

UNDERSTANDING FREE-CARRIER ACCUMULATION
IN SEMICONDUCTOR NANOMATERIALS:
PLASMONIC BEHAVIOR, CHARGE STORAGE ENERGETICS, AND QUANTUM
CONFINEMENT RESILIENCE OF COLLOIDAL INDIUM NITRIDE NANOCRYSTALS

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ABSTRACT

UNDERSTANDING FREE-CARRIER ACCUMULATION IN SEMICONDUCTOR NANOMATERIALS: PLASMONIC BEHAVIOR, CHARGE STORAGE ENERGETICS, AND QUANTUM CONFINEMENT RESILIENCE OF COLLOIDAL INDIUM NITRIDE NANOCRYSTALS

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Heavily doped semiconductor nanocrystals (NCs) are promising materials that can reversibly and substantially store electrical charges. Indium nitride (InN) is a particularly interesting semiconductor material for studying charge storage processes. Colloidal InN NCs are spontaneously degenerately doped with carrier densities large enough to lead to strong localized surface plasmon resonances (LSPR) in the infrared (IR) part of the spectrum. Unfortunately, many fundamental quantities that ultimately control the behavior of colloidal InN NCs are currently unknown. In this thesis, we focused on advancing our current understanding of the properties of colloidal InN NCs, with special emphasis on the quantification of free electron density, the LSPR behavior, the charge storage ability, the screening effect on phonon behaviors and few other important fundamental quantities such as the electron effective mass, Fermi level, conduction band (CB) edge potential and IR transition oscillator strength.

To understand the LSPR behavior of InN NCs, we first evaluated the free carrier density with a direct, model-independent quantification. We found that the number of free electrons per as-prepared InN NC is directly proportional to the NC volume, such that the free electron density is a size-independent quantity. Furthermore, we demonstrated that free electrons in InN NCs can be reversibly extracted with redox species, which leads to

a direct way to manipulate the LSPR. Importantly, the LSPR energy in InN NCs barely shifts with free electron density, a behavior strikingly at odds with what is typically observed in other semiconductor plasmonic systems. These unusual plasmonic signatures are shown to arise from the nonparabolicity of the CB dispersion, which leads to a change in the electron effective mass with the number of free electrons per NC, thus mitigating the shift of LSPR in InN NCs.

Consequently, we estimated the charge storage capability of InN NCs by pinning the chemical potential of InN NCs to redox-active molecular species. These studies directly yielded precise information on the Fermi level and on the chemical capacitance of InN NCs, which allowed the CB edge potential of InN NCs to be quantitatively determined for the first time. Surprisingly, the CB edge in InN NCs hardly showed any sign of quantum confinement effects, even for NCs sizes that were clearly smaller than the excitonic Bohr radius of InN. This “resilience to quantum confinement” effect was shown to also arise from the same nonparabolic dispersion effects described above.

In addition, the light harvesting ability of free electrons in InN NCs was evaluated by calculating the molar absorptivity per free electron. This value directly yielded the optical oscillator strength of LSPR. We found that optical oscillator strength (per free electron) is independent of NC.

Finally, the effects of free electrons on lattice vibrations were also explored. We demonstrated that free electrons weakened the $A_1(\text{LO})$ phonon mode by screening the Coulombic restoring force induced by the lattice distortion. The $A_1(\text{LO})$ mode frequency red-shifted linearly with the increasing free electron density. This relationship provided a fast way to estimate free electron density of InN NCs by measuring Raman spectroscopy.

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To My Family and Friends

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First, I would like to express my gratitude to my advisor, Dr. Rémi Beaulac for his guidance, support and patience throughout this work. His enthusiasm and serious attitude towards science is an example of how I should do research. I see in him what I want to be. Thank you for leading me to the fantastic world of semiconductor nanomaterials. You are not only a great scientist, but also a lifelong friend to me. It is an honor to be in your academic family tree.

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KEY TO ABBREVIATIONS

CB	Conduction Band
VB	Valence Band
NC	Nanocrystal
IR	Infrared
NIR	Near-Infrared
LSPR	Localized Surface Plasmon Resonances
TEM	Transmission Electron Microscopy
EPR	Electron Paramagnetic Resonance
XRD	Powder X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
OLA	Oleylamine
ODE	Octadecene

Chapter 1: Introduction

1.1 Charge Storage in Colloidal Semiconductor Nanocrystals

With the extraordinary growth in the research for renewable energy conversion methods, the increased demand to integrate intermittent energy sources has stimulated the development of charge storage technologies such as batteries and supercapacitors.¹⁻³

An ideal charge storage device is expected to meet various requirements including high current density, long cycle life, high conductivity, chemical stability, low cost, to name but a few. Among these, one of the fundamental challenges of improving the performance of energy storage devices is the development of materials with high charge storage ability.

Porous activated carbons are conventional materials for charge storage applications, arising from their large specific surface area ($> 2000 \text{ m}^2\text{g}^{-1}$) which lead to large specific capacitance (up to $200 \text{ F}\cdot\text{g}^{-1}$).⁴ The micropores provide sites for charge storage in electrolytes while the mesopores facilitate electrolyte immersion and retention. Other carbon materials such as carbon nanotubes and graphene are also promising candidates for supercapacitor applications. However, the low surface area of these materials limits the capacitance by one order of magnitude than found in porous active carbons. One strategy to mitigate this is to increase the surface area of carbon materials with an acid/base treatment.⁵⁻⁷ Another approach to enhance charge storage ability is by incorporating heteroatoms into carbon frameworks, such as nitrogen and oxygen which can greatly improve the capacitive performance by introducing a pseudocapacitance effect and promoting redox reactions.⁸⁻¹¹

Metal clusters are another family of prospective materials for charge storage applications. Metal clusters can undergo multi-electron transfer and are widely studied for redox flow batteries.^{12, 13} For instance, polyoxometalate clusters $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ can store multiple charges (up to 24 electrons) and can be converted to their super-reduced $[\text{PMo}_{12}\text{O}_{40}]^{27-}$ state. However, the “super-reduction” process is accompanied by strong geometrical distortions associated with the formation of Mo-Mo metal-metal bonds.¹⁴ Metal-free moieties such as dodecaborate clusters ($\text{B}_{12}(\text{OR})_{12}$, $\text{R} = \text{H}$, alkyl, benzyl) and *N*-ethylphenothiazine also exhibit potential for charge storage.^{15, 16} However, decomposition due to the innate reactivity of radical intermediates formed during the redox cycles is a critical drawback of these species.¹⁷ Although serious efforts have been deployed to mitigate these effects by delocalizing radical density throughout neighboring bonds and/or by sterically protecting the unpaired electron site, improving the cycle stability of these materials still remains a challenge.¹⁵

Semiconductor NCs are fascinating charge storage materials due to their ability to reversibly and substantially store electrical charge,¹⁸⁻³¹ which stems from their large density of states coupled with reduced Coulombic energetics (large dielectric constant). Semiconductor NCs can accumulate large charge densities without undergoing much structural change, which contrasts with the behavior of isolated molecular species. Early efforts toward extensive charge storage in semiconductor NCs has relied on chemical and electrochemical approaches to introduce charge carriers in metal chalcogenide¹⁸⁻²⁰

and metal oxide³²⁻³⁴ NCs. Very high volumetric capacitances ($33 \mu\text{F}\cdot\text{cm}^{-2}$, $233 \text{ F}\cdot\text{cm}^{-3}$) have been achieved in colloidal ZnO NCs through aliovalent Fe^{3+} -doping, rivaling those of the best supercapacitors.³⁰ In some other cases, the accumulation/depletion of charges is coupled with the intercalation / de-intercalation of cations (H^+ or Li^+) within the crystalline structure of metal oxide NCs.^{35, 36} With a high doping level, the introduced charges become delocalized (free) in the NC and the semiconductor NCs start to act like metals.

1.2 Introduction to Degenerately Doped Semiconductor Nanocrystals

In heavily-charged (or “degenerately-doped”) semiconductor NCs (charge carrier densities $10^{19} - 10^{21} \text{ cm}^{-3}$), the motion of the delocalized charge carriers becomes sufficiently correlated to induce the formation of plasmons.^{37, 38}

The term “plasmon” refers to the collective oscillation of free charge carriers, typically triggered by the external oscillating electric field of electromagnetic waves (light). In bulk, plasmon resonances tend to occur at metal-dielectric interfaces, interacting resonantly with impinging electromagnetic fields and resulting in strong plasmon-photon coupling effect that can propagate along the surface over tens of micrometers.³⁹ In metallic nanostructures, the motion of charge carriers is necessarily restricted in space and confined to subwavelength dimensions, resulting in nonpropagating plasmonic oscillations named localized surface plasmon resonances (LSPR).^{38, 40, 41} This important

effect is responsible for the striking colors of the gothic stained glasses of the rose window in the Notre-Dame de Paris cathedral and the Lycurgus cup, which were obviously crafted well before the scientific origin of this effect was uncovered. Common materials that exhibit LSPR are noble metals (such as gold and silver) nanoparticles, and LSPRs in such nanomaterials allow to concentrate energy into large electric fields at the surface, an effect that leads to the well-known Surface Enhanced Raman Spectroscopy,^{42, 43} deliver to heat locally,^{44, 45} or used to generate electrochemical work.⁴⁶⁻⁴⁸ In general, these various effects and applications are collectively combined under the umbrella term of plasmonics.^{38, 49} Whereas metallic nanomaterials largely dominate plasmonics studies, heavily-charged semiconductor nanomaterials are now recognized as legitimate candidates for similar applications.^{21, 23, 26, 28, 50-57}

The LSPRs of semiconductor NCs usually lie in the infrared (IR) to near-infrared (NIR) spectral region instead of the visible to UV region, typical of metallic NCs. This difference is due to the fact that free carrier densities in doped semiconductors are typically at least one order of magnitude lower than in metals. Among other things, semiconductor plasmonics attract much attention for biomedical applications since tissue and biomolecules exhibit relatively weak scattering and absorbance in NIR, allowing deep penetration of light *in vivo*.⁵⁸⁻⁶⁰

Arguably more interesting though is the potential for variable and reversible charging (“doping tunability”), which is not easily integrated in metallic systems, making

semiconductors ideal for applications such as high-storage capacitors,³⁰ smart window materials,^{61, 62} and tunable plasmonics,^{28, 50, 54, 63-66} to name but a few. The ability to store/transfer multiple equivalents of charge could also likely eventually play a major role in the design of next-generation photoredox catalysts based on semiconductor NCs.^{67, 68}

1.2.1 Spectroscopic Signatures of Free Carriers in Semiconductor Nanocrystals

The presence of excess delocalized charges in NCs is invariably associated with diagnostic spectroscopic signatures²⁴ such as optical resonances (typically in the IR), blue shift/bleach of the lowest interband transitions, strong electron paramagnetic resonance (EPR) signals, and strongly reduced radiative interband recombination due to Auger processes, to name but a few of the most ubiquitous ones.

Figure 1.1(a) illustrates the bleach of the interband transition and the intraband absorption in colloidal indium nitride (InN) NCs, which illustrate the typical behavior of semiconductor nanomaterials in the charge accumulation regime. The Fermi level (E_F) is a commonly-used parameter that corresponds to the free electron chemical potential (approximately the energy of the frontier orbital) in semiconductors.^{69, 70} In undoped semiconductors, and in the absence of effects from surfaces (However for NCs, we can never eliminate the surface effects, which can modulate the band potentials by as much as 1 V.⁷¹), E_F is approximately located in the center of the forbidden energy gap separating the occupied valence band (VB) and the vacant conduction band (CB).

