinity of the free-standing TiO₂ NT film is shown in Figure 3.11. It clearly exhibits the anatase-TiO₂ NTs staying on the Ti substrate. As discussed above, anatase-TiO₂ is considered as a suitable crystalline phase of the TiO₂ for the photocatalysis. A lot of works have been reported regarding the organic-dye degradation by use of free-standing TiO₂ NT film [^{19,28–30}]. On the basis of these progress, more studies in fabrication of free-standing TiO₂ NT film in larger area and characterization of its photocatalytic activity in various pollutants are of interest to researchers. Besides, more investigations are also desired in the modification of free-standing TiO₂ NT film using numerous doping elements in order to enhance the light absorption in visible spectra region. It can be seen that free-standing TiO₂ NT film is a promising candidate as photocatalysts.

3.2 Synthesis and application of 1D ZnO nanostructures

3.2.1 Hydrothermal synthesis of ZnO NWs for photocatalysts

ZnO is a wide bandgap semiconductor, and various ZnO nanostructures have been applied to a variety of devices, such as light emitting diodes $[^{31-35}]$, solar cells $[^{36-39}]$ and chemical sensors [^{40–44}]. Among many configurations of ZnO nanostructures, vertically-aligned NW array directly integrated onto substrates has demonstrated remarkable enhancements in the device performance. As of now, a number of techniques have been developed to synthesize 1D ZnO nanostructures (e.g. NWs) and can be roughly classified in two primary categories: gas-phase vs. solution-phase processes. Gas phase methods such as chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD) and vapor-liquid-solid (VLS) process provide well-aligned, polycrystalline ZnO NWs. However, the high-temperature nature of these processes limits the type of substrates for the NW growth. In contrast, solution-based approaches such as the hydrothermal method can be used to grow ZnO NWs at relatively low temperatures, but the quality of the NWs is not as good as the ones grown at high temperatures. In this work, we are interested in growing ZnO NWs on flexible plastic substrates, necessitating a low-temperature synthesis route. In order to maximally utilize the beneficial properties of ZnO, we first need to develop a method of growing ZnO NWs onto these substrates.

ZnO NWs grown on thermally-resistant substrates via gas-phase methods have been welldocumented [^{45–48}], which highly ordered, polycrystalline NW arrays have been obtained. Here, we mainly focus on the solution-phase hydrothermal method because it is more applicable to substrates not compatible with high temperatures. Technically, the hydrothermal method can be carried out when there are nanocrystal seeds existing on the surface and the corresponding ions in the solution. Since either Zn or ZnO crystals can be the initial seeds, there are a number of ways to synthesize ZnO NW array. In this work we will introduce two processes to grow ZnO NWs on a Zn foil and glass substrate, respectively. The relevant applications will be discussed with the integration of other fabrication techniques.

To obtain the direct-growth of the ZnO NWs from a bulk Zn substrate, a high purity Zn foil (>99%) was firstly rinsed by acetone, isopropanol and DI water, consecutively. The solution consisting of Zinc nitrates hexahydrate and ammonia hydroxide aqueous solution were prepared and transferred to a Teflon-lined autoclave. The cleaned Zn foil was immersed into the solution and followed by 12-hour heating at 95°C. The ZnO NWs were obtained and further analyzed after rinsed by DI water and dried by N₂.



Figure 3.12. (a) SEM image of the ZnO NWs on the Zn foil. (b) XRD pattern of the as-prepared ZnO NWs. (Scale bar: 200 μ m on the large view and 300 nm in the inset)

The hexagonal ZnO NWs of an average diameter about 80 nm are observed and uniformly distributed on the entire Zn foil (Figure 3.12a). As reported previously [⁴⁹], the aspect ratio of these NWs can be adjusted through the solute concentration, while the NW length is primarily governed by the reaction time. The marked peaks in the XRD pattern represents the characteristic of the wurtzite-ZnO and the intrinsic Zn, with the highest intensity in (002) plane and denoting the preferable orientation along c-axis (Figure 3.12b). Since the photocatalytic activity of these NWs have been well studied before [⁴⁹], we mainly explore its potential application in electrical devices. One advantage of the proposed synthesis method is its reliable connection between ZnO NWs and

Zn foil (i.e. substrate) as NWs directly grown from the foil. This ensures a robust electrical contact at semiconductor-to-metal interface. Here we desire to establish the top electrode onto NW bed to build a diode from vertically-aligned ZnO NW array. The top electrode of the diode can be established combining the blanket transfer (BT) technique [²⁷] followed by isotropic oxygen plasma etching and contact metal deposition. The details of this process and device performance will be discussed in the following section.



Figure 3.13. The schematic of the fabrication sequence for the patternable ZnO NW arrays on the Zn foil. A vertically-aligned ZnO NW array can be obtained as the PDMS cover is removed afterwards.

In order to extend the compatibility of the direct-growth process of ZnO NWs, a modified method has been developed for creating the predictable NWs patterns. The key strategy is illustrated in Figure 3.13. First, liquid prepolymer (PDMA-ODA) of PI 2555 (Dow Co.) was spin-coated on the surface of a cleaned thin Zn foil. After a 1.5-hour annealing at a constant temperature of 150°C, the PI film was fully covered the Zn foil with conformal contact. Then the sample was entirely embedded in the prepared PDMS solution (a ratio of 10 to 1 for prepolymer and curing agent) and solidified together at 60°C for 12 hours. Subsequently, the middle portion of the PDMS layer upon the Zn foil side was removed, exposing the Zn foil surface. The PDMS shell serves a mask layer to selectively grow ZnO NWs and can be simply removed after the synthesis. Finally,

the ZnO NWs with the Zn foil were rinsed by DI water and dried for the further characterization. The applied PI film on the back surface of the Zn foil served as another masking layer, hindering the growth of the ZnO NWs as well as the flexible substrate (Figure 3.15).



Figure 3.14. (a) SEM images of the patterned ZnO NWs on the Zn foil, (b) boundary of the patterned ZnO NWs. Scale bar: (a) 50 μ m on the large view and 10 μ m in the inset, (b) 20 μ m on the large view and 5 μ m in the inset

The SEM characterization of the patterned ZnO NWs is illustrated in Figure 3.14. Evidently, neither a PDMS masking layer nor a PI film affected the growth and quality of the NWs. Uniformly-distributed, high aspect ratio, vertically-aligned ZnO NWs have been synthesized on the Zn foil. A distinctive boundary can be observed in Figure 3.14c, indicating the transition from the ZnO growing region to the PDMS masked region. The PDMS mask layer effectively impeded the solution from seeping into the blocked regions of the foil. One future work may be related to improving the resolution and the quality of the patterns so that this modified method can be utilized to large-scale patterns of ZnO NWs.



Figure 3.15. Schematic diagrams of the fabrication for the differential growth of the ZnO NW arrays on the Zn foil.



Figure 3.16. SEM images of the ZnO NWs grown on the ZnO seeding layer. (a-b) the coated seeding layer was facing up during the reaction, (c-d)) the coated seeding layer was facing down during the reaction. Scale bar: (a) 50 μ m on the large view and 5 μ m in the inset, (b) 5 μ m on the large view and 300 nm in the inset, (c) 10 μ m on the large view and 500 nm in the inset, (d) 10 μ m on the large view and 3 μ m in the inset.

Another capability in using the modified method is growing ZnO NWs in various lengths. As illustrated in Figure 3.15, the hydrothermal method under the same condition was implemented for the as-prepared sample (Figure 3.13d) after a silicone-free blue adhesive film (denoted as blue film) was attached on the PI film. The blue tape worked as the mask layer to prevent the PI film from being attacked by the solution. We found that a fully-cured PI film was slowly dissolved in the solution, and the blue film was more resistant to the solution. The PI film is indispensable since the blue film alone cannot create a conformal contact to the foil surface and act as a supporting membrane to hold grown NWs. After a certain period of time, the various length of the NWs was obtained upon the front surface of the Zn foil. This architecture of ZnO NWs on the PI membrane can be applied to some flexible devices in the future. Despite the achievement of the direct-growth method, the alkaline solution needed for the hydrothermal synthesis limits the type of the substrates. The substrates not compatible with the alkaline solution entail other synthesis methods. Recently the in-situ growth technique based on a ZnO seeding layer gains popularity in fabricating crystalline ZnO NWs because of the cost-effectiveness and scalability [^{45–48,50–53}].



Figure 3.17. The schematics of the fabrication sequence for the patternable ZnO NW arrays on the glass substrate.

To synthesize ZnO NWs on the glass, a ZnO seeding layer should be prepared first. Herein, the seed solution consisting of zinc acetate dehydrate (Sigma Aldrich) and ethylene alcohol (200 prove) was stirred for 2 hours at 60 °C. Prior to spin-coating on a glass plate which was consecutively cleaned by acetone, isopropanol and DI water, the mixed seed solution was aged at room temperature for 1 hour. The glass coated with the ZnO seeding layer was then annealed at 150°C for 2 hours and subsequently soaked in the growth solution composed of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA). The hydrothermal method entails constant heating at 90°C for 6 hours in the oven. The as-prepared sample was rinsed by DI water and

dehydrated at 60°C in the ambient air afterwards. Note that the coated seeding layer on the glass is suggested to be placed facing down, avoiding the sediments from settling on the ZnO NW array.



Figure 3.18. (a) A SEM image of the patterned ZnO NWs via the ZnO seeding layer, (b) XRD pattern of the as-prepared ZnO NWs. Scale bar: 1 mm on the large view and 10 μ m in the inset.

The effect of a glass placement during the NW synthesis is shown in Figure 3.16. There is an obvious discrepancy in the morphology of the ZnO NWs. As seen in Figure 3.16(a-b), the NWs disorganized NWs with various lengths/diameters and orientations are originated from the sediments during the reaction when the growth substrate is placed facing up at the bottom of the solution. On the other hand, the vertically-aligned NWs with a tighter dimensional control, as shown in Figure 3.16(c-d), have been synthesized when the growth substrate is held facing down during the reaction. These NW array are uniformly distributed across the whole glass substrates. From the cross-sectional view in Figure 3.16b it clearly shows that the sediments are deposited on top of the uniformly grown, vertically-aligned NW array. Compared to the NWs in Figure 3.16d, the smaller aspect ratio of the NWs in Figure 3.16b can be found and attributed to the sediments, covering the NW array and impeding its further growth. In case of the growth substrate facing down, much fewer sediments are observed atop the NWs (see Figure 3.16d).

Similar to the ZnO NWs on a Zn foil, the NWs on a Si wafer substrate can also be patterned. The patterns in the experiment were basically created through photolithography. The key strategy of patterning NWs is displayed in Figure 3.17. A ZnO seeding layer was initially spin-coated on the cleaned glass substrate and annealed at 150°C for 1.5 hours. Afterwards, photolithography was carried out on the seeding layer by spin-coating, baking, developing and post-baking a photoresist (PR, S1813) layer, consecutively. The patterned glass substrate was then transferred to the growth solution for synthesizing NWs under the same condition as previously described.

The SEM image (Figure 2.18a) demonstrates the NWs were successfully patterned on the substrate. However, the obtained patterns were not as good as expected in term of the resolution and quality. A possible cause is the dissolution of the PR into the growth solution, resulting in the unknown side reaction. More work will be geared towards selecting a proper PR to reduce undesirable reactions and developing a technique for large-scale patterning. Figure 3.18b shows the XRD pattern of the ZnO NWs on the Si wafer via ZnO seeding layer. As discussed above, the recognized peaks are assigned to the wurtzite-ZnO, where the peak with the highest intensity implies the c-axis-preferable growth of the NWs.

With the increasing demands of the electrical devices, the NWs are expected to be synthesized not only on rigid substrates but also on flexible substrates. Solution-base synthesis techniques become more popular since the majority of the flexible substrate can only survive in the mild growth solution at relatively low reaction temperatures. In the following work, a modified hydrothermal method was employed to fabricate the NWs on the PDMS film, which has a few important advantages in term of the adhesion and flexibility.

3.2.2 Hydrothermal synthesis of ZnO NWs for electronic devices

ZnO is one of the most attractive metal oxide semiconductors due to its remarkable properties in electromechanical, optoelectronic and electrochemical, which have been widely applied to various applications such as LED, solar cell, chemical sensor and flexible and transparent electronic devices [⁴⁸]. A number of processes have been reported for the synthesis of the one dimensional ZnO nanostructures, including chemical vapor deposition (CVD), hydrothermal synthesis, electrochemical growth and vapor-liquid-solid (VLS) process. Among them the hydrothermal method allows us to grow vertically-aligned ZnO nanowire (NW) array in multiple crystalline orientations at the low temperature [⁵⁴]. To fully utilize the inherent ZnO NW structures, it is our interest to construct large parallel arrays of ZnO NW devices for various electronic and optoelectronic applications by establishing a porous top electrode. Compared to the conventional NW device architecture (i.e., individual NWs lying on the substrate between two electrodes), the vertically aligned NW device could mitigate device unreliability due to variability in NW dimensions and minimize size-dependent noise sources [⁵⁵]. One fabrication approach to 1D ZnO NW array device relies on transferring the ZnO NW array to a particular substrate which may lose certain amount of nanowires as well as the original array uniformity [⁵⁶]. It is still a challenge to efficiently use the ZnO NW arrays on its predetermined substrate.

In this work we develop a novel method for fabricating a gas sensor device directly on asprepared ZnO NW arrays. This approach is compatible with various nanowire arrays grown on their original substrates. The ZnO NW arrays in high aspect ratio is synthesized on the zinc substrate. A robust blanket transfer technique is employed to transfer a thin layer of photoresist onto the ZnO NW tips. A uniform porous electrode is fabricated onto the tips of ZnO NW arrays. The ZnO NW arrays with the porous electrode can be utilized as a gas sensor substrate for further tests.

A scheme of the fabrication of ZnO NW array with the porous electrode is shown in Figure 3.19. Firstly a cleaned zinc foil was soaked in the aqueous solution with zinc nitrite and ammonium hydroxide. After 10 hours heating at 100°C in a Teflon-lined autoclave, the foil was rinsed with

DI water and blow dry. A PDMS stamp, spincoated with a thin layer of photoresist, was brought into an intimate contact to the foil surface at 120°C. The photoresist layer was transferred onto the ZnO NW array by slowly peeling off the PDMS stamp, consequently [²⁷]. Oxygen plasma etching was then used to partially expose the tips of the ZnO NWs. A thin Aluminum film was subsequently angle-deposited to create the top porous electrode. Afterwards, a secondary oxygen plasma was applied to remove the rest photoresist underneath the Al layer. The final device only consist of porous electrode, ZnO NW array and Zn substrate.



Figure 3.19. The scheme of the fabrication for the ZnO NW arrays sensor. Highly ordered ZnO NWs were grown on the zinc substrate vertically.

The as-prepared vertical-aligned ZnO NW array in high aspect ratio is shown in Figure 3.20a. The gap between neighboring ZnO nanowires is equally, ensuring the even transferring of the photoresist layer. The continuous ZnO NW array also prevent the direct contact between photoresist and bare Zn substrate. By using focused ion beam (FIB) a pattern was created on the substrate (Figure 3.20(c-d)), where a 3 μ m thick oxidized ZnO NW layer could be identified lying on the substrate, homogenously. Apparently a number of ZnO NW arrays stack on the Zn substrate, whose crystallinity gradually increase along with the depth of substrate. A finite annealing could
change the crystalline but not the morphology of the substrate, which means the ZnO layer would permanently separate the contact of the Zn substrate and the electrode.



Figure 3.20. SEM of the ZnO NW array on the zinc substrate (a) after 10 hours hydrothermal treatment. ZnO NWs in high aspect ratio were distributed uniformly on the substrate, (b) after Al electrode fabricated. Porous is observed along each ZnO nanowires, which size is corresponding to the diameter of the nanowires. Angled view of the ZnO NW array after FIB patterning. ZnO NWs at the boundary was partially cleaved by FIB in (a). Multiple ZnO NW network layers are observed in (b). Scale bar: (a-b) 10 μ m in the large view and 3 μ m in the inset, (c-d) 1 μ m.

Due to the non-flat topography of the substrate, after the transferred photoresist layer uniformly infiltrate and encapsulate the tip of ZnO NWs, the after-etching nanowire density on the surface is lower (Figure 3.20b). The porosity and porous size of the top electrode film could be simply managed by etching the exposed tip height and the deposition angle. In this experiment the porous size of the electrode is fabricated around 300 nm in diameter and the corresponding porosity is about 10 %-12 %. The Al layer in 80 nm is compatible with this design without any collapse. With the top electrode the electrical property of the device is obtained, a smooth curve obtained in Figure 3.21 proves the robust contact between the electrode and the ZnO NWs, demonstrating the reliability of this fabrication process. This structure is proposed as a potential gas sensor, whose high porosity allows sufficient gas flowing in and contacting to the ZnO NW array, resulting a sensitive current-voltage change.



Figure 3.21. I-V curve of as-prepared ZnO NW array, which behavior is corresponding to the typical diode.

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CHAPTER 4

ZNO NANOWIRES/SI NANOCRYSTALS HETEROSTRUCTURES AS IMMOBILIZED PHOTOCATALYSTS FOR PHOTODEGRADATION

4.1 Introduction

Various forms of ZnO nanostructures have attracted considerable attention as one of the most efficient catalysts for the photocatalytic degradation due to their high specific surface-area, direct bandgap, rapid carrier transport, and strong oxidation ability [1-4]. ZnO is also an abundant, environmentally friendly material, and it is easy and inexpensive to grow its nanostructures [⁵]. Under UV light irradiation, organic pollutants in waste water streams can be decontaminated in the presence of ZnO nanostructures, where the photogenerated electrons and holes travel to the catalyst surface and produce highly oxidizing species such as hydroxyl radicals and super oxide ions [⁶] responsible for degradation reactions. Despite their remarkable photocatalytic activity, ZnO nanostructures suffer from the rapid recombination of photogenerated electron-hole pairs and low utilization of the solar spectrum due to their limited spectral response to visible light [⁶]. Considering the UV region covers a small fraction (4~5%) of the solar spectrum, photocatalysts with the better optical absorption in the visible spectrum (~ 43% of solar spectrum) will lead to the increased utilization of solar energy. The key to the improved photodegradation performance under sunlight is the development of functional materials that extend the absorbance spectrum to the visible region and enhance photoexcited charge separation for reduced electron-hole recombination. .

Tremendous efforts have been made to boost the optical response of the wide bandgap ZnO (~3.2 eV) in the visible region, including metal doping (e.g., Al[⁷], Ag[⁸], As[⁹], Fe[¹⁰], Mn[¹¹], Sb[¹²], Li[¹³]), non-metal doping [¹⁴] (e.g., N-ZnO [^{15,16}], C-ZnO [^{17,18}], S-ZnO [¹⁹]), dye sensitization [²⁰], noble metal decoration (e.g., ZnO/Au [²¹], ZnO/Ag [²²], ZnO/Cu[²³]), and

coupling with narrow-bandgap semiconductors [⁵]. Among them, the latter two approaches have been investigated as promising hybrid materials for photocatalysis because ZnO-metal or ZnOsemiconductor heterojunctions suppress carrier recombination by trapping electrons at the interface and enhance the optical absorption by effectively narrowing down the bandgap $[^{24-28}]$. However, noble metal nanoparticles are relatively expensive, and the metal loading and deposition method need to be carefully controlled for optimal performance (especially important for a ZnO core decorated with metal nanoparticles). Instead, hybrid materials of ZnO and semiconductor nanostructures with a narrow bandgap exhibit superior charge separation as well as enhanced light absorption capability since both base and add-on materials can directly absorb light energy ⁵. Up to now, ZnO has been coupled with various narrow-bandgap semiconductors for better photocatalytic functionality, including CuO/Cu₂O [^{29,30,27}], CdS/CdTe/CdSe [^{31–33}], WO₃ [²⁸] and Fe₂O₃ [³⁴]. Here, a relatively unexplored element that forms a hybrid structure with ZnO will be investigated in the context of photocatalysis – ZnO/Si heterogeneous nanostructures. Si is highly advantageous because of its abundance and environmental friendliness, and its nanostructures are well studied in terms of its fabrication and characterization. In particular, Si nanocrystals (Si NCs) have been extensively investigated as a non-toxic, chemically-stable, and bandgap tunable component for solar cells $[^{35,36}]$, light emitting devices $[^{37-40}]$, and other optoelectronic applications [^{41,42}]. Therefore, Si-NCs are a promising material to form ZnO-based heterostructures for environmentally-friendly and visible-light active photocatalysts.