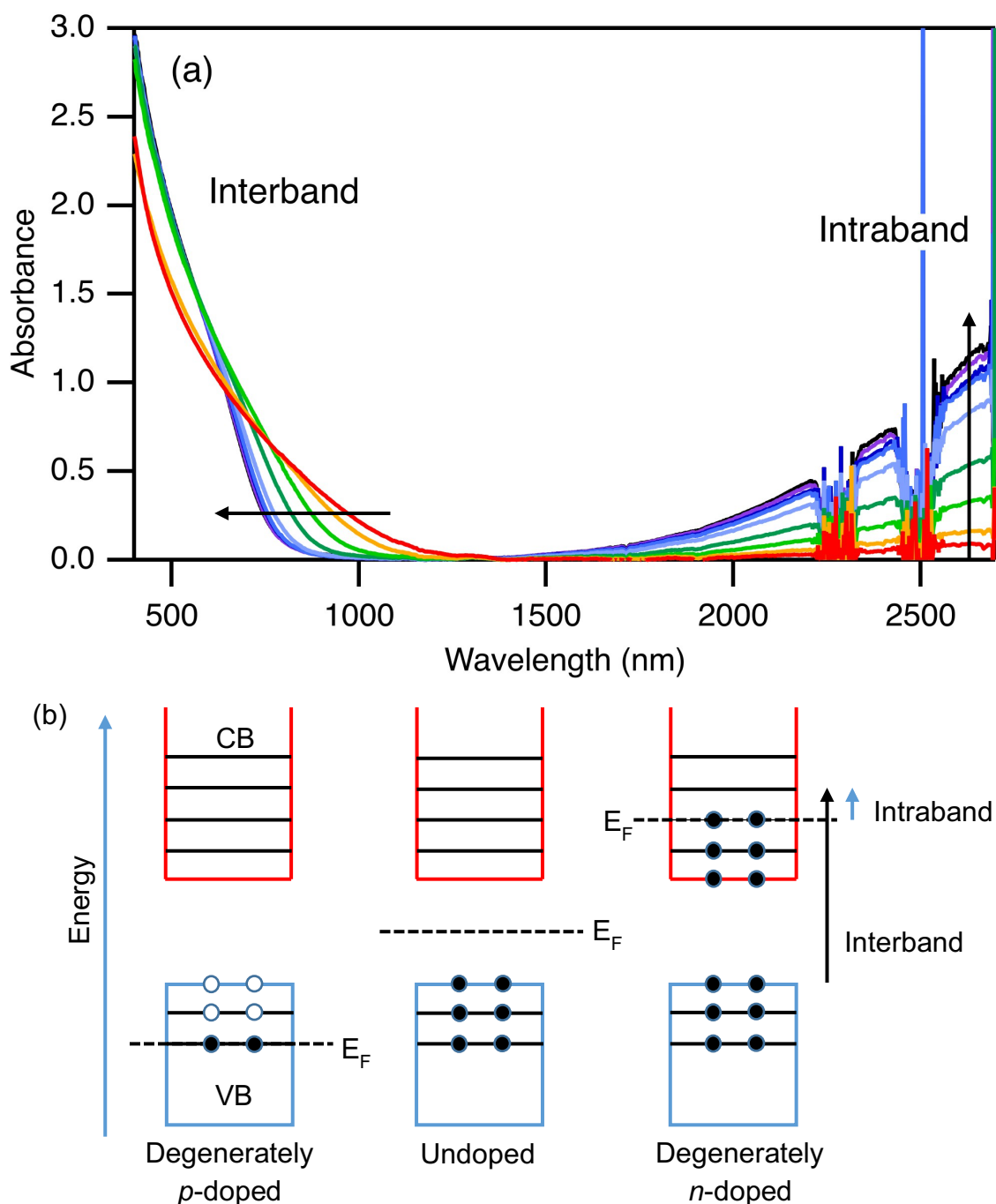


Figure 1.1. (a) Absorbance spectra of colloidal InN NCs ($d = 4.9$ nm, $[NC] = 0.66$ μM in acetonitrile) at various electron density levels. Arrows show increased electron accumulation from 5-46 electrons per NC. The addition of CB electrons to InN NCs leads a blueshift of interband transition and a growth in the IR absorption. See Chapter 6, section 6.3 for experimental details. (b) Schematic representations of E_F , interband and intraband transitions in degenerate doped semiconductor NCs compared to undoped semiconductor NCs.

However, as excess electrons start to fill the open states in CB, E_F is raised above the CB edge energy, causing the bleach of band-edge transitions, as illustrated in Figure 1(b). These new delocalized electrons can be excited to higher states, resulting in a new absorption feature in the IR region (so-called intraband transition, or LSPR), with energy and intensity that depends on the carrier density, as illustrated in Figure 1.1(b) (see chapter 4 for the theory underlying this effect). For instance, in Figure 1.1(a), $d = 4.9$ nm InN NCs are doped with 5-46 electrons per NC (the direction of arrows indicates an increase in the electron density accumulated per NC). In charged NCs, the band-edge transition is absent, and as the number of CB electron increases, a blueshift of the interband transition and a growth of IR absorption is clearly observed.

Excess carriers generally shorten or even eliminate radiative recombination process (aka photoluminescence) by introducing ultrafast nonradiative Auger recombination processes in the excited state that the electron-hole recombination energy is transferred to another hot carrier.^{72, 73} Even at relatively low carrier densities, the photoluminescence quantum yield of doped CdSe⁷⁴ and HgSe⁷⁵ NCs decreases dramatically, and at the high doping levels found in InN NCs, the photoluminescence intensity is likely too weak to be detected even with modern equipment.

In addition to changing the optical spectrum, excess charge carriers can be identified in electron paramagnetic resonance (EPR).⁷⁶⁻⁷⁸ Figure 1.2 shows the EPR spectrum of as-prepared colloidal 6 nm InN NCs with a g -value ~ 2.006 . The appearance of EPR signal

confirms the existence of unpaired electrons making EPR signal a strong indication of excess free carriers. A further discussion about the EPR spectrum of InN NCs can be found in Chapter 2.

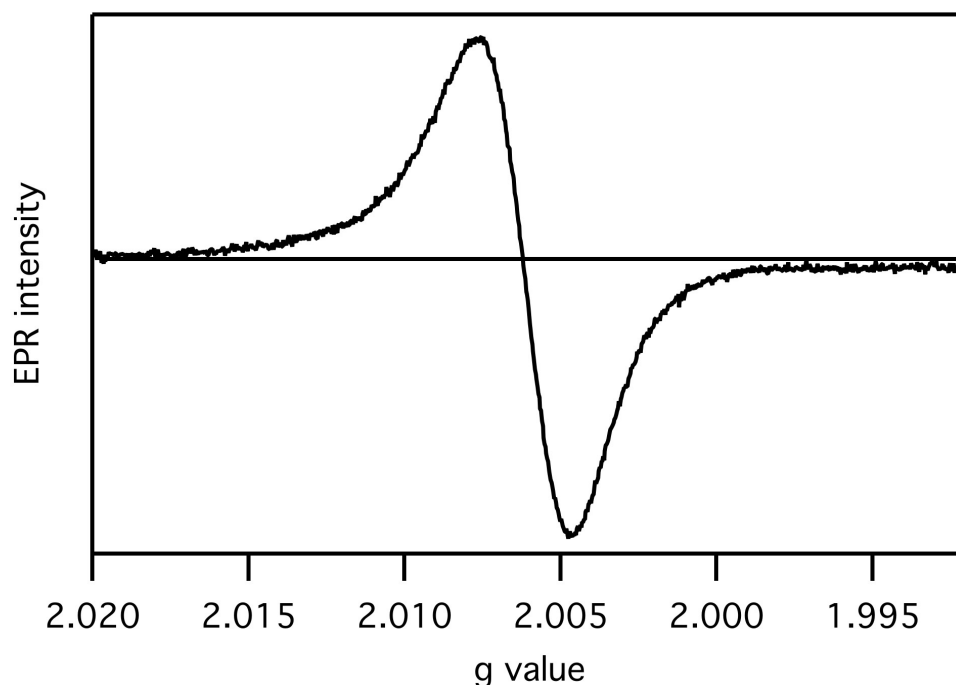


Figure 1.2. EPR spectrum of oleylamine-capped 6 nm InN NCs in toluene (full experimental details given in Chapter 2, section 2.3.2).

1.2.2 Modulation of Free Carrier Density in Semiconductor Nanocrystals

Although, the introduction of excess charge carriers in semiconductor NCs offers multiple challenges, doped NCs have now been prepared by several approaches, including aliovalent doping, vacancy doping, photodoping and electrochemical redox processes, to name but a few.

In aliovalent-doped semiconductor nanocrystals, such as Sn^{4+} -doped In_2O_3 ,⁷⁹ Al^{3+} -doped

ZnO²¹ and Nb⁵⁺-doped TiO₂,⁸⁰ the free charge carriers are stabilized by the incorporation of dopant ions. The lattice-bound impurity ion compensating source typically makes these free charge carriers very stable against oxidation.⁸¹ The LSPR can be modulated by the extent of dopant incorporation during synthesis. The doping percentage (stoichiometry) does not necessarily reflect the actual carrier density, for the reason that a decent amount of charges is often compensated by surface ligands or surface defects,⁸¹ which complicates the determination of the carrier densities. Furthermore, the dopant spatial distribution, a property which is difficult to control, has been shown to potentially impact the LSPR properties of aliovalent-doped NCs.^{82, 83}

Similar to aliovalent doping, vacancy doping can also yield very stable *n*- or *p*-type NCs, such as Cu_{2-x}S⁶³, WO_x⁸⁴ and GeTe.⁸⁵ In this case, the free charge carriers are introduced by charged defects of the native lattice, although this can be stabilized by other ions as well. For instance, in Cu_{2-x}S NCs the LSPR can be tuned by controlling the degree of copper deficiency via Cu⁺ or Li⁺ ion intercalation.^{29, 31, 86, 87}

Photodoping is a process whereby valence-band holes, generated via photoexcitation, are rapidly quenched by sacrificial reductants, leaving free electrons in the CB that are compensated by ions at the surface, and which has been demonstrated for various systems such as ZnO, ITO and CdSe⁷⁴ NCs, to name but a few. The charge-compensating species are often protons, a species that likely can easily diffuse in/out of nanocrystal lattice. In contrast to aliovalent-doped and vacancy-doped materials,

photodoped NCs are generally not very stable against oxidation upon exposure to air.³²

For ZnO NCs, the maximum charge carrier density was found to be independent of sizes, and to vary with the hole quencher species used.⁷⁸

Another common way to inject/deplete free charge carriers in NCs is by applying an external electrochemical bias to NC films.⁷⁹ It was recently shown that the modulation of the LSPR is achieved by changing the depletion width, while the extent of modulation is governed by the depletion width and inter-NC coupling.^{88, 89} A prototypical example is Sn⁴⁺-doped In₂O₃ NCs films; upon applying negative potentials, the LSPR shifts to higher energy and becomes more intense, consistent with the modulation of free carrier concentrations.⁷⁹

1.2.3 Classical Model for LSPR

The LSPR can be described as collective oscillation of the free carrier gas. A classical model due to Drude has been widely used to explain and predict the plasmonic behavior of both metals^{90, 91} and heavily doped semiconductor NCs.^{79, 92} The frequency of LSPR (ω_{Drude}) is proportional to the bulk plasmon frequency (ω_p), which depends on the free carrier density (N_e).

$$\omega_{Drude} \propto \omega_p = \sqrt{\frac{N_e e^2}{m_0 \epsilon_0}} \quad \text{eq. 1.1}$$

The constants e , m_0 , and ϵ_0 are the elementary charge, the free electron mass, and the

permittivity of vacuum, respectively.