Another important factor to be considered in developing photocatalysts for water decontamination is recyclability [^{43,44}]. Most photocatalysts, which are typically in the form of spherical nanoparticles, are synthesized and tested in a suspension, requiring an additional process to remove the photocatalysts from the treated water. Immobilized photocatalysts could eliminate

this costly separation step [^{43,44}], but their performances are limited due to the reduced surface area of the photocatalysts that are partially embedded into (or deposited onto) the substrate. One approach to increasing the effective surface area of the immobilized photocatalysts is to harness vertically-grown one-dimensional nanostructures (e.g. nanowires/nanorods [^{45–47}] and nanotubes [⁴⁸]) for improved photocatalytic performance. In particular, ZnO nanowires (ZnO NWs) are easier to directly grow on a substrate at a high aspect-ratio compared to other semiconducting photocatalysts (e.g. TiO₂) and exhibit high crystallinity for efficient charge transport. There are several reports on ZnO-NW-based heterostructures for photocatalytic applications [^{3,49,50}], but to best of our knowledge, Si NCs in conjunction with ZnO NWs have not yet been investigated for photodegration and other optoelectronic applications.

In this work, novel hybrid structures of Si nanocrystals/ZnO nanowires (Si-NCs/ZnO-NWs) were synthesized for the first time as immobilized photocatalysts for pollutant degradation. The Si-NCs, which possess tunable bandgap (1.2 ~2.8 eV), extend the light absorption of ZnO NWs into the visible spectrum and facilitate the charge carrier separation. The detailed morphology of the hybrid nanostructures seemed to have a significant influence on the photocatalytic performance; and therefore, the systematic study of the Si-NC loading effect on the light absorption, photoluminescence, and photodegradation was conducted under various illumination conditions to reveal the possible mechanism of the enhanced photodegradation from the Si-NCs/ZnO-NWs hybrid structures at the optimal Si-NC loading.

4.2 Experimental

4.2.1 Synthesis of ZnO NWs

All reagents used in this experiment were commercially available without further purification. ZnO NWs were synthesized via the hydrothermal method [⁵¹]. The detailed process

is given as follows: a ZnO seed solution was prepared by adding 10 mM Zn(CH₃COO)₂·2H₂O (99.9% Sigma Aldrich) into ethanol (200 prove, Fisher Scientific) and stirred at 58°C for 2 hours. The mixed solution was spin-coated onto a cleaned glass or Si substrate (25 mm by 25 mm in size) multiple times at room temperature. The substrate was then kept at 150°C for 1 hour to promote the adhesion of the seed particles to the substrate. The growth solution was composed of 25 mM Zn(NO₃)₂·6H₂O (Sigma Aldrich) and 25 mM hexamethylenetetramine (HMTA, Sigma Aldrich). Prior to the synthesis, the growth solution was preheated in a convection oven at 90°C for 1 hour to achieve a thermal equilibrium. The substrate was then immersed into the solution at 90°C for 6 hours for ZnO NW growth. After removal from the solution, the substrate with ZnO NWs was thoroughly rinsed by DI water and blown dry. A 3-hour-long dehydration step at 60°C was carried out for the substrate afterwards.

4.2.2 Synthesis of Si nanocrystals

Silicon Nanocrystals (Si NCs) were synthesized using a non-thermal plasma reactor in a fully gas phase process. This process was originally developed by Mangolini et al. [52] and has been well-studied for several other nanoparticles' synthesis [$^{53-55}$]. Besides producing high quality nanoparticles, gas phase synthesis has several other advantages including accurate size control, adjustable particle structure, lesser degree of agglomeration, and hydride-terminated surfaces. The flow-through plasma reactor consists of a quartz tube with varying outer diameters of 0.5 inch and 1 inch in the top and bottom parts, respectively. The lengths of the contraction and expansion region are 7 inch and 5 inch with the total length being 1 ft. Argon (Ar) was used as a background gas with silane (SiH4, 1% in Ar) as a precursor for Si NCs. The gas mixture was flown through the quartz tube around which a pair of copper electrodes are wrapped. Hydrogen (H₂) was flown

through the sidearm into the effluent of the plasma to provide additional hydrogen termination and reduced dangling bond densities [⁵⁶]. The gas flowrates were 30 standard cubic centimeters per minute (sccm) of Ar, 80 sccm of Ar/SiH₄, and 50 sccm of H₂, and the pressure in the reactor was kept constant at 2.75 Torr using a slit-shaped orifice. Radiofrequency (rf) power at 25 W was applied to the copper electrodes using a 13.56-MHz power supply and an impedance matching network. The Si-NCs synthesized using this recipe were approximately 4-5 nm in diameter.

4.2.3 Surface Functionalization Process for Si NCs

As-produced Si-NCs were surface-functionalized in a thermal hydrosilylation reactor [57]. Si-NCs were collected via diffusion onto a stainless steel mesh for this purpose. A functionalization solution was prepared by mixing mesitylene and 1-decene in a volume ratio of 5:1, and was dried and degassed using molecular sieves (size 4 Å) and nitrogen bubbling. This solution was then mixed with Si-NCs (concentration approximately 1 mg/mL) and sonicated for a few minutes (until the Si NCs were no longer agglomerated at the bottom of the container). This final solution was heated for about 2 hours under a nitrogen flow at 170°C in a refluxer to recondense any evaporated solvents. When the reaction was over, the solution became a clear colloidal liquid rather than a cloudy dispersion. These surface-passivated Si NCs were then dried and redispersed in toluene. Quantum yield (QY) measurements were performed right after the functionalization and found to be 40 – 60%.

4.2.4 Preparation of Hybrid Structure

After the surface functionalization, the Si-NCs of 5 mg/mL were spin-coated on the asprepared ZnO-NW substrate at 500 rpm for various times to control the Si-NC loading. In this experiment, three different loadings of Si NCs, i.e., $5 \mu L$, $10 \mu L$ and $15 \mu L$, were applied to the ZnO-NW substrates and named as ZS1, ZS2 and ZS3, respectively. For the comparison, a ZnO-NW substrate was prepared and denoted as ZS0. The subsequent dehydration step was performed for these hybrid structures at 40°C in vacuum for 3 hours to improve the adhesion of Si-NCs to ZnO NWs.

4.2.5 Materials Characterization

The morphology, crystallinity and composition of three Si-NCs/ZnO-NWs hybrid structures and the bare ZnO NW sample were characterized using micro-Raman spectroscopy, X-ray diffraction (XRD, Bruker-AXS), scanning electron microscopy (SEM, JEOL 6610LV, Hitachi S-4700II), energy-dispersive X-ray spectrometer (EDS, JEOL 6610LV), and transmission electron microscopy (TEM, JEOL 2200FS). X-ray photoelectron spectrometer (XPS, Perkin Elmer Phi 5600 ESCA), Fourier transform infrared spectroscopy (FTIR, Bruker Alpha). The optical response of the as-prepared samples was obtained by photoluminescence (PL) spectroscopy with the excitation wavelength at 337 nm and the emission filtered by a 345 nm long pass filter. The PL lifetime of the Si NCs was collected using a pulsed nitrogen laser excitation source ($\lambda = 337 nm$, pulse duration = 10 ns, and repetition rate = 20 Hz)_with a photomultiplier tube used for detection. The signal was filtered by a 345 nm long pass filter and a 675 nm +/- 50 nm band pass filter before detection to spectrally isolate the emission from the Si NCs. Diffuse reflectance from the samples was measured with a PerkinElmer LAMBDA 1050 UV/Vis/NIR Spectrophotometer with an integrating sphere attachment.

4.2.6 Photodegradation Assessment

Under UV light: The photocatalytic degradation was carried out in an aluminum foil-sealed case equipped with a magnetic stir plate. Two 9 W florescent tubes (Philips, $\lambda = 375$ nm) were positioned 13 cm above a dye solution container. Methylene blue (1.5%, Sigma-Aldrich) was diluted to 10 mM and used as a model pollutant. The substrate (cut into 5 mm by 5 mm) with the given Si-NCs/ZnO-NWs hybrid structure was immersed in the dye solution (12 mL). Before irradiation, the dye solution was kept in dark for 30 min to establish the absorption-desorption equilibrium. Upon irradiation, 1 mL of solution was extracted from the container at a constant time interval (typically 30 min) and centrifuged at 10,000 rpm for 2 min. The purified solution was then examined by a UV-vis spectrometer to measure the absorption of the remaining methylene blue. The experiment was repeated a few times to determine the relative error and compared to that of the substrate with ZnO NWs.

Under visible light and white light: A 250 W Halogen light was employed as a white light source. Before irradiation, a solar-filtered transparent film (ENP® ultra clear 7225) was placed between the light source and the dye solution. This film rejects 96% and 75% of UV and infrared lights, respectively, and transmits 72% of visible light. Except for the 30-cm-distance of light source, the remaining procedures were the same as that of the photodegradation experiment under the UV light. The temperatures at both sides of the transparent film were 30°C (dye solution side) and 50°C (light source side) 6 hours after light was turned on. Repeat the experiments under the same condition in the absence of solar-filtered transparent film for the white light irradiation. The temperatures of solutions in all experiments were kept below 28°C during 6-hour irradiation.

4.3 Result and discussion



Figure 4.1. Top-down and cross-sectional SEM images of the as-prepared SiNCs/ZnO-NWs hybrid structures: (a) and (e) for ZS0, (b) and (f) for ZS1, (c) and (g) for ZS2, (d) and (h) for ZS3. Scale bar: 10 μ m in (a) – (d); 500 nm in the inset of (a) – (d); 2 μ m in (e) – (h).

The ZnO NWs were synthesized on a glass or silicon substrate by the standard hydrothermal method, and the resulting NW structures were consistent with those reported in the literature [^{58–61}]. The Si NCs were synthesized via a non-thermal low pressure plasma process and subsequently functionalized to stabilize the nanocrystals and reduce the surface oxidation. The Si NC diameter was carefully controlled to be around 5 nm. Figure 4.1 shows the top-down and crosssectional scanning electron microscopy (SEM) images of the bare ZnO-NW sample (ZS0) and the ZnO-NWs/Si-NCs hybrid samples with the three different Si-NC loadings (ZS1, ZS2, and ZS3). The vertical ZnO NWs of a hexagonal shape with the diameter of 50 to 80 nm and the length of 1.5 to 2 μ m were uniformly grown on the Si or glass substrate, where the average density of the ZnO NWs is estimated to be around 10/ μ m². The Si-NC loading was adjusted by the number of times that spin-coating of a given aliquot (5 μ L) was applied onto the ZnO–NW substrates.



Figure 4.2. Top-down and cross-sectional SEM images of the as-prepared SiNCs/ZnO-NW hybrid structures with heavy Si loading, Scale bar: 10 μ m in (a); 500 nm in the inset of (a); 2 μ m in (b).



Figure 4.3. SEM/EDS elemental mapping of bare ZnO-NW and Si NCs/ZnO NWs hybrid samples: (a) ZS0; (b) ZS1; (c) ZS2; (d) ZS3. Zn in Red, O in blue and Si in yellow. The respective weight fractions of Zn and Si are: Zn 85.2% in ZS0; Zn 80.1% and Si 1.7% in ZS1; Zn 70.7% and Si 5.6% in ZS2; Zn 61.2% and Si 8.5% in ZS3. Scale bar: 5 µm.

During the spin-coating process, the Si-NC suspension partially embedded into the voids between the ZnO NWs, depositing the NCs on the NW surface. As seen from Figure 4.1(a-d), the gaps between ZnO NWs were gradually filled with Si-NCs with increasing loading. The crosssectional views (Figure 4.1(e-h)) reveal that most Si-NCs remain agglomerated around the NW tips after the deposition and tent over the ZnO NWs. The sample with the highest Si-NC loading (ZS3) shows the formation of the continuous layer (dark cloudy layer in Figure 4.1h). If the loading further increases, the extra Si-NCs fully encapsulate the entire NW array and create a thick overdeposited layer (see Figure 4.2). When this hybrid structure with the heavy Si-NC loading is irradiated, photons from both UV and visible regions are mostly absorbed by Si-NCs before reaching ZnO NWs. Therefore, it is difficult to consider it as the hybrid structure because the optical response is dominantly determined by the thick Si-NCs. This also means that there would be an appropriate Si-NC thickness (or coverage) which avoids significant blockage of the light transmitting to the ZnO NWs and yet allows the benefits of the hybrid structures.

Elemental analysis using energy-dispersive x-ray spectroscopy (EDS) was performed on these four samples (ZS0, ZS1, ZS2, and ZS3) to reveal the relative mass ratio of Zn and Si. Figure 4.3 in the Supplementary Information shows the top-down SEM views of the four samples and corresponding EDS elemental mapping spectra for Zn, O, and Si. The elemental ratios of Zn to Si for ZS1, ZS2 and ZS3 are 47.12, 12.63 and 7.2, respectively, demonstrating the increased quantity of Si for the higher loading of Si NCs. All three samples show that the signals for Si are evenly distributed across the images, indicating that Si-NCs was applied onto the substrates in a homogenous fashion. The similarity of the respective distribution between Zn and Si in ZS1, ZS2 and ZS3 also depicts the intimate attachment of Si NCs to ZnO NWs over the substrate, where the element concentration of Si fluctuates along the morphology of ZnO NW array.



Figure 4.4. TEM images of (a) bare ZnO NW sample (ZS0), (b) synthesized and functionalized Si NCs, (c) Si-NCs/ZnO-NW hybrid structure prepare from ZS2. Scale bar: 5 μ m in (a) and (c). (d) XRD patterns of ZS0 and ZS3, (e) FTIR of ZS0.

Figure 4.4a show the TEM image of the bare ZnO NW (ZS0), in which the lattice fringes (~ 0.26 nm) are in a good agreement with the distance between two (0001) planes of wurizite ZnO [⁶²]. The TEM image of one of the Si-NCs/ZnO-NWs hybrid nanostructures (ZS2) is shown in Figure 4.4b. The Si NCs of various crystal orientations were observed continuously surrounding the ZnO NWs. The lattice fringes indicate that both ZnO NWs and Si NCs in the hybrid nanostructure maintain the crystalline structures. The XRD patterns of ZS0 and ZS3 were exhibited in Figure 4.4c. All the peaks appearing on both samples correspond to the wurtzite phase of ZnO NWs [^{24,61,63}], where the peak (002) with the highest intensity depicts the preferable growth direction [0001] of ZnO NWs. The absence of Si-specific peaks from ZS3 (red) presumably ascribes to the low volume fraction of Si NCs. The Fourier Transform Infrared Spectra (FTIR) of

ZS0 was collected in the range of $500 \sim 4000 \text{ cm}^{-1}$. As displayed in Figure 4.4d, the peaks at 3393 cm⁻¹ and 1413 cm⁻¹ correspond to the stretching vibration mode and bending vibration of the O-H group, respectively. A strong peak at 1557 cm^{-1} is attributed to the C=O stretching vibration. The peaks observed at 886 cm⁻¹ and 570 cm⁻¹ indicate Zn-O stretching, while the peaks at 2361 cm⁻¹ and 2966 cm⁻¹ can be assigned to C-H stretching [^{64–66}].



Figure 4.5. Raman-scattering spectra of (a) the bare ZnO-NWs (ZSO) and three SiNCs/ZnO-NWs hybrid structures (ZS1, ZS2, and ZS3), (b) ZSO showing four Raman peaks of bare ZnO.

Figure 4.5a shows the room-temperature Raman scattering spectra of the bare ZnO NWs (ZS0) and three Si-NCs/ZnO-NWs hybrid structures (ZS1, ZS2, and ZS3), confirming their crystallinity. For ZS0, four Raman peaks are shown in Figure 4.5b, where the peak with the highest intensity at 440 cm⁻¹ is assorted to E_2 (high) [⁶⁷], associated with the characteristic of wurtzite ZnO. The three other peaks located at 340 cm⁻¹, 378 cm⁻¹, and 584 cm⁻¹ are assigned to A₁ (TO), E₁ (TO), and E₁ (LO), respectively. There is another peak obtained at 101 cm⁻¹ (data not shown) for E_2 (low), matching previous reports [^{67,68}]. The Raman spectra for the hybrid structures show one additional peak at 515 cm⁻¹, corresponding to TO of Si NCs. The peak position of the Si NCs detected at 515 cm⁻¹ is different from that of single-crystal Si at 521 cm⁻¹, which is attributed to the lattice expansion of Si NCs [⁶⁹]. The observed broadening of the peak with a large FWHM is due to the ZnO peak at 535 cm⁻¹, which belongs to A₁ (LO) mode. Furthermore, the peak with the

asymmetric shape deviated from the Lorentzian function indicates that the size of Si NCs is down to sub-micro scale in term of the electromagnetic radiation theory [^{70,71}]. By comparing the Raman peaks of each ZnO NW with different Si-NC loadings, especially A1 phonons, it can be concluded that no significant peak shift and broadening are observed, suggesting the stable formation and reproducible synthesis of the hybrid structures.



Figure 4.6. (a) Room-temperature PL spectra of the bare ZnO NW sample and three Si-NCs/ZnO-NWs hybrid samples, (b) the same PL spectra with the magnified scale to better show the peaks related to oxygen defects of ZnO; (c-e) schematic diagrams of ZSO (c), ZS1 (d), and ZS2/ZS3 (e); (f) time-resolved PL decay of the SiNCs on the ZnO NWs for the three hybrid samples (signal filtered at 675 nm +/- 50 nm), (g) a bi-exponential fit of the PL decay.

Room temperature photoluminescence (PL) spectra (see Figure 4.6a) were measured to investigate the role of Si NCs on the luminescent properties of the hybrid structures. The narrow peaks at 380 nm from all four samples can be attributed to the near-band-edge (NBE) emission of ZnO, mostly related to the recombination of free excitons through an exciton-exciton collision process [^{72,73}]. Another small and broad peak at 570 nm from ZSO (see Figure 4.6b) may originate from the recombination of electrons with oxygen vacancies and photogenerated holes in the valence band, which is typically related to the defect concentration of ZnO[^{68,74}]. Therefore, the strong NBE emission and weak green emission in the PL spectrum suggests that the hexagonal-shaped ZnO NWs have good crystallinity and optical properties. The magnified plot of Figure 4.6b shows that the weak defect-related emission peaks for ZS1, ZS2 and ZS3 are mostly overwhelmed by the strong and broad luminescence peak of Si NCs in the range between 500 and 900 nm [^{75,76}].