According to equation 1.1, the LSPR frequency varies as the square root of the free carrier density. For instance, Schimpf *et al.* showed that the LSPR frequency of 5.6 nm ZnO NCs shifts toward higher energy by over 1000 cm^{-1} as the free electron density increases from 0 to $(1.4 \pm 0.4) \times 10^{20}\text{ cm}^{-3}$ (Figure 1.3).⁷⁸ Thus, the observed shift in the LSPR frequency has often been used to quantify indirectly the free carrier densities of heavily doped semiconductor NCs.⁷⁹

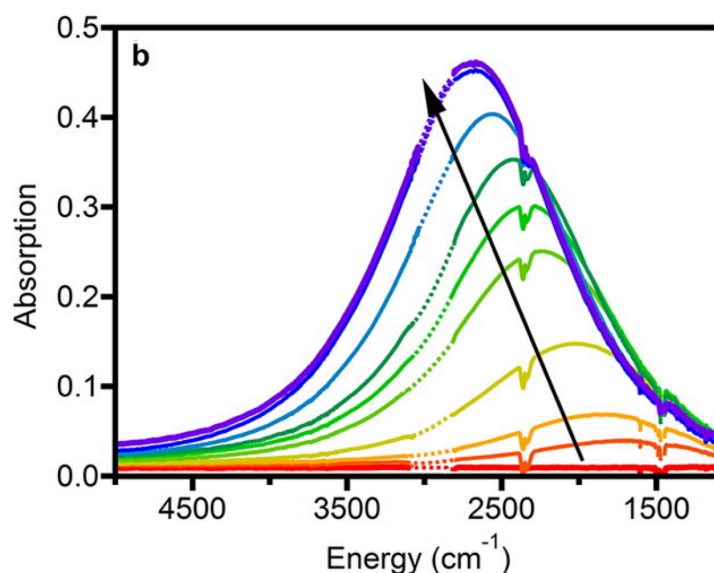


Figure 1.3. Photochemical addition of CB electrons leads to growth of IR absorption of $\sim 10\text{ }\mu\text{M}$ in 1:1 toluene/THF colloidal TOPO-capped $r = 2.8\text{ nm}$ ZnO NCs with ethanol as hole quencher. The arrow indicates increased UV irradiation time. The region of intense ligand and solvent C–H stretches ($\sim 2800\text{--}3100\text{ cm}^{-1}$) has been interpolated for clarity (dotted lines). Reprinted with permission from Reference 78. Copyright (2013) American Chemical Society.

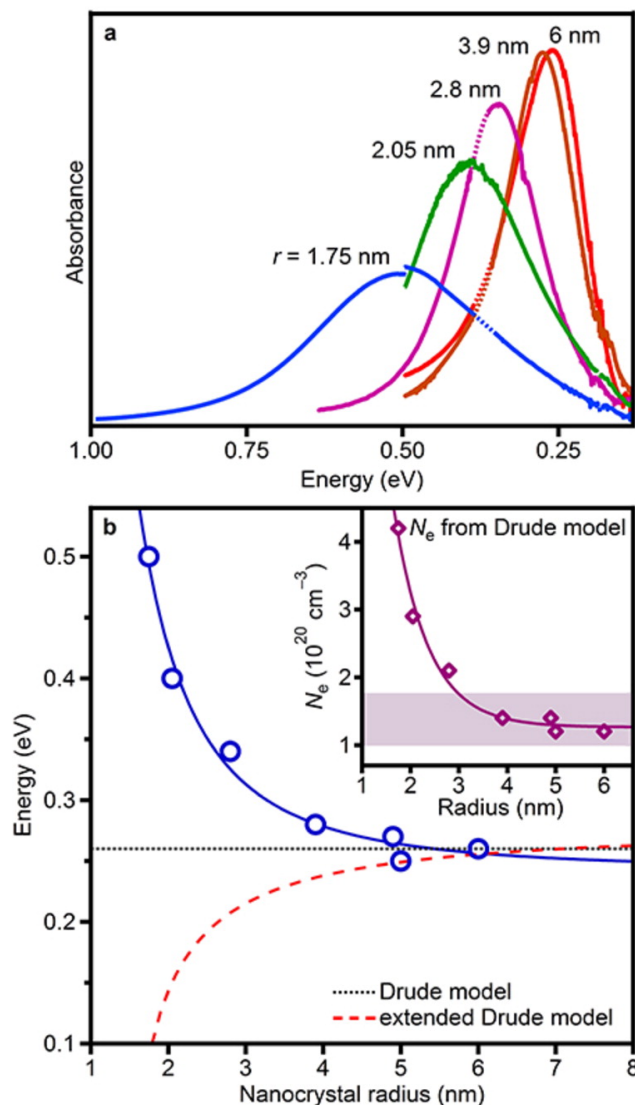


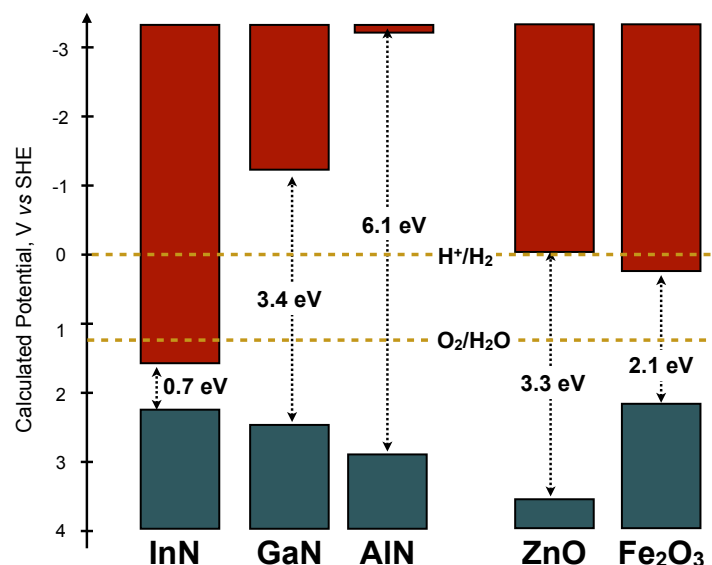
Figure 1.4. (a) IR absorption spectra of a series of colloidal ZnO NCs with different radii, each photodoped to an average carrier density of $N_e = (1.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$. Dotted lines indicate the region of intense C–H stretches. (b) IR peak maxima *versus* nanocrystal radius (blue circles). The dotted black line shows the Drude model prediction for LSPR energies at $N_e = (1.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$. The dashed red line extends this model to account for increased surface scattering in small nanocrystals. Inset: Predicted (diamonds) and experimental (shaded region) carrier densities plotted *versus* nanocrystal radius. Solid lines are guides to the eye. Reprinted with permission from Reference 23. Copyright (2014) American Chemical Society.

Many groups have now shown that the Drude model fails for small semiconductor NCs in which electron wave functions are confined.^{23, 50, 57} For instance, the data from Schimpf *et al.*²³ in Figure 1.4, several samples of colloidal ZnO NCs with radii ranging 1.75 – 6 nm were all photodoped to same free electron density, $(1.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$. However, at a constant carrier density, the LSPR energy blue shifts substantially with decreasing sizes (figure 1.4 (a)). This is not predicted by the classical model, in which the LSPR energy should be size independent. Figure 1.4 (b) plots the LSPR energy as a function of NC radius (blue circles). The Drude model (dotted line) predicts accurately for the largest size NCs but fails for small NCs. Furthermore, a modification of surface scattering (extended Drude model) that accounts for size effect also deviates from the behavior of doped ZnO NCs. We will discuss the shortcomings and limitations of the classical model in Chapter 4.

1.3 Indium Nitride: A Promising Material for Charge Storage

Whereas any semiconductor nanomaterial can in principle be designed to accumulate charges, in practice most studies in this area have involved stable transparent oxide nanomaterials such as ZnO,²¹ TiO₂^{80, 93, 94} and In₂O₃.^{26, 28, 52, 56} Group III-nitride semiconductor nanomaterials are interesting alternatives for such purposes in view of their small effective electron mass which results in a high electron mobility, but have so far remained unexploited in that respect, likely due to challenges associated with their

synthesis in the colloidal form.⁹⁵



Scheme 1.1. Bandgap of InN compared to other semiconductors (adapted from ref 96).

InN is a particularly interesting candidate with regards to its strong tendency to accumulate electrons.^{96, 97} In the bulk, InN exhibits high *n*-type conductivity and carrier densities that are generally in the 10^{17} - 10^{21} cm⁻³ range,⁹⁸⁻¹⁰⁰ a phenomenon which is attributed to its unusually low-energy CB¹⁰¹⁻¹⁰³ (as illustrated in Scheme 1.1) and an exceptionally large electron affinity that brings the charge-neutrality level well into the CB:^{98, 99, 101, 104} in simple terms, the surfaces of InN are spontaneously unstable relative to the accumulation of electrons in the CB. Whereas the dielectric constant of InN matches closely those found typically in oxides,^{103, 105} stemming from similar lattice ionicities, InN is a narrow, direct bandgap material ($E_g \sim 0.7$ eV),^{103, 106-108} starkly contrasting with most oxides, which generally possess very large bandgaps (Table 1.1).

For nanometer-sized InN NCs, this surface-accumulation effect transposes into degenerate-doping conditions, and InN NCs have been shown to indeed exhibit many of the signatures associated with charged NCs, including strong plasmonic-like resonance and Burstein-Moss shift of the optical bandgap, as discussed above (Chapter 1.2.1).^{96, 97,}

109, 110

Table 1.1. Comparison of Physical Constants of InN, ZnO and CdSe

	InN	ZnO	CdSe
bulk bandgap, $E_g(\infty)$	0.69 eV ^{100, 111, 112}	3.4 eV ^{113, 114}	1.74 eV ¹¹⁵
electron effective mass, m_e ^a	0.055 m_0 ^{100, 116-118}	0.3 m_0 ^{113, 114, 119}	0.12 m_0 ¹²⁰
heavy-hole effective mass, m_h	0.59 m_0 ^{100, 121, 122}	0.59 m_0 ^{113, 114, 119}	2.05 m_0 ¹²⁰
static dielectric constant, ϵ_s	10.5 ^{123, 124}	8.5 ^{113, 114, 119}	10.2 ¹²⁵
optical dielectric constant, ϵ_∞	6.7 ^{105, 123, 124}	3.7 ^{113, 114, 119}	6.3 ¹²⁵

^a at the Γ -point; the electron effective mass of InN varies strongly across the CB.

This thesis will focus on advances in understanding the properties of colloidal InN NCs, with special emphasis on the quantification of free electron density, the LSPR behavior, the charge storage ability, the screening effect on phonon behaviors and few other important fundamental quantities such as the electron effective mass, Fermi level, CB edge potential and IR transition oscillator strength. Following this Introduction, Chapter 2 will detail the synthesis and characterization of InN NCs and the main optical spectroscopic tools that are used throughout this thesis. The reversible modulation of free carriers using redox chemistry will be discussed as well. Chapter 3 will then present a

direct, model-free method that allowed to precisely quantify the density of excess electrons in colloidal InN NCs. Chapter 4 will discuss the ‘abnormal’ plasmonic behavior we found in InN NCs, which deviate from classical model predictions and other well-studied heavily doped metal oxide NCs. Chapter 5 and 6 will present several important fundamental quantities of InN NCs such as the oscillator strength, Fermi level, CB edge potential and chemical capacitance. The resilience to quantum confinement will also be discussed. Finally, Chapter 7 will report an interesting observation that longitudinal-optical phonon frequency can shift with free electron density in InN NCs. A direct relationship between phonon frequency and free electron density will be presented, as well as the phonon frequency of undoped InN NCs.

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**Chapter 2: Reversible Modulation of Localized Surface Plasmon Resonance and
Interband Transitions in Colloidal Indium Nitride Nanocrystals**

2.1 Overview

In contrast to metallic nanomaterials, the free carrier density of heavily-doped semiconductor NCs can be modulated, making them promising materials for tunable plasmonic applications. In this chapter, we show that as-synthesized InN NCs are spontaneously degenerately-doped, with carrier densities large enough to lead to strong LSPR effects in the infrared. We also demonstrate that the LSPR intensity and interband absorption onset can be reversibly tuned with redox chemistry. This chapter serves as a bridge to connect the general structural characterizations and optical signatures of InN NCs to the modulation of free electron density in these materials.

2.2 Introduction

Group III-nitride semiconductors NCs are promising candidates for light-emitting diode,^{1, 2} solar cells,^{3, 4} and biosensing⁵ applications due to their strong light-harvesting ability, narrow emission bands and low toxicity. In principle, alloys of III-nitrides with various ratios should cover a continuous, wide spectrum from IR all the way to deep UV. However, III-nitride NCs are not as commonly studied as II-VI semiconductor NCs, likely due to challenges associated with their synthesis in the colloidal form.⁶ Among III-nitrides, the preparation and characterization of pristine InN NCs are notoriously challenging. The bandgap energy of InN was originally reported to be $\sim 2\text{eV}$.⁷ Only in 2002, with the progress in high quality InN thin films preparation, the actual bandgap energy was revised

to its well accepted value of 0.7 eV.⁸ The overestimated value has been shown to have been caused by the surface accumulation of free electrons, which rises the Fermi level and results in Burstein-Moss effect.^{9, 10} Nanoscaled colloidal InN have recently been successfully synthesized.¹¹⁻¹³ Intriguingly, InN NCs are also degenerately-doped and show an intense LSPR in the IR region.