It can be observed that the ZnO NBE emission peak was initially suppressed at the lowest Si-NC loading (ZS1) and was then significantly enhanced at a higher loading (ZS2). But the further increase in the loading (ZS3) reduced the NBE emission. To account for this irregular trend, the different morphological models of the hybrid nanostructures are shown in Figure 4.6(c-e) as a function of Si-NC loading. The model in Figure 4.6c corresponds to the bare ZnO NWs (ZS0) while two models of two different Si-NC loadings are constructed in Figure 4.6d and e based on the SEM images (Figure 4.1b and f). When incorporated with a small quantity of Si NCs, the ZnO NWs in ZS1 was partially covered by the NCs. In this case, both ZnO NWs and SiNCs were simultaneously activated under light irradiation. The Si/ZnO junction facilitated the separation of photogenerated charge carriers, resulting in the quenching of NBE emission [⁷⁷]. In addition, the surface passivation of the ZnO NWs derived from the Si NCs may have reduced the surface defect sites (i.e. recombination centers) and led to lower radiative recombination. On the other hand, ZS2

and ZS3 (Figure 4.1e and h) can be represented as the model in Figure 4.6e, where the tips of ZnO NWs are completely covered by the Si-NC layer. It has been reported that charge carriers transportation in ZnO/TiO_2 hybrid nanostructures may cause the ZnO conduction band (CB) to bend upwards due to electron trapping at the interface, which acts as an energetic barrier impeding further electron transfer from the TiO₂ [⁷⁸]. Likewise, the majority of photons were absorbed by Si NCs and the excessive electrons generated within the Si NCs accumulated at the Si-NCs/ZnO-NWs interface, which formed a barrier to hinder the transportation of charge carriers across the Si/ZnO junction. Consequently, radiative recombination within ZnO NWs was promoted, leading to the stronger NBE emission of ZnO. A further comparison of the PL intensities at 380 nm for ZS2 and ZS3 (see Figure 4.6a) indicates that the NBE emission intensity decreases as the Si-NC loading further increases. Note that only the Si NCs in direct contact with or close proximity to ZnO NWs are highly effective in surface passivation and charge injection. The reduced PL intensity from ZnO with a higher Si-NC loading can be attributed to extra Si NCs blocking photons reaching the ZnO NWs and excitons emitting from ZnO. This "screening" effect undercuts the gains obtained from the enhanced charge transfer at the hybrid interfaces. For example, SEM imaging from the sample with the heavy loading (ZS3) shows the thick Si-NC layer deposited on top of the NWs (see Figure 4.1(g-h)). Incident photons would be first absorbed in that layer and create the electron-hole pairs within the Si NCs. But the charge carriers that were generated far away (even a couple of NCs away) from the NWs would be recombined within the Si NC layer and could not get injected into the ZnO NWs. Now fewer photons are available to excite the ZnO NWs while the emitted energy has to pass through the Si-NC layer, thereby causing a net negative effect on NBE emission. Meanwhile, the characteristic PL peaks for Si NCs are observed around 730 nm (\pm 170 nm) for all hybrid structures. As expected, the sample with the higher Si-NC loading produced the increased PL intensity (i.e., ZS3 > ZS2 > ZS1).

Figure 4.6f shows the time-resolved PL decay of the Si NCs on the ZnO NWs (signal filtered at 675 nm \pm 50 nm). Each PL decay is normalized by its maximum intensity for ease of comparison. The corresponding fast and slow decays of the three hybrid nanostructures were identified through a bi-exponential fit (R² > 0.99 for all fits) using $y = y_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) +$ $A_2 \exp\left(-\frac{t}{\tau_2}\right)$. According to Figure 4.6g, the fitted fast PL decay time constants (τ_1) are 4.78 µs, 5.96 µs and 6.32 µs for ZS1, ZS2, and ZS3, respectively, while the corresponding slow PL decay time constants (τ_2) are 42.64 µs, 46.06 µs and 55.45 µs. Previous studies from literature have correlated the fast PL decay in the Si NCs to the average carrier lifetime of a non-radiative recombination process while the slow one describes the radiative recombination process [^{79,80}]. The latter mechanism is more relevant to the NBE emission, and therefore, an emphasis is placed on τ_2 . Note that the average exciton lifetime of the room-temperature PL process in pure ZnO NWs is reported to be around hundreds of picosecond to few nanosecond $[^{81,82}]$ whilst the average exciton lifetime of Si NCs is approximately 80 μ s [⁸³]. In the current system, a shorter lifetime of τ_2 was observed at the lower Si-NC loading possibly because the photogenerated electrons in the Si NCs, after being injected into ZnO, would undergo the recombination process at a faster rate. This reduction in PL lifetime for the Si-NCs can be explained as the result of electron transport from the NCs into the ZnO NWs, as has been observed for quantum-dot-sensitized solar cells (QDSSCs) and other hybrid NC/receptor materials based on cadmium chalcogenide nanocrystals. At high Si-NC loading, the PL lifetime is dominated by the long lifetimes that are typical for silicon

nanocrystals. At lower Si-NC loading, the PL lifetime is reduced as a result of exciton dissociation

and electron transport into the ZnO NWs, driven by the energy band alignment between the two materials which is favorable for electron transfer to ZnO.

Therefore, the exciton lifetime of the hybrid nanostructure is statistically shorter than that of the pure Si NCs, and an extent of the lifetime reduction is a function of the percentage of Si NCs involved in the effective charge transfer from Si to ZnO at their interface. In other words, ZS1 has the lowest τ_2 because the majority of Si NCs in ZS1 is interfaced with ZnO NWs, resulting in the fastest exciton recombination. τ_2 was then steadily recovered to that of the pure Si NCs at a heavier Si-NC loading. Since the quantum yield of the Si NCs is approximately 40%, the radiative energy transfer lifetime of ZS1, ZS2 and ZS3 can be estimated to be 11.95 µs, 14.9 µs and 15.8 µs, respectively [⁸⁴].



Figure 4.7. UV-Vis diffuse reflectance spectra of the bare ZnO NW sample (ZS0) and three Si-NCs/ZnO-NWs hybrid samples (ZS1, ZS2, and ZS3). (a) diffuse reflectance spectra, (b) corresponding Kubelka-Munk plot as a function of the exciting light energy.

Figure 4.7a displays the diffuse reflectance spectra of the bare ZnO NWs as well as the Si-NCs/ZnO-NWs hybrid structures. In the given UV-vis region, the diffuse reflectance of ZS0 is greater than the hybrid structures (in fact, ZSO > ZS1 > ZS2 > ZS3), indicating the stronger absorption for a higher Si-NC loading. The plot of the modified Kubelka-Munk function, $(F(R)hv)^{1/2}$, vs. the energy of exciting light (*hv*), can be employed to calculate the optical band gap before and after the SiNC decoration [^{28,85}] (see Figure 4.7b). Here, $F(R) = (1 - R)^2/2R$ (where R is

the reflectance), *h* the Planck constant, and *v* the frequency of light. The x-intercept values from the extrapolation of the linear slope to photon energy in Figure 4.7b can be related to band gap energy. The calculated band gap energies of ZS0, ZS1, ZS2, and ZS3 are 3.22 eV, 3.10 eV, 3.14 eV and 3.07 eV, respectively. The maximum bandgap narrowing of 0.15 eV has been observed upon the formation of ZnO/Si hybrid structures, which is similar to the other ZnO-semiconductor-based hybrid structures [²⁸]. In this paper, the narrowed band gap of the hybrid structures is expected to extend the spectrum response of the catalyst and enhance photodegradability under visible light.



Figure 4.8. Degradation profiles of methylene blue dye solution for the bare ZnO NWs (ZS0) and SiNCs/ZnO-NWs hybrid samples (ZS1, ZS2, ZS3) under (a) UV light, (b) visible light and (c) white light. (d) Schematic energy band diagram of charge carrier movements in Si-NCs/ZnO-NWs hybrid structure.

Figure 4.8 shows the photodegradation performance of bare ZnO NWs and three Si-NCs/ZnO-NWs hybrids under UV light, visible light and white light. Here the MB dye solution was used as a model pollutant which was brought to absorption equilibrium after keeping in dark for a few hours. Note that the degradation testing was performed on the SiNCs/ZnO-NW hybrid structures on a Si substrate that was immersed in the solution. Therefore, the photodegradation performance from this immobilized catalyst platform is inferior to that of the slurry catalyst system [⁸⁶], and it is not our intention to compare results from these two very different platforms. Rather, the emphasis is placed on the comparison between the bare ZnO-NW sample and hybrid samples under various lighting conditions. The absorption spectra (i.e. peak height) taken from the dye after being irradiated for different time intervals represent the degraded concentration of MB. The degradation profile is thus the concentration (*C*) at the degradation time normalized by the initial concentration (*C*₀). Photolysis of a clean MB dye solution was performed without catalyst to measure a degree of photosensitization of the dye. This control experiment was carried out under the same degradation conditions and compared to the catalyst-added ones. Less than 8% degradation was observed for UV and visible light conditions when irradiated for 6 hours. For white light, 16% of MB was degraded within 6 hours.

As shown in Figure 4.8a, the degraded MB concentration from ZS0 and ZS3 reached the maximum and minimum absorption of 55% and 35%, respectively, during the first 6 hours. The bare ZnO NW sample (ZS0) exhibited a degradation rate similar to ZS1 but higher than ZS2 and ZS3 under UV light. As discussed earlier from the PL data, the thick Si-NC layer atop ZnO NWs may block the incident UV light for ZS2 and ZS3, in which the ZnO NWs in the hybrids absorbed fewer photons and generated fewer charge carriers in comparison to the pure ZnO NWs. The observation of ZS1 and ZS2 having better performance than ZS3 suggests the dependence of Si-NC layer thickness on the degradation rate. Another possibility originates from the generation efficiency of the charge carriers under the UV light irradiation. The UV wavelength at 365 nm corresponded to ZnO bandgap (3.37 eV), which can generate electron-hole pairs more efficiently

than that of SiNCs. The enhanced degradation rate will be also highly dependent on the ZnO surface areas exposed to the dye molecules. Thus, ZS3 is less favorable to serve as a catalyst under UV light irradiation. The electron accumulation could occur due to the slow charge carrier transport under UV light irradiation, which will be discussed in the band alignment of the hybrid structures.

The Si NCs with a narrower band gap broadens the spectrum response of the photocatalysts, while the ZnO NWs alone, with a wide band gap, limited in response to the UV region of the spectrum. The photocatalytic degradation under visible light (Figure 4.8b) was carried out in order to further investigate the mechanism of the hybrid photocatalysts. The major fraction of UV and IR light were filtered (around 97% blocked) and the intensity of the visible light was reduced approximately by 30%. The trend of the degradation behavior is opposite to that of the UV light condition (see Figure 4.8a). The maximum degradation of MB was seen with ZS3 while the minimum one is with ZS0. The straightforward explanation of this trend is that the bare ZnO sample (ZS0) does not absorb the visible light efficiently due to its large band gap and thus produce fewer charge carriers and oxidants for photodegradation. The three hybrid structures show essentially little (or minor) difference in degradability. But the fact that ZS3 shows slightly higher degradability than ZS1 or ZS2 may suggest that the charge transfer/injection between Si NCs and ZnO NWs does not play a significant role and that the oxidants generated on the Si-NC surface are more important.

The photodegradation performance of the bare ZnO NWs and SiNCs/ZnO-NWs hybrids under white light (IR cut off) exhibits the different trend (see Figure 4.8c) in comparison to those under UV or visible light only. The overall degradability follows the sequence of ZS1 > ZS2 \approx ZS0 > ZS3, respectively. Since white light consists of both visible and UV spectral regions, the photodegradability under white light exhibits the combined effects from either spectral case. In essence, the higher the Si NC loading the hybrid structure, the poorer the degradation performance became for the UV case. But the opposite trend was observed for the visible light case. The net effect is the results seen in Figure 4.8c, but the detailed explanation will require deeper understanding in the hybrid structures. Preferential light absorption of ZnO or Si in each spectral region is compounded by the relative placement of nanostructures (i.e., the incident light is always absorbed by the Si-NC layer first, thus creating the shadowing effect on the ZnO NWs) and the overall absorption efficiency. It is interesting to note that the degradation performance of ZS1 was significantly better (more than 15%) than that of ZS0 or ZS2. The enhanced charge separation and corresponding photogenerated excitons, possibly related to the low ZnO NBE PL intensity of ZS1, may be responsible for the improved behavior.

In general, photodegradation activity is governed by the amount of participating oxidants such as superoxide anions ($\cdot O_2^-$) and hydroxyl radicals ($\cdot OH$) available for degradation reactions. Figure 4.8d shows the possible mechanism of generating highly oxidizing species in Si-NCs/ZnO-NWs hybrid structure. This schematic may be applicable to the near-optimal hybrid structure of ZS1, where a very thin layer of SiNCs were covered over the ZnO NWs. Then we can assume that the recombination of the photogenerated excitons in Si NCs is not significant. Upon irradiation, the Si NCs absorb the photons prior to ZnO NWs and release photogenerated electrons that either travel to the Si-NC surface to take part in the reduction reaction – converting oxygen molecules in water into superoxide anions – or transfer to the hybrid interface and get injected into conduction band (CB) of ZnO NWs. Since the mobility of free electrons is higher than holes in the semiconductor, the enhanced electrons will contribute to the effective recombination of electron-hole pairs of ZnO NWs. Meanwhile, the valance band of Si NCs adopts additional photogenerated

holes transferred by ZnO NWs, oxidizing H₂O to \cdot OH for the further pollutant oxidization. On the other hand, excess photogenerated electrons of ZnO NWs supplied by Si NCs yield \cdot O₂- from O₂. Obviously, the facilitated charge carriers producing abundant oxidants to degrade the pollutant, resulting in improved photocatalysis.

As abovementioned, a barrier caused by the charge carrier transportation impeded further electron transfer from the Si NCs. This phenomenon tends to emerge seriously at higher concentrated Si NCs, decreasing the enhancement of the Si NCs towards the photocatalytic degradation, which may an alternative to explain the trend that heavier Si NCs loading caused slow degradation rate [⁷⁸].

4.4 Conclusion

In this work we have described the synthesis and characterization of Si-NCs/ZnO-NWs hybrid structure as promising sunlight-harnessing photocatalysts. Hydrothermal synthesis and low-pressure non-thermal plasma growth techniques were utilized to create highly crystalline ZnO NWs and Si NCs, respectively. The morphological, compositional, and crystalline nature of the ZnO NWs and the hybrid nanostructures were studied using the SEM, TEM, XRD, and FTIR, confirming the formation of well-defined hybrid structures on the substrates. The optical properties and functionality of the hybrid structures were also studied as a function of the Si-NC loading by means of the microRaman spectroscopy, PL, time-resolved PL, and diffuse reflectance spectroscopy. The photodegradation performance of the bare ZnO-NW and hybrid samples were tested on the immobilized platform under different lighting conditions, including UV, visible, and white light, to investigate the effects of hybrid structures on source light dependent photocatalysis. The improved photocatalytic activity of the hybrid sample with the optimal Si-NC loading was

attributed to the presence of the proper amount of Si NCs that decorated ZnO NWs, extending the light sensitivity of hybrid from the UV to visible region, promoting the effective charge separation (i.e., suppressing exciton recombination), and increasing the exciton lifetime. The bare ZnO-NW and Si-NCs/ZnO-NWs hybrid samples were immobilized on a flat substrate that provided a common platform for measuring both photocatalytic performances and optical characteristics, which made the comparison and analysis more meaningful. We believe that these novel Si-NCs/ZnO-NWs hybrid structures may find their usefulness beyond photodegradation and in fact even more effective in improving the performance of various optical devices.

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CHAPTER 5

IMMOBILIZED FLOATING PHOTOCATALYSTS: A NOVEL CONFIGURATION OF ZNO/PDMS HETEROSTRUCTURES

5.1 Introduction

ZnO nanostructures have attracted considerable attention as active components in electronic devices $[1^{-3}]$, water splitting $[4^{-6}]$ and environmental remediation $[7^{-9}]$ thanks to their excellent electrical, optical and chemical properties. Especially, a growing interest in water decontamination via photocatalytic degradation promotes the further development of ZnO nanostructures as photocatalysts. The state-of-the-art reports have demonstrated the remarkable performance of ZnO in decomposing organic pollutants [10-13]. Electrons and holes can be excited on ZnO nanostructures when absorbing appropriate energies from photons, which reacting with water and oxygen in an aqueous solution are able to produce hydroxyl radicals (·OH) and superoxide anions (O_2^{\bullet}) , respectively. These two chemical groups working as the primary oxidants are capable of decomposing organic contaminants into water, carbon dioxide and other inorganic molecules through complex chemical reactions. There are two basic kinds of photocatalysts can be recognized in term of their configurations: (i) slurry photocatalysts [^{14–16}] and (ii) immobilized photocatalysts, which involves immobilized films/nanocomposites [17-19] and immobilized vertically-grown NWs [²⁰⁻²²]. Slurry photocatalysts, including particles and 1D nanostructures, are the most common studied configuration, which is considered possessing high degradability thanks to their large surface-area-to-volume ratios and high homogeneity in aqueous solution. With proper modification the superior photocatalytic activities of these photocatalysts can be achieved which are comparable to that of Degussa P25 $[^{23-25}]$. However some challenges such as easy-agglomeration, complicated recovery from liquids and increased absorption along the penetration depth of UV light hindered these photocatalysts in practical use. As an alternative

route, immobilized film-like photocatalysts are preferable to practical option. This type of configurations possess great recyclability, whereas their limited active surface area and masstransfer restraint became additional drawbacks. Recently, photoreactor, especially microchannelbased photoreactor, is suggested as one effective way to improve the performance of immobilized photocatalysts by increasing the surface-to-volume ratio and mass transfer and reducing the molecular diffusion distance. These photoreactors serving as tools for the degradation of organic pollutants have been demonstrated with excellent reproducibility, stability and degradability [^{26–} ²⁹]. Moreover, the modification towards this design, such as employing immobilized NW photocatalysts, further improves its photodegradation rate owing to the larger active surface area in comparison with that of film $[^{30,31}]$. However most of these reactors require external power to drive polluted solution across the reaction chamber, and specific platform is usually built to bring it closer to the light source, which inevitably increase the cost in scalable water cleanliness. In this regards, a configuration possessing immobilized NW-like photocatalysts both autonomously floating and freely moving atop the water is desired to improve the utilization of sunlight and release the mass-transfer issue.

In this paper we report a configuration with ZnO NWs vertically grown on the flexible polymer substrate (ZP film). The thin polymer was transparent and able to freely move on top of water while floating. The ZnO NWs were securely fixed on the polymer substrate via a two-step synthesis (hydrothermal growth on rigid substrate and second hydrothermal growth on flexible substrate), where ZnO NWs had the uniform distribution and ordered orientation on the entire surface. The photocatalytic activities of the floatable configuration before and after the secondary growth of ZnO NWs were investigated to reveal the impact of surface area to photocatalysts. Two different pollutants, MB dye and crude oil, were employed to evaluate ZP

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film. And the durability capability of the floatable configuration towards particular pollutant was also examined. To date, other than the conventional external stimuli that utilizing photons to activate photocatalysts, piezoelectric effect has also been demonstrated to be effective to dye-decomposition. In view of the above, numerous photocatalysts basing on the mechanism of piezocatalysis have been investigated [^{32–35}]. In particular, ZnO as a superior piezoelectric and photocatalytic material whose piezo-photocatalytic mechanism have been revealed [^{36–38}]. In this study the piezoelectric and photocatalytic properties of ZP film in MB dye decomposition was also verified and a proper configuration in using ZP film was also discussed.

5.2 Experimental

5.2.1 Synthesis of ZnO nanowire array

All chemicals were of analytical grade and used without further purification. ZnO NWs was synthesized via the hydrothermal method as previously described by others. In the first step, 10 mM Zn(CH₃COO)₂·2H₂O (99.9% Sigma Aldrich) was dissolved into methanol (Fisher Scientific). Followed by vigorous stirring at 60°C for 2 hours, the mixed solution was spin-coated onto a glass substrate at 1000rpm for 30 seconds. Prior to the seed deposition, the glass substrate was cleaned by acetone, isopropanol alcohol, and deionized (DI) water, consecutively. A subsequent annealing was carried out for the seeded glass substrate at 150°C for 1 hour for dehydration. The growth solution of 25 mM Zn(NO₃)₂·6H₂O (Sigma Aldrich) and 25 mM hexamethylenetetramine (HMTA, Sigma Aldrich) was prepared and preheated in convection oven at 90°C for 1 hour to achieve the thermal equilibrium. The annealed substrate was then immersed into the growth solution at 90°C for 6 hours. Consequently, vertically-grown ZnO NWs were obtained on the glass substrate after thoroughly rinsed by DI water.

5.2.2 Secondary growth of ZnO nanowire array

In the second step, a certain amount of Polydimethylsiloxane (PDMS) solution (10 parts of SYLGARD 184 pre-polymer and 1 part of the curing agent, Dow Corning Co.) was fully covered and spin-coated on the NW-grown glass substrate. The spin-coating speed was varied in term of the desired thickness of the PDMS layer. As an example, spin-coating of 1000rpm for 90 seconds produced a PDMS film of around 300 µm thickness. The PDMS layer was thermally cured at 60°C for 12 hours and cooled to the room temperature overnight. The PDMS layer was then detached from the glass substrate. To facilitate the peeling of PDMS, we utilized a polyester (PET) film as a backing layer. The PET film was brought to intimate contact with the PDMS layer prior to its detachment. The as-fabricated PET/PDMS stack was subsequently placed atop the ZnO growth solution with the embedded NWs facing down at 70°C for 12 hours. The sample was thoroughly rinsed in DI water and completely dried. Finally, the PET film was separated from the PDMS layer to obtain the vertically-aligned ZnO NW array on the PDMS membrane (ZP film).

5.2.3 Materials characterization

The morphology, crystallinity and composition of ZnO NWs both on glass and PDMS substrate were characterized by scanning electron microscopy (SEM, JEOL 6610LV, Hitachi S-4700II), X-ray diffraction (XRD, Bruker-AXS) energy-dispersive X-ray spectrometer (EDS, JEOL 6610LV), and photoluminance spectrometer (PL, Ocean Optics, Inc. USB spectrometer and optical fiber) with the excitation laser at 337 nm.

5.2.4 Photocatalytic assessment and activities

Under UV light: Photocatalytic degradation was carried out in an aluminum foil-sealed case with a magnetic stirrer stage inside. Two 9 W florescent tubes (Philips λ =375 nm) were placed 30cm above the dye solution container. A 10mM methylene blue (MB, 1.5%, Sigma-Aldrich) aqueous solution was prepared as a model polluted water. Four pieces of ZP film (1" x 1" per one piece) were utilized afloat on top of 40mL of the dye solution (with the ZnO NW side facing down). Prior to the irradiation, the dye solution was kept in dark for 30min to establish the absorption/desorption equilibrium. A 1-mL of solution was extracted from the container in every 30 min as the photodegradation progressed. The extracted solution was centrifuged at 10000 rpm to remove any impurities and examined for the absorbance in a UV-Vis spectrometer (Lambda). The absorption peak at 667 nm corresponds to MB and the peak height can be correlated to the MB concentration. The photodegradation experiment was repeated three more times under the same working condition to test reusability/recyclability. The same degradation experiment (but only one 1" x 1" ZP film used for comparison) was carried out to evaluate the role of the secondary growth of ZnO NWs on its photocatalytic performance. The mechanical stability of ZnO NWs on the PDMS film allowed us to bend and stretch the film and place it on the surface of a small rod (8 mm). Experimental setup details for the photodegradation experiment using the overhead mixer. For testing the vertically-aligned ZnO NWs as piezocatalysis, ultrasonic bath (FisherScientific, 160W, 40KHz) and overhead mixer (Dragon Lab, OS20-S) were used to vibrate ZnO NWs when 1 piece of ZP (1" x 1") were utilized to treat the dye solution (40 mL). In the test of oil degradation, each sample had 50mg crude oil (Saudi Arabian Berri crude oil) dispersed onto 2 ml DI water. 1 piece of ZP film (circular, 16 mm-diameter) was utilized floating on top of the oil solution. After degradation, 5ml Petroleum ether (Sigma-Aldrich) was used to dilute the rest crude oil prior to UV/Vis measurement.

5.2.5 Residue inspection

In the end of the experiment, the remaining MB dye solution was filtrated through a filter paper (MCE, mixed cellulose ether membrane, hydrophilic, 0.22 μ m, Millipore Co.) in order to check if the ZnO NWs were dislodged from the PDMS substrate and re-suspended into the solution. A custom vacuum filtration setup composed of a filter holder, a solvent trap and a vacuum pump (Alcatel 2021I) was built. After the filter was positioned on the holder, the dye solution was poured over the filter membrane. A vacuum pressure was applied until all the solutions were completely filtrated. The filter membrane was kept overnight for the negative pressure to be fully diminished and for the membrane to be completely dried. The filter membrane was further dehydrated at 60°C afterwards. Finally, the filter membrane was imaged under the optical microscope and SEM with 3nm W deposited to search the NWs.

5.3 Result and discussion

In a typical hydrothermal synthesis process, the substrate is deposited with a seed layer by various means prior to the growth of vertically-aligned ZnO NWs. Therefore, the structural stability of NWs onto the substrate is often dependent on the adhesion between the seed layer and the substrate. When a rigid inorganic substrate (e.g. glass, silicon etc.) is used, the seed layer can be thermally treated at relatively high temperatures (often over 200°C), which significantly improves the adhesion. However, this high-temperature treatment cannot be applied for polymer substrates. Therefore, the NWs directly grown on the polymer substrate typically suffer from weak adhesion and are easy to be detached from the substrate.



Figure 5.1. Schematic of the proposed two-step fabrication process of a vertically-aligned ZnO NW array on a polymer substrate. (a) A ZnO NW array was vertically grown on the glass slide via the hydrothermal synthesis, (b) a certain amount of a PDMS solution was spin-casted onto the ZnO NW array and thermally cured afterwards, (c) a PET film was brought into intimate contact with the PDMS film, (d) the PDMS/PET stack was detached from the glass slide simultaneously, (e) the PDMS/PET layer became flat due to the recovery of PET film, (f) the ZnO NW array embedded in the PDMS film was re-grown to a desired length via the same hydrothermal process, (g) ZP film was obtained after the PET film was removed from the PDMS film, (h) the photograph of as-prepared ZP film (1" x 1").

Our approach to improving NWs' adhesion to the polymer substrate is to utilize the two step hydrothermal growth and secure the NWs by partially embedding them into a polymer matrix. Figure 5.1 shows a schematic of the proposed method to fabricate a robust ZP film via the two-step, hydrothermal synthesis. In the first synthesis step (Figure 5.1a), vertically-aligned ZnO NWs with reasonable aspect ratios were grown from a seeding layer on a glass substrate [³⁹]. A thin PDMS layer was then uniformly spin-coated onto the ZnO NWs to fully encapsulate the NWs (Figure 5.1b). Here the thickness of the PDMS layer could vary from 200 to 500 µm depending on a different spin-coating speed. Prior to the detachment of the PDMS layer from the glass substrate,

a PET film brought into conformal contact on PDMS surface to increase the stiffness of the PDMS layer (Figure 1(c-d)). The PET film was employed since the PDMS layer was too thin to be detached from the glass substrate undamaged. While the molded PDMS encapsulated the majority parts of ZnO NWs, their tips remained exposed and served as a seeding layer for regrowth. The PDMS/PET stack were placed on top of the same growth solution with the NW side facing down for the secondary hydrothermal synthesis (Figure 5.1(e-f)). Since PDMS/PET is lighter than water, the stacked film was afloat during the second growth step. The stand-alone ZP film was obtained after the separation of the PET film (Figure 5.1g). In the single-step hydrothermal synthesis, the adhesion strength of NWs to the substrate is fixed by the interfacial strength between the seed layer and the substrate. Therefore, longer NWs are difficult to be grown as they are easily detached from the substrate. The parts of the NWs are securely anchored into PDMS, allowing the NWs to grow much longer than ones generated by the single-step process.



Figure 5.2. SEM images of the ZnO NWs (a) on the glass substrate after first growth, and (b) on the PDMS before secondary growth, (c) on the PDMS substrate (~300 μ m in thickness) after secondary growth and (d) on the PDMS substrate after secondary growth (failed detachment). Scale bar: (a) and (c) 50 μ m in the large view and 3 μ m in the inset, (b) 20 μ m in the large view and 5 μ m in the inset, (d) 50 μ m in the large view and 2 μ m in the inset.



Figure 5.3. (a) XRD patterns of ZnO NWs, (b) photoluminescence spectrum of ZnO NWs.

Figure 5.2 shows the SEM images of the ZnO NW array at each key process. In Figure 5.2a, it is observed that the highly ordered ZnO NWs are uniformly distributed on a glass substrate. Figure 5.2b is the ZP film before the secondary growth, showing that the tips of broken ZnO NWs were exposed and could serve as a fresh seeding layer. Moreover, the re-grown NWs on the PDMS substrate (Figure 5.2c) preserved the NW density similar to that on the glass substrate (Figure 5.2a), demonstrating the successful regrowth of the majority of ZnO NWs. Note that the re-grown NWs would follow the same crystalline orientation as that of broken NWs. A ZP film in failed detachment is shown in Figure 5.2d, where the sparse NW array was obtained. The space between NWs represented the loss of NWs in the detachment of ZP film. The hexagonal shapes revealed the ZnO NWs with an average diameter of about 80 nm. It is worth noting that the morphology of the as-prepared ZnO NWs on both the glass substrate and PDMS layer were highly affected by factors such as reaction duration, temperature and solvent concentration as reported in other literatures [⁴⁰⁻⁴²].

The detailed crystalline quality of ZnO NWs on the glass (after the first growth) and PDMS (after the secondary growth) substrates was characterized by XRD analysis and photoluminescence (PL) spectrum. As depicted in Figure 5.3a, the XRD patterns of ZnO NWs were recorded from 25° to 75°. It is clearly seen that each diffraction peak from the glass substrate has the

corresponding peak from PDMS substrate at the same position, implying that the proposed twostep process offered the coherent crystalline structure of ZnO NWs. Additionally, all the diffraction peak on both substrates can be indexed to the wurtzite ZnO phase, where the peaks with the strong intensity indicate the c-axis preferred orientation of ZnO NWs [^{25,43}]. The PL spectrum of ZnO NWs on both substrates (Figure 5.3b) has a good agreement with the previous reports [^{20,24}], where the near-band-edge (NBE) emission and defect-related peaks are observed around 390 nm and 490 nm, respectively. It is worth noting that the intensity of the defect-related peak is comparable to that of the NBE peak, denoting the significant defect level of the NWs. The defective NWs may be beneficial to their photocatalytic activity owing to the decreased surface-state-related recombination of photogenerated electro-hole pairs [²⁴]. More interestingly, the ratio of the NBE peak to defect-related peak on glass is close to that on PDMS, which also reveals the coherent crystal structure of ZnO NWs after the secondary growth. Both XRD analysis and PL spectrum confirm that the two-step process serving as an in-situ growth method enables the ZnO NWs to grow consistently with the predetermined state.

ZnO as photocatlaysts have been intensively studied in last few decades [^{15,44}]. Here in order to investigate the photocatalytic activity of the as-prepared ZnO NWs on the PDMS film, MB was chosen as a probe pollutant, and its time-dependent decomposition under UV irradiation (~375 nm) was measured using the UV/Vis spectrometer. In this experiment, the ZP films were placed afloat with the ZnO NWs facing down towards the MB solution. It is known that PDMS is transparent to near-UV, and therefore, the UV light penetrates the PDMS layer and activate the underneath ZnO NWs spontaneously [^{45–47}]. The dye solution was kept in dark condition for half an hour to achieve the absorption/desorption equilibrium. The UV light irradiation was subsequently established in perpendicular and with a certain distance to floated ZP films. During

the experiment the absorbance of solution was measured in constant intervals (see Figure 5.4). After 3-hour-long experiment, the ZP films were dehydrated and reused for photodegradation in another fresh MB solution. This process was repeated for three times, and each corresponding UV/Vis absorbance was recorded at the same interval. Figure 5.4a shows the degradation profiles of MB in the presence of the ZP films for four consecutive cycles. C/C_0 on the Y axis stands for the ratio of the degraded concentration to the initial concentration of the pollutants, which was calculated from the absorbance of the MB solution using Bouguer–Lambert–Beer law [^{26,48–50}]. It is clearly seen that the degradation percentage of MB after 3 hours are 74.9%, 82.1%, 70.6% and 71.4%, indicating the reasonable reusability of the ZP films. We argue that the anchoring of ZnO NWs into the PDMS film indeed helped the NWs to be mechanically robust and thus recyclable. This reliable immobilization of ZnO NWs was also demonstrated by inspecting the remaining degraded solution. No NWs were found in the degraded solution after being centrifuged or filtrated.

The degradation kinetic of MB is used to evaluate the performance of photocatalysts. Figure 4(b) displays the corresponding degradation kinetics of MB dye in four consecutive cycles. According to the pseudo first-order kinetic model, that is, -ln(C/C0)=k*t, the apparent reaction rate constant k of the degradation in four consecutive cycles (Figure 5.4c) was 0.008, 0.0091, 0.0071 and 0.007 min⁻¹, respectively [^{24,51–53}]. The correlation coefficient (R²) in the fitting were all greater than 0.97, suggesting that the photocatalytic activity of the as-prepared ZP films in four cycles were highly durable. The studies in degradation and kinetics confirm the excellent reusability of the ZP films. The discrepancy of the degradation rates in four cycles may ascribe to the measurement errors as well as residual intermediates absorbed on the NW surface, leading to the loss of active surface area of NWs for the decomposition.



Figure 5.4. (a) degradation profiles of MB dye (at 667nm) in four consecutive cycles, (b) photodegradation kinetics of MB dye in four consecutive cycles, (c) constant k.

The recyclability of the immobilized photocatalytic system is governed by the stability and adhesion of photocatalysts to the immobilized substrate. In the present configuration, the PDMS substrate is used to hold ZnO NWs in place and keep them afloat. The floating immobilized system entails the substrate whose density is smaller than water, i.e., plastic or polymeric materials and the immobilization method to integrate photocatalysts onto those organic substrates. The previous fabrication approach to the floating immobilized photocatalytic system includes the physical vapor deposition, electrospinning, and spray/dip coating. But these photocatalysts are likely to fall off from the substrate during handling and repeated operation due to the weak adhesion. To further

prove the superior structural stability of the proposed immobilized system, we put the ZP film to various operating conditions such as bending, stretching, contact, and temperature variation.



Figure 5.5. SEM images of the ZP film (a) before thermal and mechanical test and (b) after thermal and mechanical test. (c) and (d) are the photographs of ZP films (1"x1") imaged in (a) and (b), respectively. Scale bar: 10 µm in the large view and 1 µm in the inset.

Figure 5.5 (a-b) shows the SEM images of the ZnO NWs on the PDMS film. Upon receiving photons with energy higher than the bandgap of ZnO, ZnO NWs fixed on PDMS substrate are capable of generating electron-hole pairs, which convert O_2 and H_2O into O_2^{-} and $\cdot OH$, respectively. As reported, these oxidants are able to decompose organic pollutants (e.g. MB dye) into clean water and carbon dioxide gas [^{15,16,54}]. Like other semiconductor-based photocatalysts, the photodegradation rate of ZP film was significantly affected by the working temperature [⁵⁵]. For evaluation of ZP film the dye solution was maintained under room temperature during the entire degradation experiment by placing the UV source far away. On the other hand, consider the thermal stability ZP film was tested in relatively high temperature solution. In detail ZP film was characterized before and after soaked in 60°C aqueous solution for

12 hours. As a result, ZP film retained same NW density as well as shape (see Figure 5.5 (c-d)) thanks to the reliable immobilization, which we believe would well accommodate to nature environment for practical application.



Figure 5.6. Schematics of ZP film (a) before secondary growth of ZnO NWs, (b) after secondary growth of ZnO NWs, (c) degradation profiles of MB dye (at 667 nm) before/after secondary growth, (d) degradation profiles of MB dye with/without magnetic stirring.

Many factors play important roles in photodegradation, including active surface areas of catalysts and mass transfer rate [⁵⁶]. These two factors are particularly important in the immobilized photocatalytic system because catalysts fixed on the substrate present much lower active surface areas and reactants need to diffuse to the substrate surface (thus higher mass transfer resistance) compared to the slurry suspension-based catalytic system. First, the effect of the surface area on the degradability can be evaluated by comparing two immobilized systems with different wire lengths. The schematics shown in Figure 5.6a and b illustrate the ZP film with two different active surface areas. It is anticipated that the ZP film with the secondary growth would have higher surface areas of the ZnO NWs exposed to the environment in comparison to the sample without

the secondary growth and thus present higher photocatalytic degradability. Figure 5.6c shows the photodegradation performance for these two immobilized systems with and without the secondary growth of ZnO NWs. As expected, the ZP film after the secondary growth exhibited a higher degradation rate. Since the degradability experiments were performed in the identical condition, the discrepancy in photodegradation performance can be attributed to the different active surface areas of two films. In other words, the improvement of the degradation rate was made by the longer length of secondary-grown ZnO NWs, rendering larger active surface areas for light absorption and pollutant decomposition. Secondarily, another important factor limiting the degradation performance in immobilized photocatalytic systems is a slow mass transfer rate, i.e., sluggish transport of reactants and products to and from the catalyst surface. The effect of mass transfer on the degradability was investigated with the assistance of magnetic stirring (at 700rpm, see Figure 5.6d). The degradation profiles in Figure 5.6d present that the ZP films performed enhanced degradability. Under the same working condition, this improvement was mainly derived from the magnetic stirring, which was utilized to relax the mass transfer limitation during the degradation process. Comparing the results, ZP film with secondary growth in Figure 5.6c and Figure 5.6d, it can be concluded that the mass transfer rate has a much significant impact on the degradability of ZP film. The combination of ZP film with secondary growth and magnetic stirring is favored in our experiment.

The strong adhesion of NWs to the substrate enables us to explore a new application, that is, an immobilized ZP film as piezocatalysts. It is well known that ZnO is a piezoelectric material, i.e., electric charge generated and accumulated in response to applied mechanical stresses. Degradation of organic pollutants by piezocatalysts has been previously demonstrated in a slurry (or suspension) form. Since ZnO NWs are securely adhered to the substrate, large stresses/strains can be applied to the ZP film, facilitating immobilized piezocatalysts. In detail, The ZnO bend or stretch and mount it onto a circular rod, which was rotating with the rod and ultrasonicated at the same time. As comparison, another ZP film was floating atop the polluted water which only has ultrasonic field applied. Even more interestingly, the immobilized floating catalysts can be used to degrade pollutant faster. The schematics of ZP films with/without ultrasonication for the investigation of piezocatalysis are illustrated in Figure 5(a-b), where the bended ZnO NWs was caused by ultrasonic-induced water pressure [³²].



Figure 5.7. Schematics of ZP film (a) without vibration, (b) with vibration, (c) degradation profiles of MB dye (at 667nm) in dark condition with ultrasonication, (d) degradation profiles of MB dye (at 667nm) under UV light irradiation with ultrasonication.

The piezocatalytic activity of ZP film with vibration is shown in Figure 5.7c (blue line). Under the presence of an ultrasonic field, 25% of MB dye was decomposed by a floating ZP film in a dark condition while the reference solution was kept unchanged (red line), proving the effectiveness of piezocatalysis to MB dye. The degradability of this ZP film was increased significantly when it was further assisted by UV illumination (Figure 5.7b, blue line), confirming

the piezo-photocatalytic mechanism of ZnO NWs as reported [³⁶]. The piezo-photocatalytic mechanism and potential reactions are illustrated in Figure 5.8. As can be seen that the piezocatalysis performed two functions in the degradation process, including excitation of electron-hole pairs and separation of photoinduced charge carriers. Owing to the existence of an increased number of charge carriers, more reactive oxidants were converted hence elevated the capability of degradation eventually. It is known that the performance of piezocatalysts is highly governed by vibration frequency [³⁶].