In this chapter, we describe the synthesis of colloidal InN NCs and the characterization of their crystalline structure, composition and morphology. We confirm the existence of free electrons with EPR and absorption spectroscopies, and then show that the free electron density can be reversibly modulated with molecular redox species.

2.3 Experimental Methods

2.3.1 InN NC Synthesis

A. Chemicals

Indium sulfide (In_2S_3 , Alfa Aesar, stored in N_2 - glovebox), sodium amide (NaNH_2 , Alfa Aesar, stored in glovebox), Et_3OBF_4 (Fluka, $\geq 97\%$, stored in desiccator in refrigerator), NOBF_4 (Fluka, $\geq 98\%$, stored in glovebox), oleylamine (OLA, Sigma Aldrich, 98%), triethylamine (J. T. Baker, $\geq 99.5\%$, stored in a glass bottle with 3 Å molecular sieve in glovebox), anhydrous acetonitrile (ACN, purified by running through alumina drying column, stored in a glass bottle with 3 Å molecular sieve in glovebox). Octadecene (ODE, Sigma Aldrich, technical grade, 90%) was heated overnight at 100°C under vacuum, ~ 50

mTorr, and stored in the glovebox. Toluene was purified by alumina drying column. Ethanol (Macron, absolute) and hexane (Macron) were used as received.

B. Synthesis and Purification of InN NCs

Indium nitride NCs were prepared from In_2S_3 and NaNH_2 at ambient pressure by adapting previously published methods.^{11, 12} The method was modified as follows. Under a nitrogen atmosphere, 0.5 mmol of In_2S_3 was combined with 5 mmol of NaNH_2 in 10 ml of octadecene in a 50 ml three-neck round bottom flask with a condenser, rubber sealed caps and a stir bar. The mixture was stirred and heated on a heating mantle to the desired temperature for a certain amount of time to control the size of InN NCs as listed in Table 2.1, and cooled to room temperature. Post-synthesis processing began with separating ODE from the resulting black solid by centrifugation at 4000 rpm for 10 minutes. The black solid was then sonicated with 20 ml toluene for 3 minutes and precipitated by centrifugation (4000 rpm, 10 min) followed by sonicating in 20 ml ethanol and precipitating by centrifugation, twice. The resulting black-brown solid was sonicated with nitric acid (~3.5 vol % aqueous, 12 ml) for 5 minutes before centrifugation (4000 rpm, 10 min) followed by washing with 20 ml ethanol to wash away residual acid. 12 ml OLA was added to the mixture and sonicated for 30 minutes and then precipitated with 12 ml ethanol (4000 rpm, 10 min) and dissolved in 16 ml toluene. The solution was centrifuged at 1000 rpm for 5 minutes to separate the unreacted In_2S_3 , then precipitated with 16 ml ethanol. The majority of the resulting black solid was dissolved in 15 ml hexane, while a small amount

was kept in 2 ml toluene for TEM.

Table 2.1. Average size of InN NCs at varying reaction temperatures and times (2 trials each).

Temperature (°C)	250	250	250	250	250	250	220
Time (min)	30	40	60	90	120	240	720
Diameter (nm)	3.9	4.2	4.5	5.2	5.7	6.4	8.7
Standard dev. (nm)	0.4	0.5	0.7	0.8	0.9	1.1	1.7

C. Ligand Exchange

The surface ligand exchange process was done following a published procedure.¹⁴ A solution of Et₃OBF₄ was prepared by dissolving ~1 g of Et₃OBF₄ in 15 mL of ACN. The Et₃OBF₄ solution was added to the suspension of InN NCs in hexane. The mixture was shaken for ~1 min before adding 2 ml toluene. The mixture was centrifuged at 4000 rpm for 10 minutes and the resulting solid dissolved in 16 ml ACN and precipitated again with 4 ml toluene. After which, the solid was dissolved in 15-20 ml ACN and stored in the glovebox for characterization.

2.3.2 Physical & Sample Characterization Methods

A. Transmission Electron Microscopy

TEM images were recorded on a JEOL 2200 FS microscope operating at 200 keV.

Formvar-coated copper grids (Ted Pella, 01800-F) were used as nanocrystal supports for TEM. InN-OLA toluene suspensions were drop-casted on the TEM grid prior to the measurements. Images were analyzed using ImageJ.

B. Powder X-ray Diffraction

XRD was performed on Bruker D8 DaVinci diffractometer equipped with Cu K α radiation (0.15406 nm) line source operating at 40 kV and 40 mA. Samples were placed in a PVMA sample holder with zero-background silica plates by drop-casting concentrated nanocrystal suspensions. The sample was scanned from 25° - 70° using 10 s/scan. Diffraction lines are compared to the JCPDS card number: 00-050-1239.

C. UV-vis-NIR Spectra

Absorption spectra of oxidized/reduces NCs were obtained by adding a solution of oxidant / reductant in ACN with desired amount to a solution of Et₃OBF₄-treated NCs in ACN in a 1 cm quartz cuvette with a screw-cap (Starna Cells, 1-Q-10-GL14-C) in the glovebox and let to stand for 1 h before measurement. UV-vis-NIR absorption spectra were measured on a OLIS 17 spectrometer from 400 to 2700 nm.

D. Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained from Mattson Galaxy 3020 from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹ for 16 scans. Background spectra were measured on a clean silicon window (Edmund Optics, #68-523). Films of BF₄-capped InN NCs were obtained by drop-casting the InN NCs suspension on the same silicon window.

E. X-ray Photoelectron Spectroscopy

XPS was done on a Perkin Elmer Phi 5600 ESCA system, with a Mg $K\alpha$ X-ray source at a take off angle of 45° , under ultrahigh vacuum conditions ($< 10^{-7}$ torr). Spectra were acquired with a pass energy of 187 eV for survey scans or 29.35 eV for zoomed-in scans, and a step size of 0.8 eV for survey scans or 0.1 eV for regional scans; the energy scale was calibrated with adventitious carbon at 284.6 eV. Samples for XPS were first precipitated out of solution and dried under nitrogen. Films were then prepared by spreading the nanocrystals powder on a 1 cm^2 copper tape (Ted Pella) attached to a stainless steel holder.

F. Electron Paramagnetic Resonance

EPR spectra were collected using a Bruker ESP-300E spectrometer. Samples were prepared by dissolving OLA-capped InN NCs in toluene in EPR tube. Oxygen was removed by standard freeze-pump-thaw process before the measurement.

2.4 Results and Discussion

Indium nitride NCs were prepared from indium sulfide (In_2S_3) and sodium amide (NaNH_2) at ambient pressure using the method developed by Belcher and Neale groups (described in experimental section).^{11, 12} Figure 2.1(b) shows the X-ray powder diffraction pattern of OLA capped InN NCs. The two sets of three peaks at $2\theta = 28^\circ - 34^\circ$ and $50^\circ - 64^\circ$ correspond to the wurtzite phase of InN.¹⁵ The resulting particles synthesized at 250°C for 30 min are 4.0 ± 0.5 nm from TEM analyse (Figure 2.1(a)).

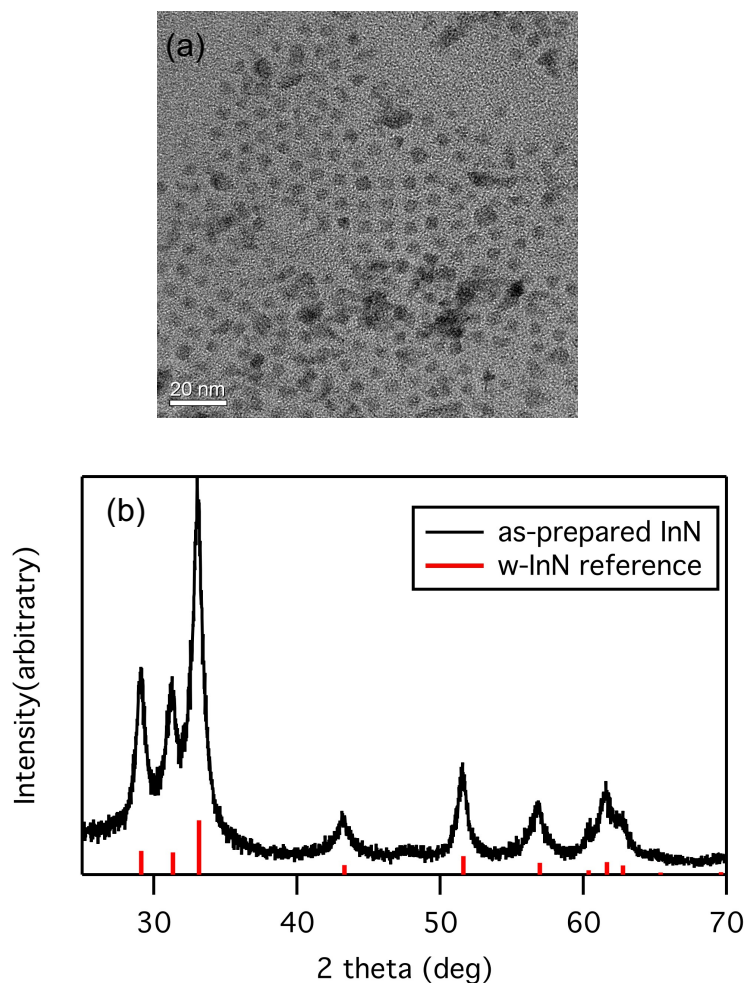


Figure 2.1. (a) TEM image and (b) X-ray diffraction spectrum of 4.0 ± 0.5 nm OLA capped InN NCs. Reference diffraction angles for bulk wurtzite InN are given as red bars.¹⁶

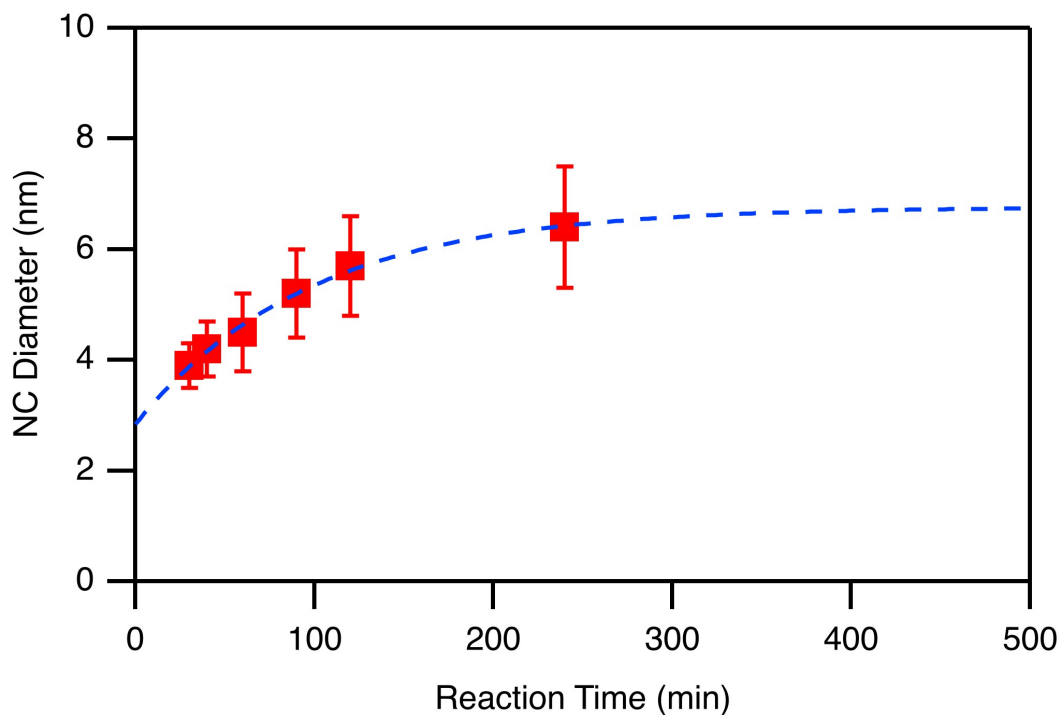


Figure 2.2. Plot of average size of OLA capped InN NCs synthesized at 250 °C with varying reaction times (data in Table 2.1). The blue dashed line is a single-exponential fit, with a time constant of 97.8 min^{-1} , a pre-exponential factor of 2.8 nm and a baseline value of 6.8 nm.

Various sizes of InN NCs can be synthesized by controlling the reaction time. At 250 °C, as the reaction time increases from 30 min to 240 min, the average NC diameter increases from 3.9 nm to 6.4 nm. Interestingly, the average sizes were fitted well with exponential function which certainly contains the information of the growth mechanism of colloidal InN NCs. Further studies to illuminate the relation between reaction time and sizes go beyond the scope of this thesis.

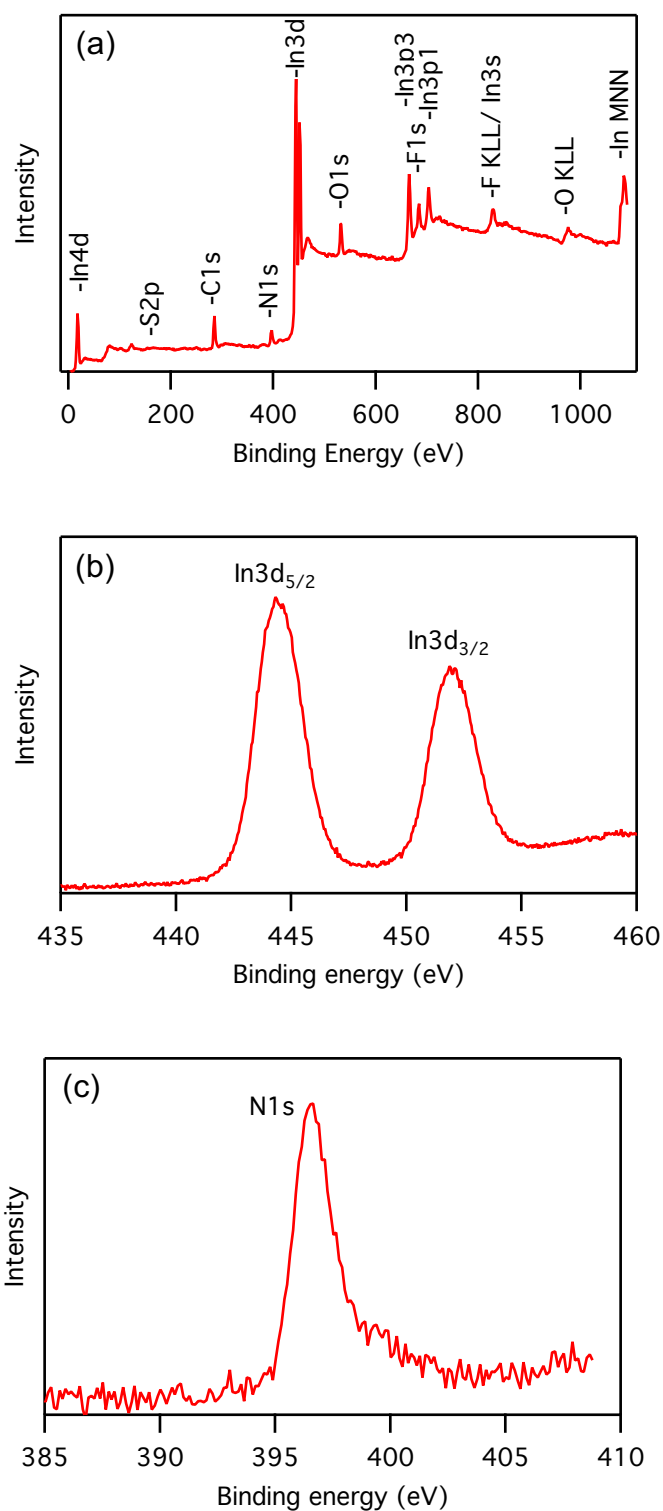


Figure 2.3. XPS spectra of 5.2 nm *i*-InN NCs. (a) Survey region (b) higher resolution In 3d region and (c) higher resolution N 1s region.

Typical XPS survey spectra (Figure 2.3(a)) indicate the presence of indium and nitrogen, as well as fluorine from the ligands, carbon from the reference and oxygen impurity from absorbed gaseous molecules. Higher resolution spectra were also recorded in the In 3d (Figure 2.3(b)) and N 1s (Figure 2.3(c)) regions. The indium $3d_{5/2}$ peak at 444 eV and $3d_{3/2}$ peak at 451.6 eV were attributed to In 3d and the peak at around 396.4 eV corresponds to N 1s of InN.^{13, 17}

Previous report on the synthesis of colloidal InN NCs shows the presence of spectroscopically-inactive sulfur species in the InN NCs sample, arising from the In_2S_3 precursor or sulfur-containing byproducts, which complicates the composition, surface conditions and further study of colloidal InN NCs.¹² Here, we adapted the post-synthesis from the published method by centrifuging oleylamine treated InN NCs at a low speed (1000 rpm for 5 min), separating unreacted In_2S_3 and other impurities from the suspension, as detailed in experimental section. The absence of sulfur (S 2p should appear at ~ 160-170 eV¹²) in the XPS spectrum (Figure 2.3(a)) demonstrates that the sulfur-containing component can be effectively removed via our modified post-synthesis.

As reported previously, the LSPR in InN NCs can be tuned with redox chemistry.¹² To effect a change in the carrier density, InN NCs were first transferred into a polar solvent with Meerwein's salt (Et_3OBF_4) treatment due to the polarizability of most redox agents. It has been demonstrated that the carrier density undergoes minimal change upon ligand exchange.¹²

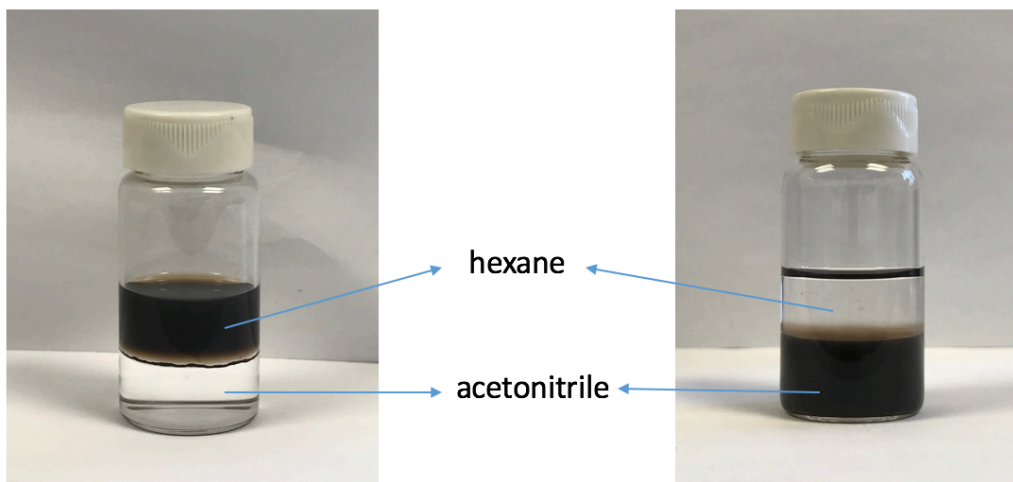
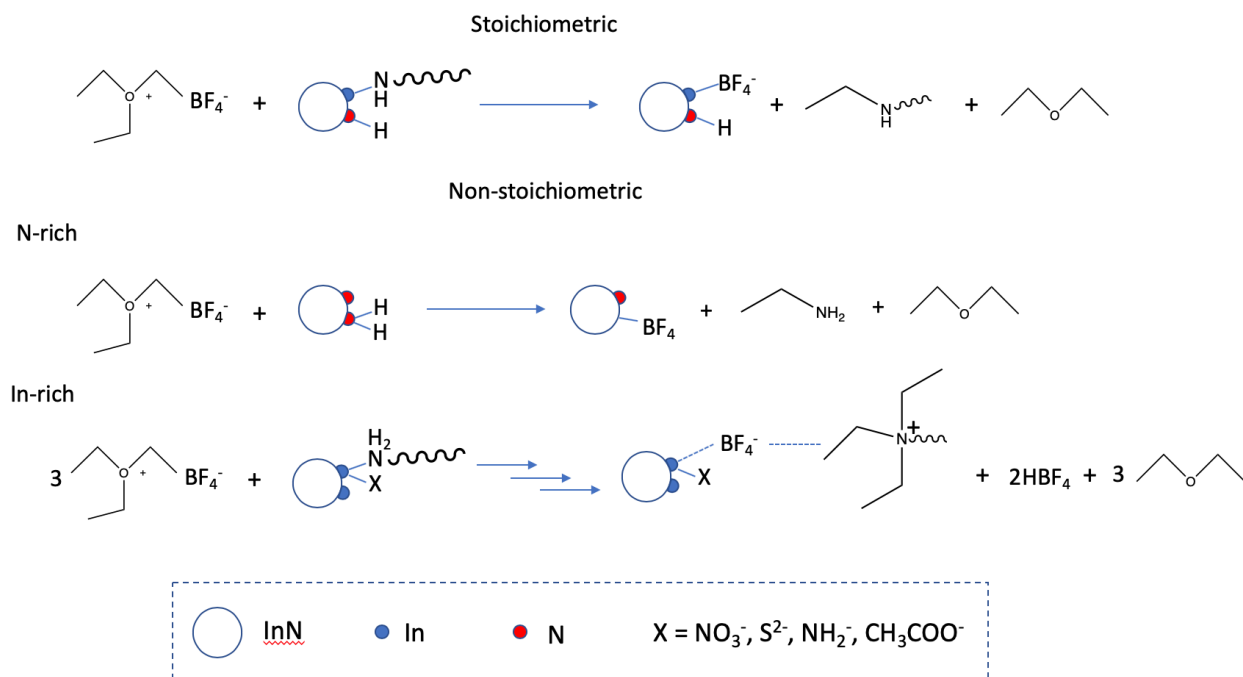


Figure 2.4. Ligand exchange process of InN NCs. OLA capped InN NCs dissolve in hexane on the left bottle, while on the right *i*-InN NCs dissolve in ACN.



Scheme 2.1 The possible mechanisms of Meerwein's salt treatment to InN NCs.

The surface of InN NCs is still unknown after treated with Meerwein's salt. There are several possibilities depending on the surface condition before ligand treatment, as presented in scheme 2.1. 1) InN NC is stoichiometric with same number of In and N atoms on the NC surface. It is likely that the original surface ligand (OLA) divided to proton and amide with proton bound to the N site and amide bound to the In site. The BF_4^- of Meerwein's salt replaces the amide group and bound with In^{3+} , leaving Et_3O^+ react with amide forming diethyl ether and secondary amine. 2) InN NC is N-rich. It is likely that N stays as $-\text{NH}_2$ on the NC surface since the nitrogen precursor is NaNH_2 . The BF_4^- from the Meerwein's salt etches the NC surface by replacing the entire $-\text{NH}_2$ and bounding with the core In^{3+} , thus stabilizing NCs in polar solvent. 3) InN NCs is In-rich. On In terminated site, surface ligand attached on In^{3+} through dative bond. Meerwein's salt react with the starting OLA ligand, forming BF_4^- and quaternary amine ion pairs stabilizing InN NCs with electrostatic interactions.¹⁸ In this case, the third hypothesis is more reasonable due to the fact that InN NCs become unstable after washing with ACN for multiply times (> 2 times), since the absorbed ion pairs can be easily washed away. In this thesis, we label Meerwein's salt treated InN NCs as *i*-InN to refer its ionic surface.