Figure 5.8. Schematic of pizeo-photocatalytic mechanism of ZP film.

As comparison, a setup was built for a ZP film to further experience enhanced vibration frequency. In the experiment the ZP film was wrapped around a glass rod which was attached on a rotator as presented in Figure 5.9. The fixed ZP film in the entire degradation process was ultrasonicated while being rotated (at 700 rpm) simultaneously. Consequently, the immobilized ZP film on the rod obtained a higher degradation rate than the floating one, which indicates that an increment of vibration frequency was applied to ZnO NWs. Likewise, the immobilized ZP film on the rod performed better degradability than the floating one under UV irradiation which may be attributed to the enhancement of piezo-photocatalytic efficiency. Notably, the discrepancy of degradation percentage between fixed ZP film and floated one in dark condition is slightly larger than that in UV illumination condition, which may ascribe to the efficiency of light utilization. As mentioned above, the floated ZP film has optimal configuration to utilization the incident light while the fixed one has limited area as light irradiating vertically. The efficiency loss derived from this diversity was diluted by improved piezocatalysis.



Figure 5.9. Schematics of (a) mixer setup and (b) float setup, (a1) and (a2) the photograph of mixer ZP film used in (a), (b1) and (b2) are the photograph floated ZP film used in (b). All the ZP films are in 1 "x 1".

As of now the considerable efforts have been devoted to treat pollutants from industrials and agriculture. In the field of photocatalysis the immobilized photocatlaysts are regarded as promising candidates in removing floating pollutants (e.g. oil spills). In this study, crude oil was used as another probe pollutant to evaluate the photodegradation capability of the ZP film, where the decomposition was validated by monitoring the concentration of particular components. Figure 5.10a shows the spectral changes of crude oil measured through UV/Vis spectrometer. As can be seen that crude oil possessed many characteristic peaks due to its complex composition. All peaks were weakened as the irradiation time increased, indicating the various organic components were indeed degraded by the ZP film. To clearly analyze the degradation performance of ZP films, degradation profile of crude oil was plotted as function of an irradiation time for two peaks at 288 nm and 293 nm, respectively (Figure 5.10b). The concentration of crude oil was observed declining around 20% in 6 hours in the presence of ZP film. In addition, the impact of UV light alone on decomposing this crude oil was found insignificant (Figure 5.10b, blue line).



Figure 5.10. (a) spectral changes of crude oil UV light irradiation, (b) degradation profiles of crude oil at 288nm and 293nm under UV light irradiation.



Figure 5.11. crude oil samples (a) before and (b) after degradation

The corresponding crude oil samples before and after degradation are displayed in Figure 5.11 (a-b). In Figure 5.11a, a circular ZP film was placed on top of crude oil layer, which had

approached absorption/desorption equilibrium prior to the experiment. After 6-hour degradation process, the oil concentration was clearly observed to be reduced (see color gradient in Figure 5.11b) after diluted by the same amount of petroleum ether, suggesting the valid degradation process by means of ZP films.

5.4 Conclusion

In this paper we fabricated a new type of immobilized photocatalysts for the photodegradation. The ZnO NWs securely fixed on the flexible substrate has been proposed possessing some advantages: (i) avoided the NW re-suspension, (ii) increased the active surface area, (iii) increase the utilization of the incident light and (iv) facilitated the mass transfer. As a result, the floating ZP film exhibited a considerable degradability and reusability against MB dye. According to the degradation mechanism, since the redox reaction only occurs at the interface of the solution and the NW, the longer exposed NW part may result better photocatalytic performance. In addition, a ZP film with more embedded NWs may also have a greater degradability. In the experiment we also investigated the piezocatalytic and photocatalytic properties of ZP film. Meanwhile, a proper setup was proposed to effectively improve piezocatalytic capability of ZP film. Considering the practical challenge in treating floatable pollutants, crude oil as a model pollutant was tested by ZP film. The result confirmed a slow but valid photocatalytic degradation process took place in the presence of ZP film. For better performance, the high power light source needs to be introduced to accelerate the process. Sunlight irradiation and other types of pollutants need to be introduced to further evaluate ZP film in future work.

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CHAPTER 6

MULTIFUNCTIONAL SOFT MICROMOTORS FOR PHOTOCATALYTIC DEGRADATION

6.1 Introduction

Photocatalytic degradation is one promising approach to degrading organic contaminants in water. Many photocatalysts are made of semiconductor nanostructures [¹] and typically employed in the form of suspended particles, namely a slurry system. Slurry photocatalysts are considered to be an efficient configuration in photodegradation due to their large active surfacearea-to-volume-ratio and a high mass transfer coefficient. Despite the excellent degradation performance towards numerous pollutants, these nanostructured photocatalysts suffer from the drawbacks, such as particle agglomeration and more importantly high cost associated with suspended catalyst separation/recycling limiting widespread adoption in industry. It has been generally known that up to 70% of the total cost associated with photodegradation-based wastewater treatment technology is attributed to the separation and recycling of catalyst particles.

Another photocatalytic platform is an immobilized photocatalyst system that has attracted much attention thanks to the improved recyclability and potentials for large-scale utilization. One common embodiment of the immobilized photocatalysts is an immobilized photocatalytic reactor $[^{2-6}]$, whose walls are transparent and coated with photocatalytic materials. As long as photocatalysts remain fixed in the walls, no extra step is needed to separate photocatalysts from decontaminated water, significantly reducing an operation cost. However, the immobilized system inherently possesses two drawbacks. First, surface areas of nanostructured photocatalysts are significantly reduced or masked due to the surface immobilization. One-dimensional nanostructures (e.g. nanowires and nanotubes) increase the active surface area compared to zero-dimensional nanoparticles when immobilized on the surface. Second, pollutants in bulk water need

to be transported to the reactor surface for degradation reactions, posing significant mass transport limitation. Therefore, in photodegradation reactors, continuous flow and/or stirring are often implemented to enhance the mass transfer coefficients $[^{7-9}]$ but require an external power, i.e., a higher cost. More recently, an alternative form of immobilized photocatalytic system has been introduced, namely buoyant or floating immobilized photocatalysts [10-14]. Basically, transparent substrates lighter than water and relatively hydrophobic are chosen to keep immobilized photocatalysts afloat. This configuration allows them to be effective in open surface water (i.e., no reactor required) and especially capable of decomposing floating pollutants (e.g. oil spills). Because the catalysts are floating on top of water surface in which incident radiation reaches first, it maximizes light absorption and photogeneration of charge carriers. In Chapter 5, we have proposed a novel fabrication technique to immobilize vertically-aligned zinc oxide (ZnO) nanowires (NWs) on a polymer substrate with strong adhesion. The resulting ZnO NW/polymer system was tested as a buoyant photocatalytic system, demonstrating the effective photodegradation of dyes and floating crude oil. However, similar to immobilized photoreactors, immobilized photocatalysts on buoyant substrates exhibit lower degradation efficiency due to mass transfer limitation and small surface-area-to-volume-ratio.

One approach to enhancing mass transfer rates of photocatalytic systems is to integrate a functionality of self-propulsion into photocatalysts [15,16]. The main idea is to partially decorate the surface of photocatalytic micro/nanoparticles with a noble-metal catalyst layer that generates gaseous bubbles propelling the particles. For example, hydrogen peroxide (H₂O₂) in water is catalytically decomposed into H₂ and/or O₂ on a Pt or Ag surface, and these bubbles propel the microparticles in an opposite direction [$^{17-19}$]. This catalytic micromotors with photocatalysts have shown excellent degrability for organic-dye degradation [15,16]. It is worth mentioning that for

catalytic micromotors, light is not only working as stimuli to induce the photocatalytic reaction but also to promote catalytic reaction for bubble generation and thus accelerating propulsion $[^{15,16}]$. The geometry is another factor that governs the speed and direction of micromotor movement $[^{16,20-24}]$. The Su group $[^{25}]$ recently reported that solid cylindrical micromotors with precise geometry control fabricated by a template-based method performed multiple functionalities of photocatalysis and self-propulsion, together improving the overall photodegradability. The Mei group $\begin{bmatrix} 26 \end{bmatrix}$ developed tubular-shaped catalytic micromotors based on a rolled-up technique, demonstrating high speed movement of tubular micromotors owing to the bubble-recoil mechanism and providing possibilities to salt concentration-independent approaches [^{18,22,27}]. However the complex top-down fabrication process and critical conversion from 2D to 3D are challenging. Aside from the catalytic reaction, other propulsion approaches harnessing different external stimuli (e.g. magnetic $[^{28-30}]$, ultrasonic $[^{31}]$ and electrical field $[^{32}]$) have also allowed micromotors to swim under remote control and accomplish multiple tasks such as objective capture and cargo delivery. However, the aforementioned micromotor-based photocatalytic system still relies on individual particle, and to our knowledge, self-propelled immobilized photocatalysts on soft substrates have not been demonstrated. In addition, a material platform to integrate true multifunctionalities, i.e., three or more functionalities integrated onto a single entity, has been rarely reported.

Here we present a novel multi-material platform to integrate immobilized ZnO photocatalysts, a catalyst layer for improved locomotion, and magnetic nanoparticles for motion control and separation. Vertically-aligned ZnO NWs are grown on an elastomeric (polydimethylsiloxane (PDMS)) substrate with strong adhesion (see Chapter 5), forming a photocatalytic layer. This film and another PDMS layer containing various functional materials

like magnetic nanoparticles or noble metal catalysts are bonded together with strain engineering to produce 3D-shaped soft micromotors. The predetermined shapes, including semi-circular, circular and over-rolled shape, can be realized by varying the strain mismatch between two PDMS membranes. Sub-millimeter-sized, 3D soft structures whose outer surfaces are covered with vertically-aligned ZnO NWs have been fabricated with the flexibility of incorporating various functional materials. These integrated soft micromotors (ISMs) exhibit the multiple functionalities including photodegradation, self-propulsion, and magnetic control. photodegradation experiments with and without integrated functionalities are compared to prove the utility of the proposed multimaterial platform. Three mechanics models are employed to calculate the out-of-plane deformation of the ISMs, providing a guideline for the construction of the micromotors with diverse shape. We believe that the proposed multi-material integration method may open an opportunity for creating polymer-based multifunctional micromotors towards various applications.

6.2 Experimental

6.2.1 Preparation of ZnO NWs

All reagents used in this experiment were commercially available without further purification. ZnO NWs were synthesized via a hydrothermal method. The detailed process is available elsewhere (Chapter 5), but a brief account is given as follows: a ZnO seed solution was prepared by adding 10mM Zn(CH₃COO)₂· 2H₂O (99.9% Sigma Aldrich) into enthanol (200 prove, Fisher Scientific) and stirred at 58°C for 2 hours. Once cooled down to room temperature, the mixed solution was spin-coated onto a cleaned glass substrate with multiple times to achieve a uniform surface coverage. The substrate was then kept at 150°C for 1 hour to improve the adhesion of the ZnO seed layer to the substrate. The growth solution is composed of 25 mM Zn(NO₃)₂· 6H₂O

(Sigma Aldrich) and 25 mM hexamethylenetetramine (HMTA, Sigma Aldrich). Prior to the synthesis, the growth solution was preheated in a convection oven at 90°C for 1hour to achieve a thermal equilibrium. The substrate was then immersed into the growth solution at 90°C for various duration (3~12 hours) to obtain a specific NW length. Subsequently, tge substrate was thoroughly rinsed by DI water. A 3-hour dehydration step at 60°C was carried out for the substrate afterwards.

6.2.2 Fabrication of ISMs

A Sylgard 184 PDMS elastomer kit (DOW Corning) was applied to prepare a PDMS solution at a ratio of 10 parts base prepolymer to 1 part curing agent. A thin (200~400 µm) PDMS layer (1st) was spin-casted onto the as-fabricated ZnO NW substrate at 2000 rpm and solidified at 60°C for 6 hours. Another PDMS film (2nd) of 300-500 µm in thickness was prepared in a Petri dish under the same mixture and curing condition. For the magnetic response, a certain amount of Fe particles (30~40 µm in diameter) were uniformly mixed into the 2nd PDMS solution with a weight percentage around 5% prior to the solidification of film. The cured PDMS film (2nd) was pre-stretched in a custom-made uniaxial or biaxial stretcher to a desired length. Both ZnO NW/PDMS substrate and 2nd PDMS film were plasma-treated according to the literature method ³³], by Corona plasma treater, and bonded consecutively at 60°C. A laser machining system (Universal Laser System VLS 4.60) was used to dice the plasma-bonded bilayer on the glass substrate with the predetermined designs. The constructed ISMs were obtained when the bilayer sandwich was detached from the glass substrate. The released ISMs were then soaked in the 70percent ethanol solution with 5-10 mins sonication to clean the laser-induced residues and dehydrated at 60°C. In order to re-grow the ZnO NWs, the as-cleaned ISMs was dispersed in the growth solution again by following the same growth process of ZnO NWs as 6.2.1.

6.2.3 Characterization

The morphology, crystallinity and composition of ZnO NWs on ISMs were characterized by scanning electron microscopy (SEM, JEOL 6610LV, Hitachi S-4700II), X-ray diffraction (XRD, Bruker-AXS), energy dispersive x-ray spectrometry (EDS, JEOL 6610LV) and photoluminance spectrometer (PL, Ocean Optics, Inc. USB spectrometer and optical fiber) with the excitation laser at 337 nm..

6.2.4 Photocatalytic assessment and activities

Under UV light: The photocatalytic degradation was carried out in an aluminum foil-sealed case with a magnetic stirrer stage inside. Two 9W florescent tubes (Philips λ =375 nm) were positioned 30 cm above the dye solution container. Methylene blue (1.5%, Sigma-Aldrich) was diluted to 10 mM concentrated dye solution as a model pollutant. The ISMs was poured onto the dye solution (20 mL), subsequently. Before irradiation the dye solution was kept in dark for 30min to establish the absorption-desorption equilibrium. A small amount of solution was extracted from the container at the constant intervals (60, 120, 180, 240, 300 mins) and centrifuged at 10000 rpm for 2 mins to remove any residue from the extracted solution. The purified solution was then examined using the absorbance in UV-Vis spectrometer (Lambda). The photodegradation experiment was repeated a few times to determine relative errors and recyclability. In a selfpropulsion test, a 5% H₂O₂ solution was added to each MB dye solution before experiment. The free ISMs and Ag-deposited in same quantity were dispersed into a H_2O_2/MB dye solution (20) mL) under the same working condition as before. In the test of magnetic propulsion, under the same working condition, free ISMs and magnetic ISMs in the same quantity were dispersed into MB dye solution. No H_2O_2 was utilized in magnetic propulsion test.

6.3 Result and discussion

The fabrication process of the ISM (uniaxial) is shown in Figure 6.1. Two layers of PDMS were utilized to achieve curved structures using strain engineering. Vertically-aligned ZnO NWs were incorporated into one of the PDMS layer to increase active surface areas. Initially, an array of vertically-aligned ZnO NWs was hydrothermally synthesized on a rigid (glass in this study) substrate (Figure 6.1a). the substrate with the ZnO NWs was spin-coated with a PDMS solution and cured subsequently (Figure 6.1b). After the PDMS layer was thoroughly solidified (Layer Z), another pre-fabricated PDMS film (Layer P) was brought into intimate contact with the top of Layer Z (Figure 6.1c). Prior to sandwiching these teo layers, Layer P was uniaxially stretched at a given strain. Note that the contact surface on Layer P and Layer Z were treated by oxygen plasma in advance. Once two surfaces were securely bonded, the stretching force applied to Layer P was removed. Consequently, an instant shrinkage of Layer P generates a shear stress at the interface of the bilayer structure, but no deformation appears because the rigid substrate holds both layers in place. At this point, the bilayer film can be released from the substrate or laser machined prior to release. In either case, upon detachment from the substrate, the interfacial shear stress will cause out-of-plane deformation, rolling up or curling the bilayer film. An amount of the stretching force on Layer P plays an important role in ISM fabrication. For the same geometry, the structures with a larger curvature could be achieved with an increased stretching force. Besides, a reliable plasma bonding between Layer Z and Layer P is indispensable. Any un-bonded part would affect the ISM shaping. For the function of self-propulsion, a layer of Ag nanoparticles were deposited on top of Layer P prior to the detachment of the as-prepared bilayer structure from the rigid substrate.


Figure 6.1. Fabrication schematic of ISM under uniaxial SPB and producible shapes. (a) verticalaligned ZnO NWs grow on the substrate, (b) spin-cast thin PDMS layer, (c) pre-stretched one thin PDMS film and plasma-bond to ZnO-PDMS substrate, (d) pattern shapes and remove residue edges, (e) peel off the bilayer from the substrate and obtain the micromotors, (f) process for the semi-circular ISMs, (g) process for the circular ISMs, (h) process for the over-rolled ISMs. Scale bar: 500 µm.

When laser-assisted micromachining was introduced to the bilayer structure to increase the shape diversity and dimension control of ISMs. In detail, the as-prepared bilayer structure was machined into the pre-determined geometrical patterns prior to the detachment from the rigid substrate (Figure 6.1d). The specific geometry was designed in light of potential deformation which would form into a specific 3D shape as the released bilayer structure rolled up (Figure 6.1e). In this manner, a variety of 3D shapes can be conceived using different geometrical patterns. Note that the laser-assisted machining can be substituted by other similar fabrication methods. When the bilayer structure was detached from the rigid substrate, individual ZnO NWs initially grown

on Layer Z were broken near the interface between Layer Z and the glass substrate. One part of the ZnO NWs remained embedded in Layer Z and should serve as a seed layer for the re-growth of ZnO NWs on Layer Z afterwards (Figure 6.1f1, g1 and h1)). Another part of the ZnO NW array was left onto the rigid substrate which could be also used as a seed layer for new growth, i.e., promoting the recyclability of the rigid substrate. Eventually, these curved sub-millimeter structures with the embedded ZnO NWs with their tips being exposed at the surface were immersed into the same hydrothermal growth solution, resulting in the regrowth of ZnO NWs on the ISM surface on Layer Z (Figure 6.1f2, g2 and h2). We reported this regrowth process in Chapter 5, named it as a secondary growth process. Apparently, there are numerous advantages of this secondary-grown ZnO NWs array, including a strong and reliable connection to the PDMS layer (thanks to the partial embedment of ZnO NWs), a larger catalytic surface area (in comparison to a ZnO film) and selectively grown on the desired surface (only appearing on the particular surface of the ISMs). This approach is quite different from the conventional nanomaterial-based hybrid polymer film in which the nanomaterials are randomly dispersed in a matrix. Here, controllability of placing the functional materials into the target location would improve the photocatalytic degradation and versatility of the ISMs. The optical microscopic images (Figure 6.1f3, g3 and h3) shows three geometries produced by uniaxial stretched PDMS bonding (SPB), where the Layer Z (in dark) and Layer P (in transparent) are clearly observed.

Figure 6.2a exhibits an over-rolled circular ISM prepared through the uniaxial stretching, where the thicknesses of Layer P and Layer Z are about 200 μ m and 67 μ m, respectively. As shown in Figure 6.2b, the vertically-aligned ZnO NWs are distributed uniformly along the outer surface of the ISM. No loose NWs were observed after construction. From the inset of Figure 6.2b it can

be seen that approximately 2 μ m-length ZnO NWs were partially embedded in the substrate. The length of the embedded portion can be adjusted by the initial growth time.



Figure 6.2. (a-d) SEM images of the ISM produced by uniaxial process, (b) outer surface of the ISM, (c) boundary of Layer P and Layer Z, (d) side surface of Layer P, (e) Photoluminescence spectrum of the ZnO NWs on ISM and glass, (f) XRD pattern of the ZnO NW on ISM and glass. Scale bar: 500 μ m in a; 30 μ m in b, 10 μ m in c and 20 μ m in d; 5 μ m in the inset of b.