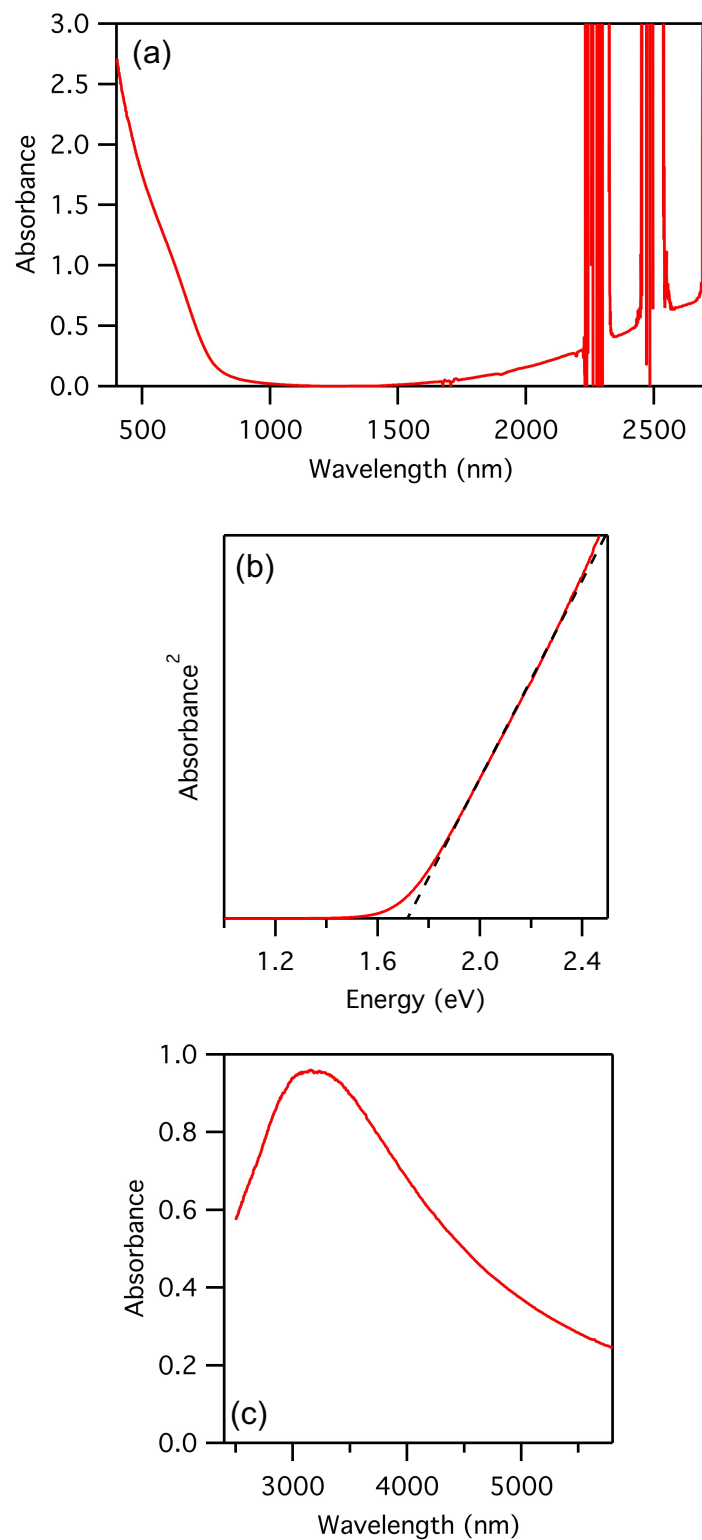


Figure 2.5. (a) UV-vis-NIR spectrum of 3.9 nm *i*-InN NCs in ACN. (b) Tauc plot of (a). Dashed line is a fit to the linear region with the x-intercept taken as the absorption onset. (c) FTIR spectrum of *i*-InN NC film.

As discussed in Chapter 1, free electron accumulation in semiconductor NCs is accompanied by a bleach of band-edge absorption corresponding to the filling of the CB, and by the appearance of a strong absorption in the near/mid-IR. For undoped InN NCs, the band-edge transition should appear at ~ 1800 nm (0.69 eV). However, the excess free electrons in InN NCs occupy the low energy states in the CB and raise the E_F above the CB minimum. The interband transition now is from the VB to the lowest vacant state in CB, resulting in a bleach in the band-edge transition and a higher energy transition. In Figure 2.4(a), the interband transition energy is ~ 1.7 eV, confirming the bleach in band-edge transition. A broad and intense peak lies between 1500 nm to 6000 nm is also observed which has been assigned to the LSPR.¹²

Figure 2.5(a) is the EPR spectra obtained at room temperature of OLA capped InN NCs in toluene with sizes 4 – 10 nm. EPR signals confirm the existence of unpaired electrons with an average g -value of 2.006, higher than other reported degenerately doped semiconductor nanoparticles such as Sn^{4+} -doped In_2O_3 and photodoped ZnO which are 1.96~1.98.¹⁹ This implies a difference in the nature of free electrons and dopants in nitrides vs oxides, which is yet to be explored. From the respect of the delocalization of extra electrons, the EPR signal of InN NCs is expected to be electron density dependent and size dependent, similar to photodoped ZnO NCs.²⁰ However, we did not observe such behavior. Instead, the g -value is nearly constant. Further studies are needed to explain such a difference. To the best of our knowledge, this is the first time that the EPR signal

of InN NCs being observed.

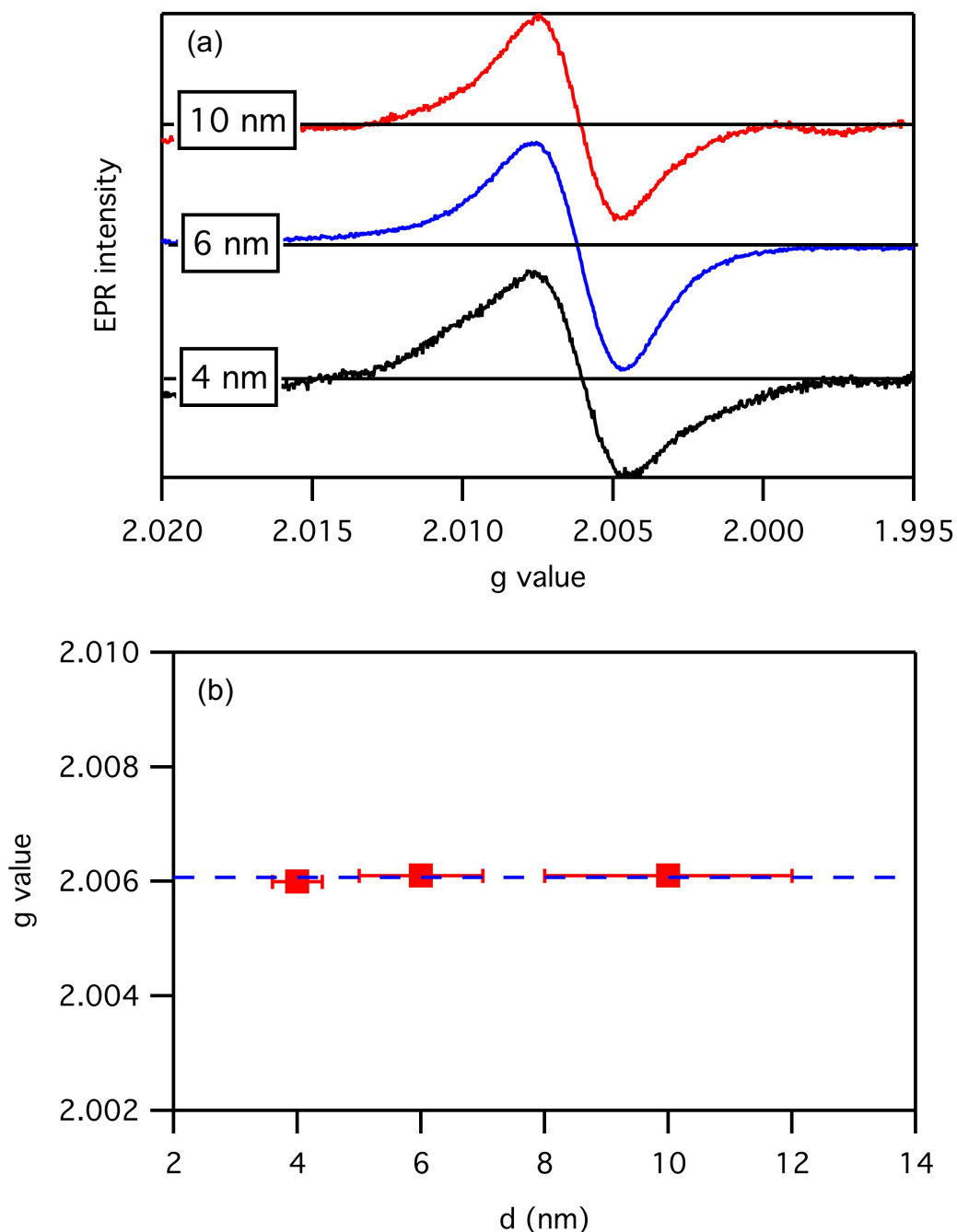


Figure 2.6. (a) Room-temperature EPR spectra of as prepared colloidal OLA capped InN NCs. Black, blue and red line corresponds the EPR signal of 4 nm, 6 nm and 10 nm InN NCs. (b) g -value of colloidal InN NCs obtained from (a) as a function of sizes. The average value 2.006 is represented as the blue dashed line. The error bar on y -axis is smaller than the size of the markers.

Following Palomaki et al.,¹² the free electron density of colloidal InN NCs can be chemically oxidized with nitrosonium (NO^+). NO^+ is a strong oxidant that can react with the free electrons in the CB and lower the E_F , thus decreasing the interband transition energy and reduce the intensity of the LSPR. In Figure 2.7(a), 0 - 5600 equiv. of NOBF_4 were added to 5.5 nm InN NCs resulting a stepwise redshift in the absorption onset and decrease in the LSPR intensity, indicative of the reduction in the free electron density. Changes in these absorption features can be fully recovered with the addition of reductant. We found that oxidized InN NCs can be reduced with amines, with full recovery of the LSPR intensity and original interband transition onset. In Figure 2.7(b), under the addition of 0 - 87000 equiv. of triethylamine, the band edge absorption shifts back to higher energy accompanied with the growth in the LSPR, and eventually overlaps with the as prepared InN NCs absorption feature (figure 2.7(c)). These changes are consistent with the modulation in free electron density and indicative of the adjustment in Fermi level.

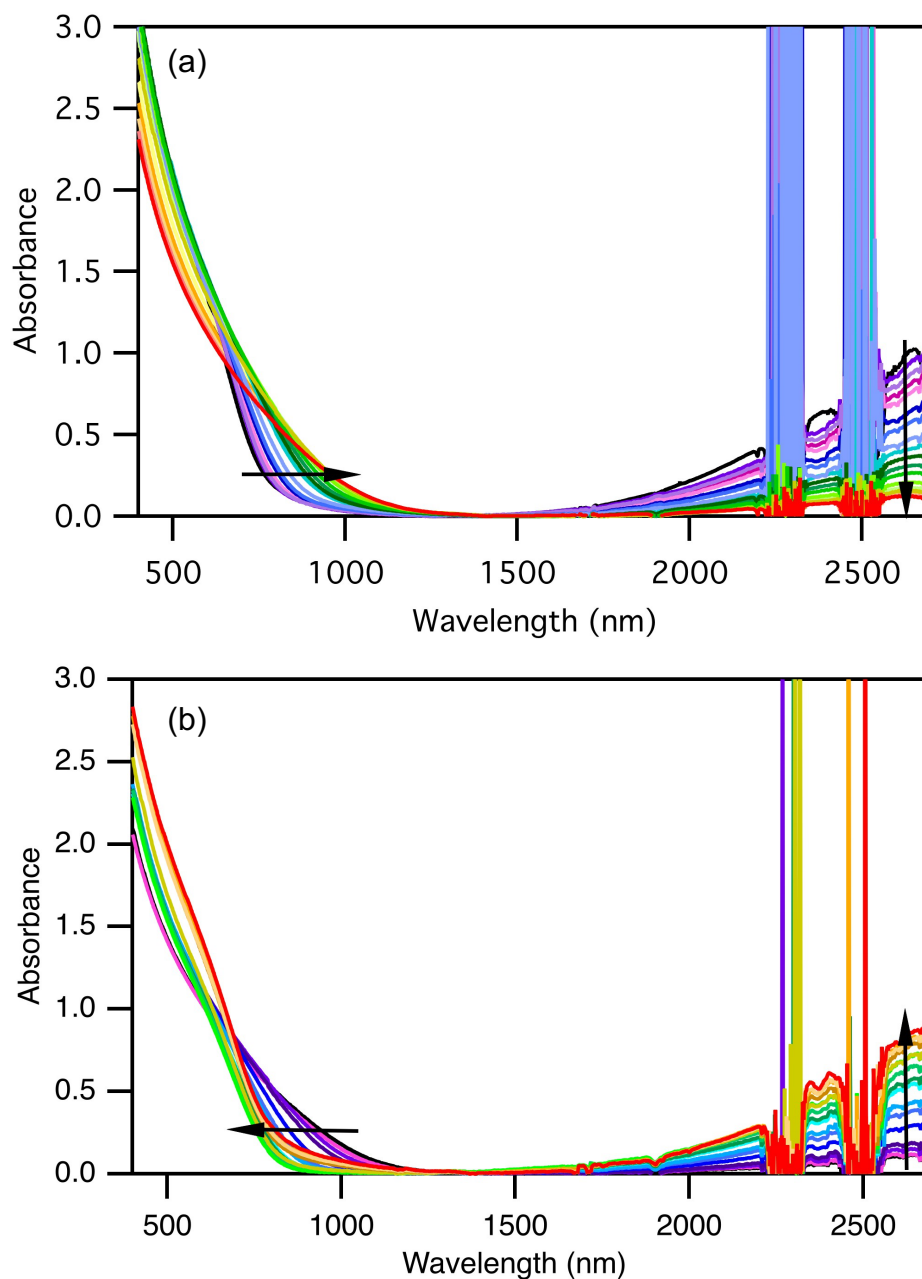
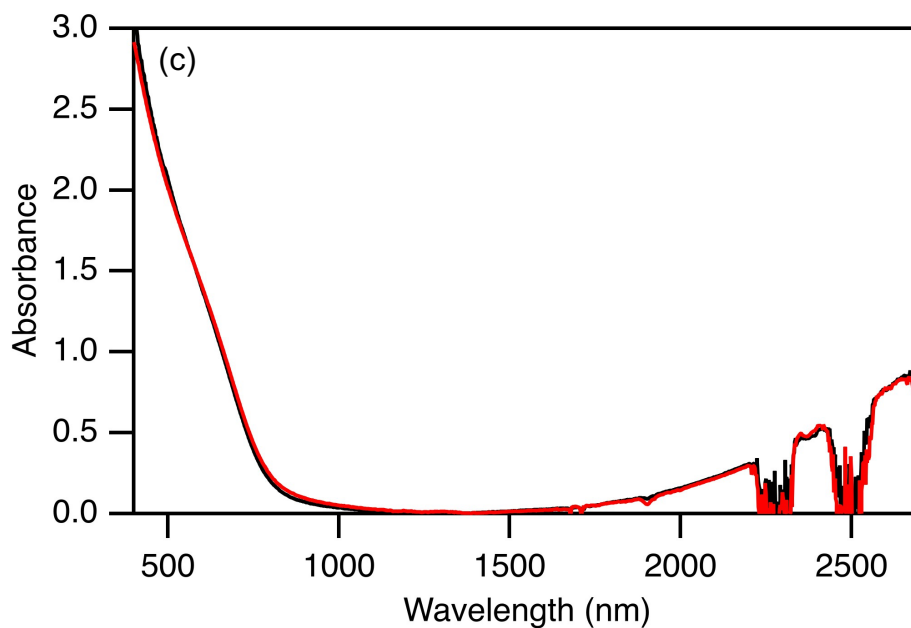


Figure 2.7. UV-vis-NIR absorption spectra of 5.5 nm *i*-InN NCs in ACN. (a) As prepared InN NCs were oxidized with 0, 6, 11, 14, 18, 25, 40, 60, 80, 160, 320, 630, 1100, 1700, 2300, 2900, 3400, 4100, 4800, 5600 equiv. of NOBF₄ (b) As prepared InN NCs were treated with 3400 equiv. of NOBF₄, followed by reduction with 0, 2800, 5000, 5300, 5600, 5800, 6100, 6900, 8300, 11000, 14000, 17000, 35000, 52000, 69000, 87000 equiv. of triethylamine. Arrows indicate the direction of change in the spectra upon oxidation and reduction. (c) Absorption spectrum of reduced InN NCs (red, treated with 3400 equiv. of NOBF₄ followed by 52000 equiv. of triethylamine) overlaps well with the as prepared InN NCs (black).

Figure 2.7 (cont'd).



Triethylamine is not the only amine could fully recover oxidized InN NCs, evidence shows that oleylamine and even ammonium gas can transfer electrons back to InN conduction band, although oleylamine easily destabilizes the InN suspension and complicates the measurement. This suggests that LSPR in OLA capped InN NCs might not be tunable with oxidants due to the surface bonding reductants. This was confirmed by the experiment of adding ferrocenium hexafluorophosphate into OLA capped InN NCs suspension in CHCl_3 which showing no changes in the absorption onset or LSPR intensity. However, ferrocenium tetraboroborate in BF_4 capped InN NCs suspension in ACN does remove a decent among of free electrons.

As mentioned before and shown in Figure 2.8, NH_3 gas also serves as a reductant to

oxidized InN NCs. The experiment was performed by simply attaching a balloon of NH_3 gas with a needle penetrating into the sealed cuvette with NO^+ oxidized InN suspension. After standing still for about 5 min, the cuvette was shaken for few times and put into the UV-vis chamber for measurement. The absorption spectra show a full recovery of interband onset and LSPR intensity. From another aspect of view, oxidized InN NCs could potentially be an alternative of ruthenium complexes²¹ and used as a catalyst in ammonia oxidation reaction at room temperature, although no evidence of dinitrogen from GC measurement, which either because the oxidized InN NCs could only reduce nitrogen to an intermediate oxidation state between -3 to 0 or the amount of N_2 is below detecting limit. Further study with higher concentration of oxidized InN suspension or InN films could be used to investigate this reaction.

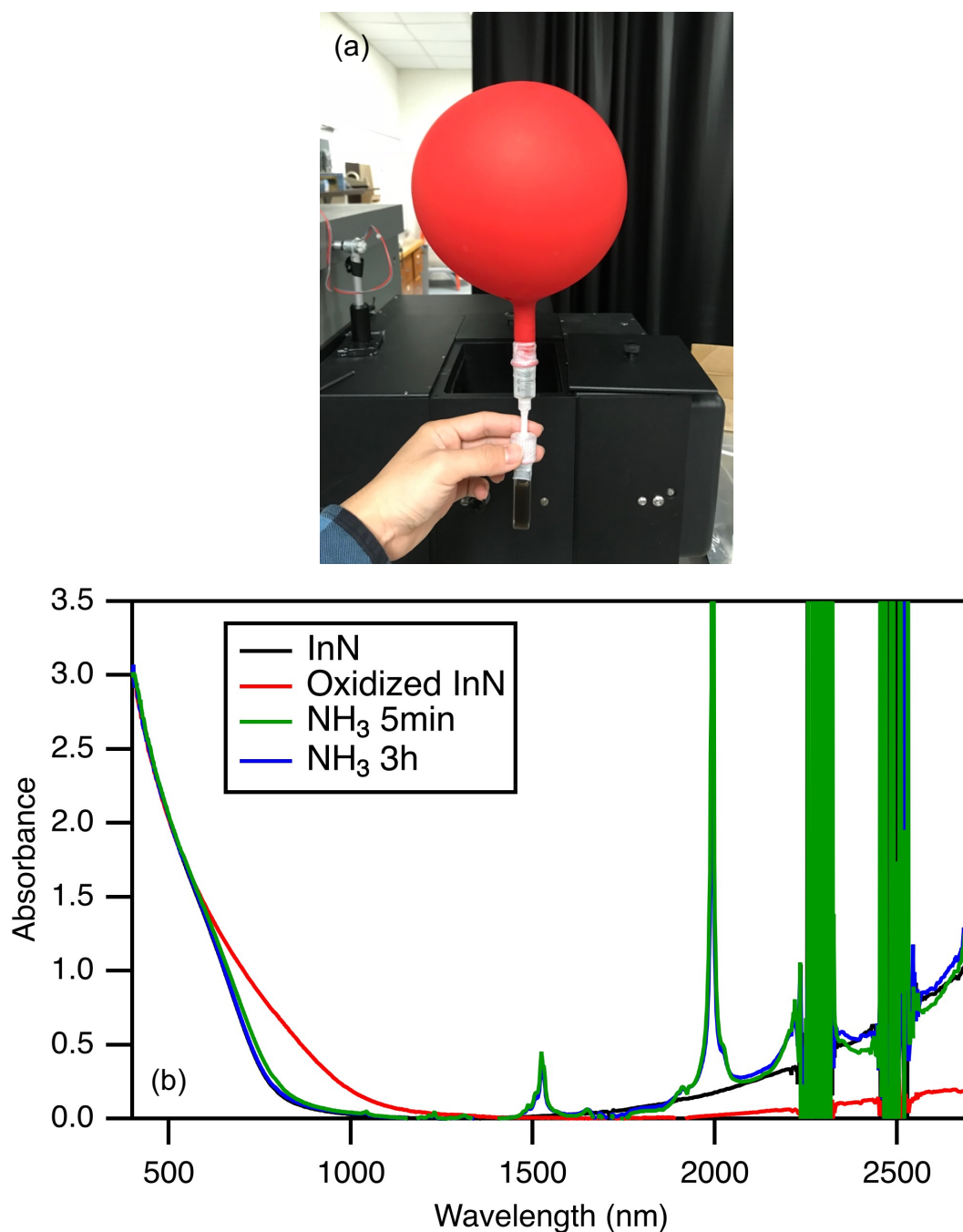


Figure 2.8. (a) A balloon of NH_3 gas attached to a sealed cuvette with oxidized InN NCs suspension. (b) UV-vis-NIR absorption spectra of reduction of 5.5 nm oxidized InN NCs in ACN (3400 equiv. of NOBF_4) with added ammonia gas.

2.5 Conclusions

Wurtzite InN NCs were synthesized and the sulfur-containing component that was previously shown to contaminate InN NCs was eliminated by adding an additional separation step in the post-synthesis. The free electrons in InN NCs were confirmed by the absorption and EPR spectrum. The reversible modulation of accumulated free electrons was demonstrated with redox chemistry using nitrosonium, amines and ammonia. Furthermore, we found that alkyl amines and ammonia can fully return oxidized InN NCs to their as-prepared level.

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**Chapter 3: Quantitative Modulation of the Electron Density of Colloidal Indium
Nitride Nanocrystals**

3.1 Overview

An oxidative titration approach based on the use of nitrosonium ions is used to directly quantify the carrier densities of colloidal InN nanocrystals, bypassing the need to rely on specific theoretical models. A size independent carrier density value of $(7.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$ is obtained for diameters varying between 4 and 9 nm, corresponding to about 30 to 300 electrons per NC, depending on size. Upon oxidation, the redox activity of each equivalent of nitrosonium ion significantly reduces at around $(3.9 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$, also independent of size. The results and discussion presented in this chapter have been reported in the literature.¹

3.2 Introduction

As its name suggests, the carrier density corresponds to the number of charge carriers per unit volume (typically expressed in cm^{-3} units). At the high charge carrier densities that characterize the metallic state ($N_e \sim 10^{22} \text{ cm}^{-3}$),^{2, 3} the motion of delocalized charge carriers becomes sufficiently correlated to induce the formation of plasmons, collective (and quantized) oscillations of the charge density.^{2, 4} In semiconductors, the carrier density is also an important quantity that depends on the doping level, the density of states and the Fermi level. As shown in Chapter 2 and previously discussed in the literature,^{5, 6} colloidal InN NCs are characterized by strong IR transitions and Burstein-Moss shifts of the interband transitions, two archetypical signatures of degenerately

doped semiconductors. However, InN NCs have so far remained unexploited for plasmonics applications, contrasting to the well-studied case of transparent oxide nanomaterials.⁷⁻¹¹

A proper assessment of the carrier density is a central prerequisite for any LSPR analysis. Many investigations have applied the classical Drude model (Chapter 4) to estimate carrier densities from the LSPR energies.^{6, 12-15} However, in semiconductor NCs, impurity doping of any type perturbs carrier wave functions,¹⁶ and surface scattering of NCs can be different from bulk.¹⁷ Additionally, quantum confinement effects are not taken into account in classical models. All these factors complicate the determination of carrier densities using classical models. A direct experimental quantification of the carrier density in InN NCs is therefore necessary for a thorough understanding of the plasmonic behavior of InN NCs.