In comparison with the ZnO NWs array on the independent PDMS film, the ZnO NWs maintained the similar quality on the curved surface, whereas the large gaps between neighboring ZnO NWs can be attributed to the substrate bending. A distinctive boundary in Figure 6.2c (same view angle as Figure 6.2a) splits the ISM into a less conducting region (Layer P) and a more conducting region (Layer Z), where only few ZnO NWs lying on Layer P whereas bunches of ZnO

NWs coming out of Layer Z. The parallel striped ripples observed in Figure 6.2d indicate that oxygen plasma treated Layer P may have undergone a uniaxial stretching process with a large strain [³⁴]. In the current case, it is worth noticing that no ZnO NWs remained on Layer P, proving the precise growth of the ZnO NWs on the selective surface. XRD patterns in Figure 6.2e exhibited the wurtzite crystallites and [0001] preferable growth direction of ZnO NWs on the PDMS film, where the marked peaks are assigned to the characteristic of ZnO, and the peak at (002) with a higher intensity indicates the preferable growth of ZnO NWs along the c-axis direction. Figure 6.2f illustrates the PL spectrum of the ISM under the excitation of 328 nm UV-LED irradiation. The PL peak location presented two respective emission bands at 389.58 nm and 490.63 nm, each corresponding near-band emission and oxygen-derived defects in ZnO, respectively. These results match those of the ZnO NWs grown on the rigid substrate [³⁵]. High crystallinity from XRD and strong PL intensity suggest the high quality of the ZnO NWs grown on the ISM via the two-step growth process. Consider the scalability of the hydrothermal method for ZnO NW synthesis reported on 4" Si wafer [³⁶⁻³⁸] and laser micromachining, thousands of diverse ISMs can be obtained within few hours, representing an efficient and low-cost process.



Figure 6.3. (a) photocatalytic activity of ISMs in different quantities, (b) numbers of ISMs with various shapes on the degradation rate of MB. Experiments proceeded at room temperature.

A series of experiments were carried out to investigate the photocatalytic degradability of ISMs under UV irradiation, where methely blue (MB) was used as a probe pollutant. The

degradation tests on semi-circular ISMs are shown in Figure 6.3a to elucidate the effect of ZnO NWs on ISM, of which the degradation efficiency varied from 45% to 55% in 6 hours with an increased amount of ISMs were applied to the photocatalytic process. The influence of various shapes of ISMs with respect to degradability was also explored which is shown in Figure 6.3b. Four different shapes of ISMs were examined under the same working condition. As can be seen that the over-rolled ISMs acquired an excellent degradation efficiency (90%) with a small quantity in four hours, while much larger quantities of other types of ISMs should be utilized to approach the similar result. As a conclusion, this discrepancy is mainly attributed to the difference of the active surface area in diverse shapes. Note that there is a positive linear correlation between the active surface area and their shapes. For example, the quantity of quarter-circular ISMs was doubled as that of semi-circular ones, which indicate that the doubled active surface offered a higher decomposition rate of MB dye. Additionally it also implies that a near-complete degradation can be achieved by either extending the reaction time or increasing quantity of ISMs. Evidently, those data above confirms the stable performance of ISMs in photocatalytic degradation.



Figure 6.4. Time-lapsed images of a micromotor in the 70% ethanol solution with 5% H2O2. (a) t = 1s, (b) t = 10s, (c) t = 20s and (d) t = 30s. Scale bar: 2 mm.

To demonstrate the versatility of ISMs, the autonomous movement in an aqueous solution was explored. Here the recoiling force was employed for the purpose of the self-propelling ISM.

The recoiling force is known to possess the high speed and the long-span spiral motion to propel the entire structure [^{24,25}]. According to the relevant reports, the recoiling force is usually realized by the generation oxygen bubbles in the presence of hydrogen peroxide (H_2O_2) in solution and noble metal (e.g. Au, Ag, Pt) layer on micromotors [25]. It is worth noticing that a noble metal layer serving as catalysts can be placed in specific locations when fabricated onto micromotors with various shapes. For tubular-like micromotors Ag is placed at the inner surface uniformly where bubbles can generate and accumulate simultaneously. In other designs such as spherical micromotors, an asymmetric Ag deposition was employed since it is efficient to power asymmetric micromotors [15,20]. In our experiment, the ISMs in various shapes were found with low Reynolds number (0.03-0.05) due to the small characteristic length, and their motions should follow with recoiling mechanism in term of asymmetric Ag locations. In the fabrication of ISMs, Ag was deposited uniformly across the entire PDMS surface (an extra step between Figure 6.1d and Figure 6.1e) prior to the secondary growth of ZnO NWs. Figure 6.4 shows the autonomous movement of the semi-circular ISM in a diluted ethanol solution in the presence of H₂O₂, where bubbles ejected from the backside surface of the ISM generated a recoiling force to propel the micromotor forward with an average speed of 125 μ m/s. The corresponding video is attached in Support Information (Video S1), in which a linear trajectory was observed during the experiment, indicating that the sustainable driving force was achieved. A constant rotation accompanied with the global movement of the semi-circular ISM can be attributed to the poor-oriented driving forces which generated asymmetrically on the backside surface. Other than the asymmetric designs, the propulsion of the tubular ISM was also carried out with the Ag film deposited on its backside surface uniformly. As reported, for a successful tube-shape micromotor O2 needs to be ejected only at one-end opening, which acted the propelling force to drive the ISM [³⁹]. In our case, since

Ag deposited at the inner wall results a symmetric structure, the tubular ISMs could not realize directional swimming as the bubbles generated on both ends make micromotor stationary [²⁴] (Video S2). Therefore a preferred asymmetric geometry is essential for a great directional motion of the ISMs in the future.

To date, multi-functional microrobots have become attractive due to its versatility and operability, and are useful in many applications [⁴⁰]. For instance, autonomous movement could improve the performance of micromotors for drug delivery and photocatalytic degradation $[^{16,41}]$. Apart from the recoiling force, other propulsion strategies based on external fields (e.g., ultrasonic, electric and magnetic), have been developed in realizing movement of micromotors [⁴⁰]. Amongst, the magnetic field are considered as an effective external stimuli to guide the motion of the ISMs remotely [⁴⁰]. In this work, magnetic materials were employed to create desired ISMs with the proper response of the stimuli. The magnetically-controlled movement of the semi-circular ISM in water is displayed in Figure 6.5 (Video S3). As shown, within 60 seconds the ISM was remotely controlled to move around the "MSU" letters. The ISM during the experiment performed linear trajectory and the moving speed of ISM varied in terms of the applied magnetic field. The ISM could freely swim due to the sufficient magnetic force provided by embedded magnetic materials in comparison to the drag resistance in water. In current case the remote distance of the ISM was maximally 2 cm. A stronger magnetic field is required to further increase this distance. It can be imaged that ISMs coupled with magnetic materials is able to be navigated towards desired objectives, which is advantageous to drug deliver and photocatalytic degradation. More works need to be done in term of the geometry effect and sustainable against the long-term navigation.



Figure 6.5. Time-lapsed images of a micromotor atop water. (a) t = 1s, (b) t = 20s, (c) t = 40s and (d) t = 60s. Scale bar: 2 mm.

The autonomous movement of Ag-ISMs with respect to their enhanced degradation rate was evaluated. In Figure 6.6 (a), the same concentration of H₂O₂ was added in MB dye solution prior to the experiment, which worked as a catalyst accelerating the decomposition of MB dye for all three scenarios [¹⁶]. Obviously, the function of self-propulsion further promoted the degradation rate in comparison to free Ag-ISMs thanks to the lower mass transfer resistance (Figure 6.6a). Moreover, both original ISMs and self-propelled Ag-ISMs performed higher degradability than that of the reference one, confirming the valid photocatalytic capability of ZnO NWs fixed on these ISMs. This result validates the synergetic effect of the combined functionality, i.e., photodegradation and self-propulsion. The experiment in Figure 6.6b presents the comparison of magnetic-propelled ISMs to original ISMs. A magnetic field was applied to the solution placed on a stir plate without a magnetic stirrer inside. Instead the solution was populated with magnetic ISMs and thus mixed by the movement of ISMs. As a result, the magnetic-propelled ISMs have the best photocatalytic performance, which, likewise, ascribes to the reduction in the mass transfer resistance derived from the magnetic movement. The all three scenarios in Figure 6.6b exhibit lower degradation rate than that in Figure 6.6a due to the absence of H_2O_2 , which has a significant effect to MB dye degradation. Taking account the toxicity of H₂O₂, magnetic-propelled ISMs are more promising as photocatalysts regarding the environmental remediation while self-propelling ISMs are suitable for other applications.



Figure 6.6. Photocatalytic activity of ISMs (a) with/without self-propulsion, (b) with/without magnetic propulsion. Experiments proceeded at room temperature.



Figure 6.7. Schematics of the SPB process. (a) Layer P was stretched at a certain ratio, (b) the bilayer structure was formed between Layer P and Layer Z, (c) The deformation of bilayer structure took place right after the releasing of stretching force on Layer P, (d) The deformation process stopped until bilayer structure was fully relaxed, where a curved bilayer structure was obtained.

The ISM was converted from a 2D film to a 3D structure arises from the mismatch strain of the two PDMS layers. The stretching ratio of Layer P with respect to Layer Z is regarded as one key parameter in the fabrication process. PDMS is known that can be uniaxial stretched over 200% [⁴²], whose elastic recovery is the major force in inducing SPB for the fabrication of ISMs. Briefly, the shrinkage initially occurred on Layer P brings linear compression to Layer Z, resulting the folding motion of the bilayer structure after it is detached from the glass substrate. We noticed that the resulting curvature of the micromotors is governed by the initial stretching ratio of Layer P. In other words, the more Layer P is stretched, the larger curvature will be resulted to the micromotors. Layer Z consisting of the PDMS layer and ZnO NWs was plasma bonded to pre-stretched Layer P, which would maintain flat until the bilayer structure is formed and detached from the glass substrate. Upon the investigation of the free body diagram (FBD) of Layer Z and Layer P, we found that the bilayer structure should be always folding upwards because of the moments at the interface. The resulting curvature is calculated using various Stoney formula expressions.

The Stoney formula as one developed theory has been widely applied to calculate the mechanical properties of the bilayer structures [$^{43-46}$]. Modified expressions in response to various assumptions and geometrical parameters can be introduced to describe the curvature of the ISM as a function of its residual strain. The Stoney formula results from the film-substrate bending model based on a few important assumptions. : (1) the thickness of both substrate and film are very small in comparison with their lateral dimensions; (2) the thickness of the film is much smaller than that of the substrate; (3) both the substrate and the film are homogenous, isotropic and linearly elastic; (4) the rotations and deformations are infinitesimally small; and (5) edge effects are negligible. In this work, three models, involving the Stoney formula expression for internal film stress and two modified expressions based on vary assumptions were applied to our structures. The main

difference is the suppression of Assumption (2), non-negligible thickness of Layer P in the model. In addition, the initial stress of Layer Z is negligible in comparison with that of Layer P, which is the extra assumption in the following analysis for the models.

 $\sigma_p = \frac{1}{6} \frac{E_z}{(1 - v_z)} \frac{h_z \kappa}{H}$ $H = \frac{h_p}{h_z}$ $m = \frac{M_p}{M_z} = \frac{\frac{E_p}{1 - v_p}}{\frac{E_z}{1 - v_z}}$

Where κ represents the curvature of the ZCM, ε is the strain of the layer, σ stands for the stress of the layer, M, E, v and h are the biaxial elastic modulus, Young's modulus, Poission's ratio and thickness of the PDMS layers, where z and p as the subscripts refer to layer Z and layer P, respectively. Model 1 is the Stoney formula for the calculation of the internal film stress [^{43,44}]. Model 2,

$$\kappa = \frac{6\delta}{H}F(m,H)$$
$$F(m,H) = \frac{(1+H)^2}{mH^3 + m^{-1}H^{-1} + 4H^2 + 6H + 4}$$

Where δ is the relative reduction of linear dimension. Model 2 is derived considering Timoshenko beam theory [⁴⁶].

Model 3,

Model 1,

$$\kappa = \frac{6\Delta\varepsilon}{h_z} Z(m, H)$$
$$Z(m, H) = Hm[\frac{1+H}{1+Hm(4+6H+4H^2)+H^4m^2}]$$

Where $\Delta \varepsilon$ is the mismatch strain between layers. Model 3 is the general expression of Stoney formula for a given bilayer structure with uniform mismatch strain [⁴⁷].

The comparison of experimental results and modeling ones is displayed in Figure 6.7, where the Poisson's ratio substituted in the models was presumed as $0.5 [^{49-51}]$ for the both layers due to the same mixture ratio of PDMS films. In model 2 and model 3 we respectively employed F(m,H) and Z(m,H) as a dimensionless term to describe the correlation of layer thickness and Young's modulus, where the Young's modulus as a thickness-dependent parameter that was recorded in term of the respective thickness of Layer P and Layer Z, as found by the reported experimental results $[5^{2}]$. It is worth noted that all input parameters in the analysis were originated from the initial status of Layer P and Layer Z before forming into the ISMs. Here consider a bilayer structure consisting of a thick film (Layer P) with tensile stress and a thin relaxed film (Layer Z) with an original length of interface (L1), an opposite shear force instantly generates at their interface when releasing, offering an inward moment and a shrink motion simultaneously, leading a smaller intermediate length with larger deformation. In other words, L obtained at the final state is always smaller than L_1 arising from the tangential shrink of Layer P, which constitutes the major part governing the mechanical properties. The intimately plasma-bonded Layer P and Layer Z have to compress along with the interface, resulting the discrepancy of the real axial strain. In the modelling study we noticed that this issue was partially released by employing L, L_p and L_z simultaneously into the model as the replacement of L₀, although a undesirable deviation would occur, which needs to be addressed in future work.

It is known from Figure 6.7 that the stretching ratio of Layer P is one key factor influencing the geometry of the ISMs. As depicted in Fig 6.8(a-b), both curvatures from the analysis and

experiment exhibit a linear proportion to εp , demonstrating that apparent deformation took place at heavy stretched Layer P.



Figure 6.8. (a) the comparison of experimental curvatures and analytical curvatures as a function of the stretching ratio of Layer P, (b) detail comparison of model 2 and model 3, (c) circular ISM with $L=1500 \mu m$, (d) over-rolled ISM with $L=2000 \mu m$. Scalebar: 100 μm .

From Figure 6.8a it can be concluded that, model 1 has quite large error to fit experimental data in comparison to other models, which expresses an increased discrepancy at larger stretching ratio. This deviation is attributed to the limited assumptions which needs further modification. Model 2 and Model 3 as two modified Stoney formula perform better result-fitting in the range of current stretching ratios. However, serious deviation emerges in Model 2 at larger stretching ratio while excellent result-fitting is found on Model 3 all the time, indicating that Model 3 is the most suitable model for predicting deformation of ISMs in current situation. The further, we noticed that all three models are not able to predict ISM at sharp shape (over-rolled ISMs). Figure 6.7e shows two ISMs with similar H and M, apparently, the shape of the ISM constructed via SPB correlates highly with L under the same κ where the circular shape can be obtained only when

 $2\pi/\kappa \ge L \ge \pi/\kappa$. In practical, the region around the ends of the circular ISMs could not deflect as much as the other parts due to the unbalanced self-constrain, which became thicker and more flat, resulting an error of κ in analysis. Similarly, the κ of over-rolled ISMs (inner circular) differs from that of the circular ISMs owing to the extra bending arisen from the overlapped free ends. In view of the above, some volume-dependent factors should be considered in further modifying model 3 in future.



Figure 6.9. (a-g) schematics of biaxial SPB process. (h-l) hollow and semi-closed ZCM with various shapes and sizes, Scalebar: (h-j) 500 μ m, (k,l) 1 mm.

In addition to the circular shapes shown above, the capability of SPB in constructing hollow (and semi-closed) ISM has been proved. As depicted in Figure 6.9, a number of shapes was achieved with the assist of biaxial stretchable stage. Similar as uniaxial SPB, Layer Z was prepared and plasma bonded with stretched Layer P, whose stretching ratio upon two directions varies according to the geometry design (as shown in Figure 6.9 (a-g)). After detaching from substrate, the bilayer structure deformed by shear force immediately, which shrink along two perpendicular axis towards the body center. In our experiment, the symmetric shapes (i.e. spheres and cubes) could be obtained through equally stretching Layer P on two directions. In contrast, asymmetric shapes were originated from different stretching ratio of Layer P on both directions. Obviously, the biaxial SPB method is promising to pursue the complex shape of ISM. After the investigation of those ISMs, we found that some particular complex shapes approached by varied stretching ratio could be analyzed by employing uniaxial model respectively to the priority shrinking direction and secondary shrinking direction.

For instance, the semi-sphere ISM in Figure 6.9i was achieved by biaxial SPB method with the equal stretching ratio of Layer P on both direction. This scenario was found to be very close to the fabrication of circular ISM using uniaxial SPB method (Figure 6.8b, $\varepsilon_p = 1$). The comparison of analytical curvature (using Model 3) to experimental curvature shows a similar error as the case shown in Figure 6.8b (purple line vs. red line, $\varepsilon_p = 1$), indicating the accuracy of Model 3. Nevertheless, Model 3 is failed to match the hollow-sphere ISM in Figure 6.9j. This difference may be attributed to the constitution of structure. The half-sphere ISM reaches relaxation status whose fingers have no contact to each other, while the fingers on hollow-sphere ISM suffer the stress from neighbors which prevents the further deformation. This difference is also applicable to asymmetric ISMs (i.e. Figure 6.9l vs. 6.9k). In addition, the dimension of complex ISMs is determined by the smaller stretching ratio in current case.

Other than shape diversity, the functionality is expected to be extended using biaxial SPB. For the hollow-sphere ISM, the cavity inside the structure is able to be used as a cargo. The manageable cargo transportation regarding micromotors has been investigated extensively in recent years which has been rendered a variety of capabilities such as objective capturing and unloading [^{25,40}]. Taking account the developed mechanisms for autonomous movement, the hollow-sphere ISM is a very promising candidate in the application of cargo transportation. Furthermore, since the deformation is originated from the elastic recovery of PDMS film, the fabricated ISMs will memory the shape all the time in ambient condition, which guarantees its long lifetime and stability. Finally, to our knowledge, ISM is the first micromotor that has 1D ZnO NWs fixed on its surface. This unique structure not only benefits for the photocatalytic degradation but also paves a way to immobilize 1D nanostructures to other soft micromotors. More potential applications will be explored in the future.

6.5 Conclusion

In conclusion we have developed a new type of micromotors that has ZnO NWs array embedded in the particular surface. Plasma treatment is utilized as a reliable method to combine PDMS films. The remarkable performance in photocatalytic degradation of ISMs has been demonstrated and few strategies were introduced to integrate the function of autonomous movement to ISMs. Besides, few mathematic modelling was developed to analyze the deformation of ISMs in fabrication. Comparing to other polymer-based micromotors, the flexible construction regarding numerous shapes and sizes of ISM enables the integration of multiple functions to satisfy diverse working conditions, which is a promising candidate for both environmental remediation and drug delivery fields. Other than the current components, many other materials will be employed as heterogenous structure to further improve the photocatalytic performance of ISMs in the future. More functions will also be integrated by use of particular structures. REFERENCES

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CHAPTER 7

RAPID AND LARGE-SCALE ASSEMBLY PROCESS FOR 1D NANOSTRUCTURES 7.1 Introduction

One dimensional (1D) nanostructures (NSs), mainly including nanowires (NWs), nanotubes (NTs), nanorods, and nanobelts, have been widely considered as important building blocks for future nanoscale devices [1]. Initial proof-of-concept devices such as transistors/logic circuits $[^{2-6}]$, sensors $[^{7-9}]$, light emitting diodes $[^{10,11}]$, and solar cells $[^{12-14}]$ were fabricated from individual 1D NSs using serial and resource-intensive approaches, which are not adequte for largescale production. Apart from the fabrication limitation, individual 1D NSs devices may not meet operation requirements due to their low driving current, low lumens, low signal-to-noise ratio, and significant device-to-device performance variation [¹⁵]. Instead the networks of 1D NSs with random orientations have been considered a promising path for realizing high performance thinfilm transistors (TFTs) for macro- and flexible electronic applications. Random networks of 1D NSs solves the scalability problem, improves the current-driving capability of the resulting devices due to the large number of conducting materials incorporated into the device channel, and greatly improves the uniformity of the device performance. The common assembly methods used to obtain random networks of 1D NSs include spin coating $[^{16,17}]$, dip coating $[^{18,19}]$, vacuum filtration $[^{20,21}]$, and printing $[^{22,23}]$. The first three methods, while suitable for large-area fabrication, typically entail the subsequent photolithographic pattern and selective etching/liftoff. Considering the size of the active components (on the order of a few percent aerial coverage), most of the NS areas need to be etched away or lifted-off, causing a significant amount of nanomaterials to be wasted or needed to be recycled.

Many attempts have been made to genetrate an array of well-defined, random network patterns directly from solution-processed 1D NSs with the maximal material utilization. One approach is a use of an external (e.g. electrical $[^{24-27}]$, magnetic $[^{28,29}]$, and acoustic $[^{30,31}]$) field for NS localization. Most, if not all, of NSs are deposited onto the target regions on the substrate. While these field-based methods often accompany the benefit of NS alignment $[^{32,33}]$, a large-area patterning may still be time-consuming and costly. On the other hand, the template-based assembly like solution-based self-assembly [^{34–36}] can be readily implemented in a wafer scale. However, controlling the NS density and uniformity in the patterns across the entire substrate is still challenging because the surface-mediated interaction with the functionalized NSs extends only to the first layer. The deposition of the subsequent layers is less controllable, leading to the greater variabilities in the network thickness and corresponding film properties. Here we consider filtration-guided assembly (FGA) as a scalable, inexpensive assembly platform that creates 1D NS patterns without generating any waste stream of nanomaterials and minimizes the environmental footprint. FGA is based on a vacuum filtration method that uses filter membranes with nanometersize pores. Since the pionerring work by the Wu's group $[^{37}]$, vacuum filtration has been extensively utilized for the preparation of macroscopic random-network films from various 1D or 2D NSs such as carbon nanotubes (CNTs) $[^{37-42}]$, nanowires $[^{20,21,43,44}]$, graphene/graphene oxide $[^{45-49}]$, organic micro/nanofibers $[^{50-52}]$, and a mixture of these nanoscale building blocks $[^{53-55}]$. FGA utilizes selective filtration of NSs through the open windows on the nanoporous filter membrane whose surface is patterned by a polymer mask for guiding the NS deposition. CNTs [⁵⁶], organic microfibers [⁵⁷], and biological samples [^{58,59}] were patterned via FGA and used as functional elements for electronic devices or bioassay. In all of these previous work, anodized alumina oxide (AAO) membranes were the choice of the filter membrance. But they are

expensive, fragile, and difficult to handle, and thus not suitable for the large-area fabrication. The pattern resolution of FGA has been also limited to tens to hundreds of microns (for the reasons to be discussed later).

The objective of this work is to create a template-like FGA platform on robust nanoporous membranes with high-resolution (sub-10-micron) patternability and demonstrate the homogeneity (density control) of the patterned 1D NS network over 20 cm² area. We will utilize the blanket transfer (BT) method, a modified soft-lithography technique previously developed by our group ⁵⁰], to pattern the surface of the filter membrane. Akin to dry film photoresists (PRs), BT laminates a PR layer onto various substrates, but at a much smaller thickness than dry film PRs, facilitating the generation of the patterns as small as 5 μ m. During filtration, the PR pattern will serve as a template, guiding the deposition of the nanomaterials into the opened regions of the filter membrane. We will employ a mixed cellulose ester (MCE) membrane as our FGA platform, which is much more flexible and inexpensive compared to the AAO membranes. The MCE membrane has been used to assemble large-area random-network films of nanomaterials in the past [^{37,60}], but selective filtration of FGA has not been explored with the MCE membrane. The challenges associated with patterning the MCE membrane surface will be addressed. High-purity semiconducting single-walled CNTs (SWCNTs) will be used as a model 1D NS to demonstrate the concept of the proposed FGA. A simple technique to pick up and transfer the SWCNT network film will be presented for the transistor device applications.

7.2 Experimental

7.2.1 Blanket transfer process



Figure 7.1. A schematic diagram of the fabrication sequences showing a versatility of PR blanket transfer in different settings; (a) a PR film spin-coated and partially cured on a flat PDMS stamp; and the fabrication of exemplary multilayer or freestanding microstructures using the PR BT process such as (b1-b4) multilayer polymeric structures, (c1-c4) free-standing polymeric structures, (d1-d4) PR patterns on a porous membrane.

As mentioned above, BT is a modified soft-lithographic process; that is, transferring a spincoated PR film from a flat elastomeric stamp to a substrate (Figure 7.1). The elastomeric stamp is highly compliant, bringing the PR film into intimate contact with the substrate and eliminating the need of large lamination pressure. Upon peeling of the stamp, the film can be transferred to a variety of substrates; flat, etched, curved, fragile, and porous substrates. In addition, the thickness (submicron to tens of microns) and tone (both positive and negative) of the PR film can be judiciously adjusted for the target applications. One utility of the PR BT process is to apply a PR layer on top of porous substrates without damaging or blocking the pores. If the PR solution is directly spin-coated or sprayed, excessive PR would flow into the pores, making it difficult to be exposed and developed. Moreover, porous AAO membranes are difficult to be patterned because of their brittle nature [⁵⁸]. The PR BT process entails very small lamination (or rolling) pressure, facilitating the transfer of PR to the fragile AAO substrates. Here the same PR transfer principle can be applied except that a low surface energy of the alumina surface makes the PR transfer to the AAO membrane more challenging. Surface modification prior to transfer including a short deposition of metal (e.g. Cr) film helps to increase the surface energy of the alumina membrane and improve the transfer yield. In addition, the positive-tone PR (e.g. AZ 1518) is preferably used over the negative PR because the positive PR does not require the post exposure step and can be removed relatively at ease in the ensuing processes. Once the PR is transferred, the film can be patterned using photolithography. We observe that parts of the PR film were pressed into the pores during the transfer, and a higher exposure dose and a longer development time compared to a film on a flat, rigid substrate are needed to ensure the openness of the pores after patterning. Figure 7.2a shows line patterns of PR AZ 1518 with the nominal line width and spacing of 5 μ m on the AAO membrane. One of these line patterns is imaged using SEM (see Figure 7.2b) to reveal the openness of the pores after patterning. Individual pores of average 220 nm are clearly seen in the inset image without the PR residues. The openness of the pores in the patterned AAO membrane can be further tested by filtrating a nanomaterial suspension through the filter membrane. If pores in the patterned windows are not blocked, the suspension solution will flow through these open windows and nanomaterials will be preferentially collected over them. A SWCNT suspension is vacuumfiltrated through the AAO membrane patterned with an array of square openings. The dark jade

regions in Figure 7.2c represent an array of SWCNT mats while the light green areas are the PR layer on the AAO membrane. The SEM image of a single opening and the inset image in Figure 7.2d also suggest that SWCNTs are deposited only on the patterned window. This selective deposition of the SWCNT mats imply a scalable approach to deterministically assemble nanomaterials on the substrate [^{56,57}].



Figure 7.2. (a) An optical micrograph of an array of PR 1518 lines patterned on the AAO membrane; light jade – PR lines, dark jade – AAO membrane, (b) an SEM image of the PR patterns in (a) showing the open porous structures; scale bar in inset image is 500 nm, (c) an optical micrograph of an array of SWNT mats after the vacuum filtration of SWNT suspension through the PR-patterned AAO membrane; light green – PR pattern, dark jade – SWNT mat on the AAO membrane, (d) an SEM image of the single square window on which the SWNTs are selectively deposited to form a CNT mat; scale bar in inset image is 500 nm.

7.2.2 Patterning of the MCE membrane

A 3-mm-thick PDMS stamp was firstly prepared by casting the mixed solution (10 parts of SYLGARD 184 pre-polymer and 1 part of the curing agent, Dow Corning Co.) on a clean Si wafer. Photoresist (Shipley 1813, MICROCHEM Co.) was then spin-coated on the PDMS stamp at 5000 rpm for 1min. After 30 sec softbaking at 60°C, the PR layer on the PDMS stamp was

brought into an intimate contact with a MCE membrane (Hydrophilic, 0.22 μ m, 47 mm in diameter, Millipore Co.) at 110°C for 3 mins. Prior to the PR transfer, the MCE membrane is prebaked at 110°C for 2 mins and mounted onto a rigid substrate (e.g., a flat, 3-mm-thick aluminum plate). Sometimes a thin (~20 nm thick) Cr layer (sputtered under 50 mPa background pressure) can be deposited onto the MCE membrane to enhance the adhesion of the PR. The PDMS stamp was then slowly (< 0.1cm s⁻¹) peeled away from the MCE membrane, leaving the PR layer onto the membrane. Before cooling down to room temperature, another 1 min soft-baking at 110°C was performed to improve the adhesion of the PR film to the membrane. Standard photolithography, including the UV exposure (AB-M mask aligner, dose: 180 mJ·cm⁻²) through a photomask and the subsequent development (Shipley 352 developer, Dow Co.), were carried to accelerate the development speed and completely open the pores in the patterned windows. Upon the development, the patterned membrane was rinsed thoroughly with DI water, dried, and stored in a dust-free environment.

7.2.3 SWCNT solution preparation and vacuum filtration

Two different SWCNT solutions were used in the experiment. For the general FGA experiment, unsorted SWCNTs (purified HiPCO, Unidym, $0.8 \sim 1.2$ nm diameter, $100 \sim 1000$ nm length) were suspended in 1% sodium dodecyl sulfate aqueous solution. The typical concentration ranges from 0.5 to 10 mg·L⁻¹. For the transistor experiments, a 95% pure semiconducting SWCNT solution was purchased from Nanointegris Technology Inc. and diluted in an ionic surfactant solution (1%) for filtration. A vacuum filtration setup was purchased from Fisher Scientific (47 mm filter holder) and connected to a solvent trap and a vacuum pump (Alcatel 2021I). The

configuration for filtration is based on the dead-end flow similar to the popular benchtop chemistry labware (Figure 7.3).



Figure 7.3. (a) The schematic diagram of the filtration system for depositing SWCNTs. (b) Photo of the filtration system in the experiment.

The dead-end flow filtration allows the uniformly distributed pressure to be applied over the filter membrane, leading to higher spatial uniformity. Before the patterned MCE membrane (the patterned side facing up towards the solution) was positioned on a flat glass frit, the glass frit was made wet by a few water droplets. Applying a vacuum pressure briefly would bring the membrane into a conformal contact with the frit and remove any air bubbles that may have been trapped. The prepared SWCNT solution (20~100 mL) was then poured over the filter membrane. A vacuum pressure was applied until all the solutions were completely removed. The vacuum pressure was kept for additional 3-5 mins after the filtration, and the filter membrane was retrieved after the negative pressure diminished. The membrane was further dried overnight, or oven drying at elevated temperature (~ 80°C) expedited the drying process.

7.2.4 SWCNT transfer and transistor fabrication

A commercial PVA film (3M Inc.) was first laminated over the MCE membrane towards the filtrated side. In order to improve the conformal contact between the PVA film and the SWCNT patterns, we kept the stack under a low vacuum (~ 100 Pa) about 30 mins. By gently peeling the PVA film off from the MCE membrane, the SWCNT patterns were picked up along with the PR layer. Meanwhile, an n++ doped Si wafer (University Wafer, <100>, phosphorous, 0.001~0.005 Ω cm) with a 100-nm-thick SiO₂ layer was used to pattern the Ti/Au electrodes with various gaps $(5, 10, 20, 50 \,\mu\text{m})$ using the standard photolithography followed by metal lift-off. To improve the adhesion of SWCNTs onto the receiving substrate, the SiO₂ surface was functionalized with 3-(aminopropyl)triethoxysilane (APTES, Sigma-Aldrich) as an amineterminated self-assembled monolayer. Prior to the APTES functionalization, the substrate was cleaned using the standard cleaning procedure (5:1:1 vol. % of DI water, ammonium hydroxide and hydrogen peroxide) to terminate the SiO₂ surface with hydroxyl groups. After laminating the SWCNT-PR/PVA stack on the APTES-treated SiO₂ substrate under the slight pressure and elevated temperature (~ 90°C), the stack was transferred to a warm water (~ 60° C) bath until the PVA film was completely dissolved. A brief acetone soaking was then carried out to remove the transferred PR layers.

7.2.5 Materials and device characterization

All the optimal images were obtained from the upright microscope (Nikon LV100) under the reflection mode. The SEM images were collected from Hitach S-4700 Field Emission Scanning Electron Microscopy. The pattern height measurements were performed using Dektak3 Surface Profiler. The s-SWCNT transistor characteristics were measured using an Agilent B1500A semiconductor parameter analyzer.



7.3 Result and discussion

Figure 7.4. A schematic of the filtration guided assembly (FGA) process; (a) spin-coating of PR on the flat PDMS stamp, (b) conformal contact between PR/PDMS and the MCE filter membrane, (c) slow peeling of PDMS transferring the PR layer onto the membrane, (d) patterning PRs using photolithography, (e-f) vacuum filtration to guide nanomaterials onto the pattern openings.

Creating large-area patterns on the surface of porous substrates with sub-10-micron resolution proves to be challenging. For example, during spin-coating, the pores in the membrane can be blocked by PR when a negative pressure is applied to a spinner chuck to hold the porous substrate. Even with the extended exposure and/or PR development times, the PR layer embedded in the pores cannot be completely removed, hampering the subsequent FGA step. Dynamic spin-coating [⁵⁶] or a special membrane holder [58] was used to reduce the PR flow into the porous structures, but the pattern size smaller than 10 µm has not been demonstrated on porous substrates. Another challenge is the extremely brittle nature of some porous substrates like the AAO membrane, which excludes the option of using dry PR films due to high pressure required for lamination. On the other hand, spin-coating of PR is not compatible with the MCE membranes

because the solvents in PR attack the membrane. Below we shall show how we utilize the PR BT to create high-resolution patterns on the MCE membrane, which will serve as the FGA template.

Figure 7.4 illustrates the sequence of the proposed FGA method. First we transfer a uniform PR film onto a MCE membrane via BT. A thin (2~5 µm) PR layer is spin-coated onto a flat elastomeric (e.g., polydimethylsiloxane (PDMS)) stamp (Figure 1a). A highly compliant PDMS stamp allows the PR film to be brought into intimate contact with the MCE membrane without the need of large lamination pressure (Figure 7.4b). The detailed description of the BT technique has been reported elsewhere [⁵⁰]. The PR layer transferred onto the MCE membrane is then subject to the standard photolithography process (Figure 7.4c and 7.4d). Depending on the BT parameters, the transferred PR layer can be partially embedded into pores in the filter substrate. In order to construct completely opened patterns in the porous membrane, relatively longer (1.5 times the standard recipe) UV exposure and development time are employed with a gentle sonication. Next, the patterned MCE membrane is placed on a vacuum filtration setup, and the suspended SWCNTs of a known volume is filtered through the membrane. Almost all SWCNTs are deposited only onto the opened patterns while the solvent (e.g. water) gets removed through the filter membrane (Figure 7.4e and 7.4f). The resulting SWCNT network patterns are to be transferred to the target substrate for further characterization.

Figure 7.5 shows the optical microscope images of the various PR patterns (Shipley 1813, $1.4 \sim 1.6 \,\mu\text{m}$ thick) on the MCE membrane before and after the SWCNT filtration. The brighter portions of each image in the left column of Figure 7.5 are the opened patterns on the MCE membrane while the darker areas in the right column are the filtrated SWCNT networks. As the SWCNTs are guided by the water flow and stacked on top of one another, they form a random network structure inside each pattern. Lines, circles, and squares have been patterned on the MCE

membrane with the minimum feature size of 5 μ m, which corresponds to our previous report [⁵⁰]. FGA combined with BT is capable of producing an arbitrary shape of the nanomaterial network because the pattern is photolithographically defined.



Figure 7.5. Optical microscope images of the PR-patterned MCE membrane before SWCNT filtration (a),(c),(e) and after filtration (b),(d),(f). Various SWCNT patterns were formed onto the opened regions of the MCE membrane. Scale bars are 100 µm in the large views and 10 µm in the inset.

The line pattern in Figure 7.5b also demonstrates the high density array, where the proportion of the opened region to the blocked region is about 1 to 1. An extent to which FGA maximizes the nanomaterial utilization (i.e., minimizing its wastes) can be investigated by the careful inspection of the patterned filter membrane and the filtrated solvent waste. First, the PR patterns on the filter membrane are imaged at high resolution in the optical microscope and HRSEM, corroborating that no apparent residues of SWCNTs were deposited atop the PR surface

(see Figure 7.5 and 7.6). This means that SWCNTs were faithfully guided towards the openings on the filter membrane. Secondly, the wasted solvent from the initial filtration was collected and re-filtrated over a new MCE membrane.



Figure 7.6. Photographic images of the 47-mm MCE membrane patterned with the PR layer (a) before filtration and (b) after filtration of the SWCNT solution; SEM images of the individual linearray pattern (c) before SWCNT filtration and (d) after the filtration; (e-g) SEM images of the SWCNT films deposited on the opened pattern for three different SWCNT loadings – 0.1, 0.25, 0.8 mg/L, respectively. Scale bar: 8 mm in (a) and (b), 100 μ m in large view of (c) and (d), 20 μ m in the inset (top right) of (c) and (d), 200 nm in (e-g).

The MCE membranes after the initial filtration and re-filtration were imaged and compared to each other (Figure 7.7). Few SWCNTs were observed on the re-filtrated membrane, indicating that most of SWCNTs, if not all, were filtered onto the membrane during the initial filtration. It has been also shown that the characteristic Raman peak for SWCNTs is missing in the re-filtrated membrane (see Figure 7.7c). This near-100% filtration result represents a route to maximal nanomaterial utilization in assembling 1D NS networks.



Figure 7.7. Photographs of the 47-mm-diameter MCE membranes (a) after filtration of 40 mL of highly concentrated (~8 mg/L) SWCNT solution and (b) after filtration of the waste solvent collected from (a). (c) Raman spectroscopy measurements performed on the bare MCE membrane, after 1st filtration of the SWCNT solution (a) and after re-filtration of the wasted solvent (b). The characteristic Raman peak (G band) is missing in the re-filtrated MCE membrane.

To systematically study the FGA process and explore its applicability for device fabrication, we designed an array of line patterns (16 of 20 µm wide, 500 µm long as shown in Figure 7.8) and distributed them over a 47-mm-diameter MCE substrate. Each line array would serve as a channel layer for SWCNT-based transistors. Figure 7.6a and 7.6b show the photographs of the PR-patterned MCE membrane before and after SWCNT filtration. It is estimated that the

MCE membrane has an open area of approximately 1.2 cm², which corresponds to 6.9% of the entire filter membrane. As filtrated with the SWCNT solution, the opened regions of the MCE membrane became darker. The amount of the SWCNTs deposited onto the membrane can be estimated from the volume and concentration of the SWCNT solution, which were 40 mL and 0.25 mg/L for the sample images shown in Figure 7.6b. From the high resolution SEM image in Figure 7.6c, the porous structures of the MCE membrane is observed – the nominal average pore size is 220 nm.



Figure 7.8. (a) A photograph of the 47-mm MCE membrane patterned with the PR layer before filtration, (b) an optical microscope image of the individual line array pattern from (a), (c) the same MCE membrane as (a) but after filtration of the SWCNT solution, (d) the SWCNT line-array pattern from (c). Scale bar: 8 mm in (a) and (c), 100 μ m in (b) and (d).

One of the key metrics to determine the pattern quality of the proposed technique is the relative amount of the SWCNTs deposited atop the PR film vs. ones deposited onto the patterned windows. From the optical and SEM images of the filter membrane (Figure 7.6d and 7.8), no SWCNTs (black dots in the optical image) are found outside the patterned windows, demonstrating
a high yield of patternability (> 99%). Comparing the top right insets of Figure 7.6c and 7.6d, we can conclude that a conformal contact between the PR layer and the MCE membrane guarantees the side-sealing and funneling a solvent flow only onto the openings in the filter membrane. Figure 7.6(e-g) shows the zoomed-in SEM images of the SWCNT patterns, where a number of distinctive SWCNT bundles can be readily recognized. The total amount of SWCNTs in each pattern opening can be controlled by the concentration of the SWCNT suspension and its volume.

On a separate note, one may consider a FGA's potential to align 1D NSs. In fact, the FGA method was demonstrated in the past for aligning organic microwires [⁵⁷]. One of the key requirements for alignment is that the FGA pattern width should be comparable to the length of NSs, so that the NSs would be aligned to the pattern direction to minimize the flow resistance exerted by the filtration-induced flow field. Since the length of commercially available sorted SWCNTs including ones used in this study is rather short (< 0.5 μ m), the pattern width on the filter membrane needs to be submicron to achieve some degree of alignment. Due to the limited pattern resolution (as mentioned earlier, the best resolution so far attained is 5 μ m), we think that the alignment of SWCNTs would be impractical. Instead, one can explore the possibility of using longer1D NSs for aligning experiment.

Since the SWCNT line patterns are formed simultaneously over the entire membrane surface within a few to tens of minutes, the FGA platform presents a facile approach to the largearea assembly of 1D NSs. Figure 7.9(a) shows the measured average filtration speed as a function of the solution concentration. The filtration speed is reduced with the increasing concentration of the SWCNT solution because the SWCNTs would be deposited at a faster rate for the higher concentrated solution, slowing down the subsequent filtration. Since the instantaneous filtration speed is a function of time, measured experimentally is in the range of the predicted values for a given filtration condition. Note that if a constant pressure is applied across the filter membrane, the filtration speed will be slowed down as the SWCNT filter cake is formed within the open window. For the dead-end filtration process in this experiment, the modified Darcy's law equation can be used to express a filtration speed or a flow rate through the membrane. An inverse of the filtration flow rate (t/V), where t and V are the filtration time and (total solvent) volume, is given as [⁶¹],

$$\frac{t}{V} = \frac{\mu c \alpha}{2A^2 \Delta P} V + \frac{\mu L}{\varsigma A \Delta P} \tag{1}$$

where \varkappa , *A*, *L* are the intrinsic permeability, open area, and thickness of the filter membrane, respectively. ΔP is the pressure drop across the membrane, μ is the viscosity of the SWCNT solution, *c* is the concentration of SWCNTs by weight, and α is the specific cake resistance of the SWCNT pattern. In Equation (1), the first term on the right hand side indicates the flow resistance due to the filtered SWCNT pattern while the second term is related to the flow resistance imposed by the filter membrane. For the MCE membrane ($L \approx 150 \,\mu$ m), \varkappa can be estimated from the flow rate measurement of pure water for a given pressure drop and was found to be $4.21 \times 10^{-11} \text{ cm}^2$ (consistent with the data sheet, GSWP04700, https://www.emdmillipore.com/US/en/product/). The solvent of the SWCNT solution is deionized water whose μ is around 0.89 mPa·s at 25°C. As mentioned above, *A* is calculated to be $1.2 \,\text{cm}^2$. During the experiment, the applied vacuum pressure amounted to 100 Pa, indicating a maximum pressure difference of around 10⁵ Pa across the filter membrane. *V* is fixed at 40 mL. Based on these parameters, the specific cake resistance of SWCNTs, α , can be estimated and ranges from $2.82 \times 10^{13} \sim 5.33 \times 10^{13} \text{ m/kg}$ [⁶²].

The MCE membrane is a commercial filter with high porosity and hydrophilicity and commonly used to separate solutes from solvents like water. Quite a few reports including this work have employed the MCE membranes for nanomaterial filtration thanks to their high porosity and filtration speed $[^{37,60}]$. The main disadvantage is that MCE can be easily attacked by alcoholbased or other organic solvents, which makes the FGA process limited to aqueous solvents. If nanomaterials suspended in non-aqueous solvents are of interest for the FGA process, anodic aluminum oxide (AAO) or polycarbonate (PC) membranes can be viable options. As AAO is an inorganic membrane, it is resistant to most of organic solvents. PC is not as resistant as AAO and yet more stable with alcohol-based solvents than MCE. The AAO membrane has high-density and straight pores, exhibiting an ultrahigh filtration speed (several folds faster than MCE) $[^{63-66}]$. However, it is extremely fragile and difficult to perform the BT process, resulting in a lower FGA yield. On the other hand, the PC membrane is highly flexible, easier to handle, and amenable for recycling, but has a much lower porosity than the other two, i.e., requiring a much longer filtration time for the same amount of the solvent. This lower solvent flux also undermines the pattern quality of FGA. The choice of the filter membrane, therefore, depends on the solvent type, required pattern resolution, and available transfer method. The comparison among these filter membranes is summarized in Table 7.1. For FGA of SWCNTs, we conclude that the MCE membrane is the best choice in terms of the ease of handling and patternability.

Once completely dried, the SWCNTs on the filter membrane were transferred onto a target substrate using a water-dissolvable adhesive tape such as polyvinyl alcohol (PVA). The similar transfer processes have been reported for micro-/nanoscale structure transferring [$^{67-70}$]. The main advantage of the PVA-based transfer is that it can pick up almost all the filtrated SWCNTs. However, it took a long time (> 60 min) to dissolve PVA after transfer, and sometimes the organic residues were left on the target substrate. Alternatively, a viscoelastic stamp made of polydimethysiloxane (PDMS) was utilized to pick up only the SWCNT patterns, which were then transferred onto the APTES-treated SiO₂ substrate. The use of PDMS leads to a faster transfer

without any chemicals; but it is difficult to pick up all the SWCNT patterns in its entirety. It can be attributed to the fact that the SWCNTs are slightly recessed compared to the protruded PR layer, hampering intimate contact between the PDMS layer and the SWCNT patterns. This issue becomes worse as a lower amount of SWCNTs is filtrated (i.e., the smaller patterned height). Therefore, in this study, we employed the former approach for the pattern transfer.

	MCE	AAO	Polycarbonate
FLEXIBILITY	medium	low	high
POROSITY	high	high	low
SOLVENT RESISTANCE	low	high	medium
SURFACE HYDROPHOBICITY	low	low	high
BT COMPATIBILITY	high	medium	low
FILTRATION RATE	medium~high	high	low
REUSABILITY	high	medium	high
COST	low	high	medium

Table 7.1. Comparison of the MCE, AAO and polycarbonate membrane in SWCNT filtration tests.

Figure 7.9b shows the topography of SWCNTs patterns transferred onto the SiO₂/Si receiving substrate. The thickness (or height) of the periodic patterns for the SWCNT concentration of 0.25mg in 1 L water and a filtration volume of 40 mL is around 400 nm. The standard deviation of < 10% in the thickness measurements indicates the excellent uniformity of the pattern thickness, which is one of the desired features. The gap distance between the SWCNTs

patterns are also uniform and close to the original gap from the PR pattern on the membrane, demonstrating that the patterns were not disrupted during the transfer process. The spatial uniformity of the transferred SWCTN patterns have been also investigated and discussed in Figure 7.10. In general, the maximum thickness of SWCNT patterns is limited by the thickness of PR layer. When excessive SWCNTs are filtrated, they would deposit over the PR patterns and bridge the neighboring patterns, creating a continuous network film. The SWCNT patterns in Figure 4a were transferred from the filter membrane possessing the 1.5-µm-thick PR layer, indicating a success filtration was accomplished.



Figure 7.9. (a) The average filtration speed measured for the various SWNT loadings with the fixed filtration volume (40 mL), (b) the surface profilometry scan of SWCNT patterns, (c) the sheet resistances of the unsorted SWCNT patterns from the five locations indicated in the inset (after transferred onto the glass substrate), (d) the percolation behavior of unsorted SWCNT pattern.

A set of sheet resistances of the unsorted SWCNT patterns (~ 400 nm thick) from the different positions across the 47-mm transferred area were measured and plotted in Figure 4c, manifesting a small resistance deviation along their positions and further proving the spatial uniformity of the SWCNTs patterns. The assembly homogeneity is guaranteed by the process

itself [37,45]. As the SWCNTs accumulate on the filter membrane, the filtered network impedes the solvent flow rate. Therefore, if SWCNTs are deposited more at a particular region of the porous membrane, the rate of filtration will decrease, allowing more materials to be collected at thinner or uncovered regions. This self-regulating feature facilitates highly uniform patterning over the filtration membrane and is one of the reasons why vacuum filtration is widely used to deposit thin films of various nanomaterials [45]. The unsorted SWCNT patterns of several loadings have been used to create the conductance as a function of the SWCNT loading, namely a percolation curve, as shown in Figure 7.9d. The dependence of the loading on conductance (exponent ~ 2.01) follows the standard percolation theory, demonstrating the percolation in the 3D film [63].



Figure 7.10. The surface profilometry scans for 6 SWCNT line patterns at 4 different random locations. The SWCNT patterns were transferred to the silicon surface before the measurements. The 6 line patterns at each location have the following averages and standard deviations of the measured heights: (average = 330 nm, standard deviation = 34 nm), (325 nm, 44 nm), (358 nm, 21 nm), (344 nm, 27 nm)

The SWCNT patterns assembled by FGA and transferred onto the substrate can serve as channel layers for CNT-based transistors. High-purity (~95%) semiconducting SWCNTs (s-

SWCNTs) were filtrated on the patterned MCE membrane. An array of s-SWCNTs was then picked up by the PVA film. Prior to the s-SWCNT transfer, Ti/Au source/drain electrodes were created on a SiO₂/Si substrate with different sizes of the electrode gap. The gap distance corresponds to the transistor channel length. The s-SWCNT pattern array on the PVA film was manually aligned and transferred onto the electrode surface to form bottom-gate transistor devices. The transferred s-SWCNT line pattern bridging onto the source and drain electrodes is shown in the inset image of Figure 7.11a. The cracks (white lines) on the s-SWCNT pattern usually came from the bending of the PVA film during the transferring, which did not affect the property of the s-SWCNTs patterns. The proposed FGA platform is particularly cost-effective when the 1D NSs of interest are expensive and the active pattern area is small. For example, a 95% pure s-SWCNTs solution is sold at around \$300 for 1 mg/mL, and a 99% pure one at over \$800 for the same amount. The FGA method effectively minimizes the nanomaterial waste and maximally utilizes them for the device application. In the experiment, 40 mL of 0.25mg/L SWCNTs can produce over two hundreds devices simultaneously by using FGA.

Figure 7.11a shows the source-drain current, I_{sd} , versus the gate voltage, V_g , of the s-SWCNT device at different source-drain voltages, V_{sd} , demonstrating the typical p-type transistor characteristics. The on/off current ratio (I_{on} / I_{off}) is measure to be around 10². Figure 7.11b presents the corresponding plots of I_{sd} versus V_{sd} on the same device, which also exhibit clear modulation of the channel conductivity by the applied gate voltage. The histograms for the distributions of the on/off current ratios and field-effect mobilities are shown in Figure 7.11c and 7.11d, respectively.



Figure 7.11. Electrical characteristics of the bottom-gated SWCNT transistors. (a) Transfer characteristics of a representative device (channel length = 5 μ m, width = 20 μ m) measured with VDS varying from -5 to 0 V (Inset image – the false-colored SEM image of the transferred SWCNTs patterns bridging on the electrodes; The golden color region represents the Au contacts and three horizontal strips are the SWCNTs patterns. The dark vertical strip in the middle indicates the gap space between two electrodes, which corresponds to the transistor channel length; Scale bar = 20 μ m). (b) Output characteristics of the same device with VGS varying from 20 to -20 V. Histogram of the distributions of transistor performance of the on/off current ratio (c) and field-effect mobility (d).

The mobility of those devices was deduced from the transfer curve (e.g. Figure 7.11a). In detail, the mobility was calculated using the following equation $[^{71-73}]$.

$$\mu = \frac{L}{C_q V_{SD} W} \frac{\partial I_{SD}}{\partial V_q} \tag{2}$$

where μ is the mobility, C_g is the capacitance. *L* and *W* are the length and width of the SWCNTs channel, respectively. For the given I_{SD} , V_{SD} and V_g , the mobility can be determined. These statistical data were collected over 30 devices on a single 2" wafer and demonstrates that the dispersed s-SWCNTs in the channel have relatively good electron mobilities but low on/off ratios. This low on/off ratios can be attributed to the relatively thick (400 ~ 420 nm) transferred s-SWCNT layer in which 5% metallic SWCNTs play an important role on the device performance

- dramatically reducing the gate-effect. More work is geared towards using s-SWCNTs with better purity and improving both FGA and transfer techniques to effectively pick up and transfer SWCNTs of small thickness (< 50 nm), which will in turn improve the device's on/off ratio performance.

It is worth mentioning that quantitative comparison between FGA and other assembly techniques (e.g. traditional lithography combined with etching or lift-off, surface-mediated directed assembly, and field-assisted assembly) would be highly desirable based on the key metrics such as cost, throughput, feature size, waste material disposal, and eventual device performance. However, it is often not feasible, if not impossible, to quantitatively compare these assembly methods because the metrics have to vary significantly depending on the type of the nanomaterials, assembly volume and speed, and the target assembled structures. Therefore, more careful study can be devised as future work to make direct and quantitative comparison across the multiple assembling techniques for a given nanomaterial and device structure.

7.4 Conclusion

In this work we investigated a scalable yet inexpensive nanomaterial assembly method, namely filtration-guided assembly (FGA), which provides an array pattern of homogeneous 1D NS network films. The BT process allowed us to create the various PR patterns of sub-10-micron resolution on the nanoporous filter membrane. The choice of the filter membrane is mixed cellulose ester (MCE), which possesses high permeability for fast filtration as well as flexibility for easy handling. Selective filtration through the PR-patterned MCE membrane provides an approach to assembling few hundreds of individual SWCNT networks under 10 minutes. Combining FGA with the PVA- or PDMS-based transfer process, we created an array of the

semiconducting SWCNTs random network onto the SiO₂/Si substrate with a minimal material loss. The thickness and electrical resistivity of the transferred SWCNTs were measured over the 20 cm² substrate, demonstrating the uniformity with less than 5% variance. These semiconducting (95%) SWCNT networks were tested as the back-gated field-effect transistors. Good electron mobility but with relatively low on/off current ratios (< 100) was observed mainly due to the large thickness of the transferred SWCNT layer. More work should be carried out to improve the FGA and transfer methods to diverse substrates.

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CHAPTER 8

CONCLUSION AND OUTLOOKS

TiO₂ and ZnO attracted considerable attention not only because their superior electrical, chemical and optical properties but also their high capability with other nanomaterials, which result the prominent performance in numerous applications. In this chapter, we primarily introduced the synthesis strategy of TiO2 NWs and ZnO NWs and their application in photocatalysis. In Chapter 1, we briefly reviewed the mechanism of the photocatalysis and the well-developed TiO-based and ZnO-based nanostructures. One special application, micromotors/micromotors was regarded as a promising platform for the use of TiO₂ and ZnO. The main content in Chapter 2 is the summarization of the recent approaches about ZnO-based photocatalysts in aspects of foreign materials and photocatalysis systems. As a detail literature review, we identified the feasibility of a potential foreign material (i.e. Si nanoscrystals) and an efficient photocatalysis system (i.e. micromotors), which were developed and studied in the following chapters, respectively. The Chapter 3 mostly focused on our recent approaches in synthesizing one-dimensional nanostructures of pure TiO₂ and ZnO via solution-base method and their numbers of modifications against the drawbacks. We learned that solution-base method offered high chance to grow varied geometries of TiO₂ and ZnO on most of the substrates, which has a variety of prospective applications. To verify the enhancement of the photocatalytic properties of ZnO, a ZnO NWs/Si NCs heterogeneous structure was fabricated in Chapter 4, which the electronic mechanism was studied to interpret the enhanced photocatalysis phenomenon. In this chapter we also understood that the obtained improvement may not be only applied to the pollutant decomposition but also good for other optoelectrical devices with the similar driven principle. With those knowledge we believed that it is worthwhile to combine those distinguished nanostructures with an interesting appliance, micromotors, to further raise its performance in environmental remediation and extend its functions in other fields. Chapter 5 introduced a novel type of floating catalysts which consisted of ZnO NW array and transparent polymer film. The embedded ZnO NWs possessed reliable connection to polymer substrate and exhibited remarkable degradability to probe pollutant as well as crude oil. As the support, PDMS film was found to be always floating atop water which was advantageous to maximally receive incident light for photocatalysts. The pizeocatalysis property of ZnO NWs was also investigated with a proper setup which suggested a way to further improve the degradability of ZnO NWs. On the basis of the technique in Chapter 5, we first developed a novel platform to efficiently produce soft micromotors in Chapter 6, which has extraordinary capability in constructing desired complex shapes and very harmony with ZnO NWs. As one realized function, ISMs assembled with the ZnO NWs provides excellent photocatalytic degradation against the model pollutant. As a promising device, the functionalization mainly in autonomous movement was discussed in Chapter 6. It is clearly seen that the self-movement as a particular capability lead to a significant improvement of photocatalytic performance. Therefore, we are expecting that the ISMs will eventfully possess multiple functions which is adapt to most of cases. The reinforcement of the ISMs as our major future work will be continued in terms of other applications. Since the inspiration of the wonderful works in the photocatalysts, we will work on coupling valid and efficient heterogeneous structures and the functional ISMs in the future. Apart from the photocatalysis, another key application, 1D nanostructure-based electronic devices was introduced in Chapter 7, where a novel assembly method, FGA, was developed with the assistance of BT method. In this work, SWCNTs was fabricated as high-performance transistor arrays on wafer scale. As known, nanostructures, especially TiO₂ and ZnO, possess unique electrochemical properties, which can be utilized as the

building blocks for the high performance components in the scalable integrated circuits. Since the FGA-BT method introduced in Chapter 7 has been demonstrated as a cost-effectiveness and easy-to-handle strategy for the assembly of low-dimensional materials onto predetermined substrates, the next step is to test TiO₂ NWs and ZnO NWs as the extension. To enrich the field of our research, we also discussed the compatibility of FGA for other 1D and 2D nanostructures at the end.

Presently we have developed few reliable and reproducible solution-base synthesis methods for both TiO_2 and ZnO 1D nanostructures. The ongoing modification process towards the compatibility for the substrates, manageable diverse geometry and large scale fabrication is expected to be used not only in micromotors but also in other extended applications such as solar cells and electrical devices. Moreover, the patternability of those 1D nanostructures is extremely significant in multi-functional micromotors, which is presumed as an advanced technique to confer additional heterogeneous materials to extend the functionality with the combination of the optimized SPB platform. In next we will also work on the materials synthesis and the modification of the platform to obtain catalyst with better degradability. And we will also test the catalysts in other harsh pollutants except for MB dye and crude oil. A variety of desired catalysts will be fabricated with suitable platform in the future.