In this chapter, we provide a direct (*i.e.* model-free) quantification of the carrier density of InN NCs by analyzing the IR absorption spectra, and describe the size dependence of their plasmonic behavior.

3.3 Experimental Methods

3.3.1 InN NC Synthesis

The synthesis, purification and ligand exchange of InN NCs were described in Chapter 2, Section 2.3.1.

3.3.2 Physical & Sample Characterization Methods

A. Absorption Spectra

400 to 2700 nm was measured with *i*-InN suspension in a sealed quartz cuvette with UV-vis-NIR spectrometer. 4000 to 400 cm^{-1} was measured with FTIR. (More details could be found in Chapter 2, section 2.3.2.) The UV-vis-NIR and FTIR spectra for one same sample were connected by matching the overlapping region (4000 – 3704 cm^{-1}).

B. Inductively Coupled Plasma Optical Emission Spectroscopy

ICP-OES was used to calculate the concentration of the suspension of InN NCs. 50 μl InN NCs in ACN was dried under vacuum, and the sample was calcined in air at 500°C for 2 h, then digested in 2 ml aqua regia (1.5 ml of HCl and 0.5 ml of HNO_3) and diluted to a 100 ml in volumetric flask with deionized water. The concentration of In was determined by the method of standard additions. 10 ml sample solution was added to each 25 ml volumetric flask to make 5 standard solutions of 0.1, 0.5, 1, 2, 5 ppm.

C. Other Instrumentations

TEM and XRD instrumentation and measurements were described in detail in Chapter 2, Section 2.3.2.

3.4 Results and Discussion

Following Palomaki *et al.*,⁶ colloidal InN NCs were oxidized chemically using nitrosonium (NO^+), a strong one-electron oxidant. The addition of NO^+ to colloidal suspensions of InN NCs reduces the intensity of the LSPR absorption and redshifts the interband transitions,⁶ as shown in Figure 3.1.

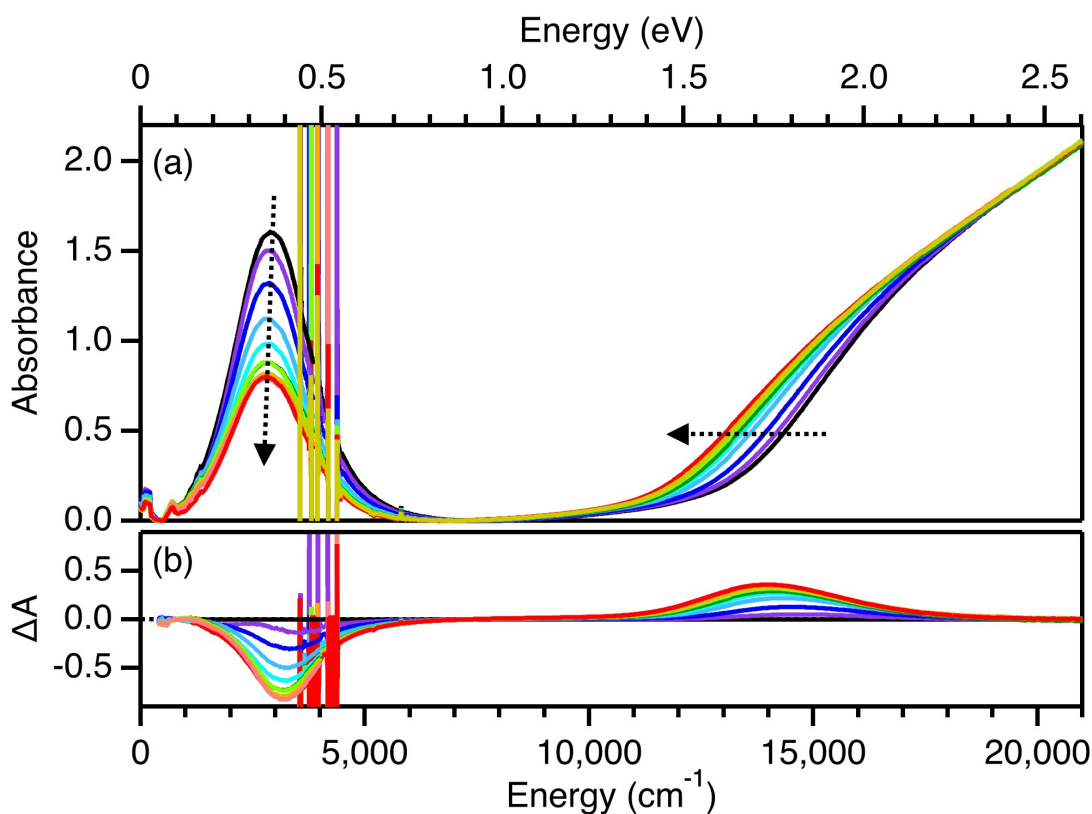


Figure 3.1. Spectroscopic signatures of colloidal InN NCs at various oxidation levels. (a) Absorbance spectra of InN NCs ($d = 4.2$ nm, $[\text{NC}] = 1.8$ μM), with various amounts of NOBF_4 oxidant added (0 – 30 equivalents per NC). The arrows indicate the direction of the shifts upon oxidation. The sharp features between 3,800 and 4,500 cm^{-1} are due to solvent overtone modes. All absorption spectra have been corrected for dilution effects. (b) Differential absorption spectra, $\Delta A = A_{\text{oxidized}} - A_0$.

Interestingly, we note here that the reduction of the integrated cross-section of the LSPR matches closely the integrated increase in the visible (Figure 3.1b), which points to the large oscillator strength of the IR transition, on par with that of the fully allowed direct interband transitions. We will further discuss the oscillator strength of the IR transition in Chapter 5. The intensity of the LSPR band is directly proportional to the number of oscillators (that is, the number of free carriers) involved in the resonance and provides a direct probe to quantify the carrier density in these colloidal NCs using titration methods similar to those that have been applied extensively to study *n*-doped ZnO NCs.¹⁸⁻²¹

Figure 3.2 summarizes the quantitative change in the integrated absorption cross-section of the IR transition of InN NCs ($d = 4.2$ nm) as a function of the oxidative reaction with NO^+ . The reduction of the IR band intensity initially drops linearly with each equivalent of added oxidant, suggesting that a fast equilibrium is reached in that regime, whereby electrons are quantitatively extracted from the NCs by NO^+ . Beyond that point, the ability of each additional equivalent of oxidant is significantly reduced, leading to “plateaus” around 50% of the original absorption cross-section. The same relative “plateau” relative value was found consistently for all samples we investigated, and does not depend on the NC size. We also observed extremely slow dynamic changes in the optical spectra of samples prepared in the plateau regime (see Appendix). Although these time - dependent shifts in the plateau region are quite small compared to the overall changes reported here, we cannot unambiguously eliminate the possibility that the observed plateaus (given here

as the value observed after 1h, see experimental section for further details) arise from slow electron transfer kinetics. Further studies to illuminate the origin of such slow kinetic processes in the plateau regime go beyond the scope of this contribution, and we concentrate here exclusively on the linear titration regime, where equilibrium is quickly reached upon addition of the oxidant.

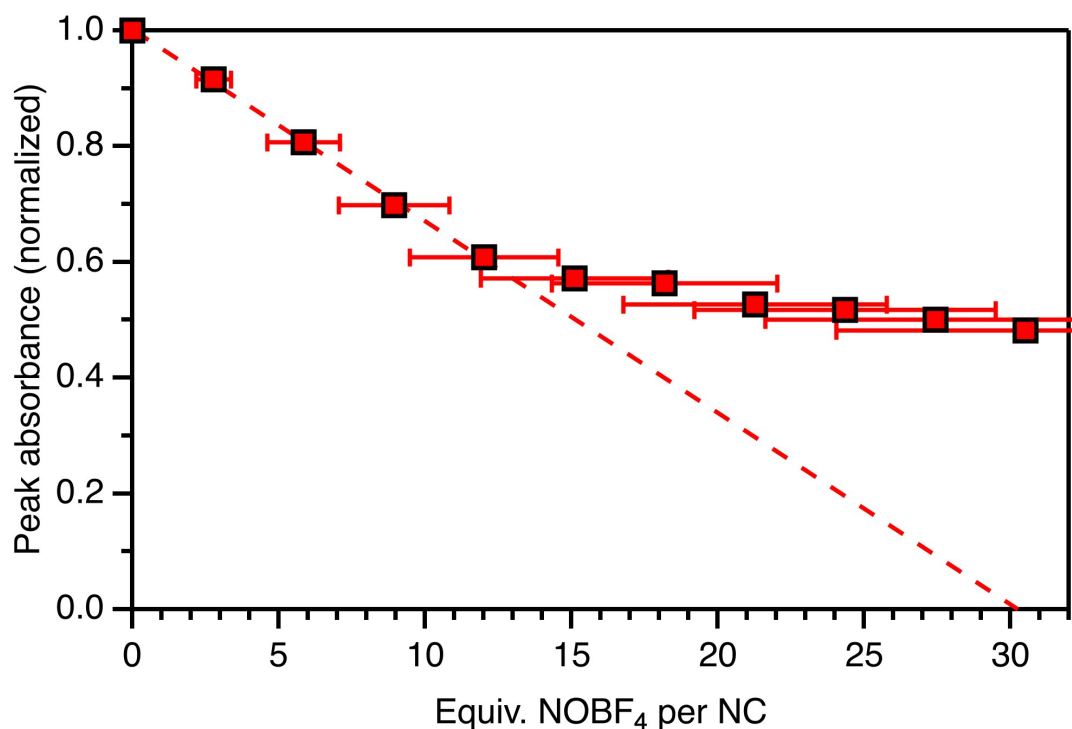


Figure 3.2. Quantitative determination of the free carrier density in InN NCs. The relative integrated LSPR absorption InN NCs ($d = 4.2$ nm) is reported as a function of added NOBF₄; the intensity of absorption initially decreases linearly with each equivalent of oxidant added, then plateaus. The dashed line is a linear regression to the first five points, $y = (1.002 \pm 0.005) - (0.0033 \pm 0.0007)x$. The abscissa intercept yields an extrapolated average electron density of 30 ± 7 e^-/NC , or $\langle N_e \rangle = (7.7 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$ (we note that experimentally, the carrier density is obtained independently of the NC volume, which is why the standard deviation on the volumetric density is lower than the per NC one; see Appendix for further details)

A quantitative estimate of the electron density can be obtained from the data in Figure 3.2 by extrapolating the linear trend to zero absorbance, yielding an average value of $30\ e^-/\text{NC}$, or $7.7 \times 10^{20}\ \text{cm}^{-3}$ for the $d = 4.2\ \text{nm}$ sample. Oxidative titrations such as that shown in Figure 3.2 have been carried for a range of InN NC sizes ($4\ \text{nm} \leq d \leq 9\ \text{nm}$), allowing for the evaluation of the size dependence of the carrier density (Figure 3.3).

This value is comparable, on the higher side, to the highest densities observed in other plasmonic colloidal NCs,^{19, 20, 22} and underlines the predominance of native dopants in colloidal InN NCs, just as is observed in the bulk.²³⁻²⁵ The fact that the carrier density does not vary with NC size suggests that the chemical processes associated with the (unintentional) doping of InN NCs are likely regulated here by thermodynamic factors during the synthesis of InN NCs, rather than by kinetically limiting processes. Interestingly, the “plateau” oxidation level that each sample reaches is equally independent of size, reaching an average value across all sizes of $(3.9 \pm 0.3) \times 10^{20}\ \text{cm}^{-3}$.

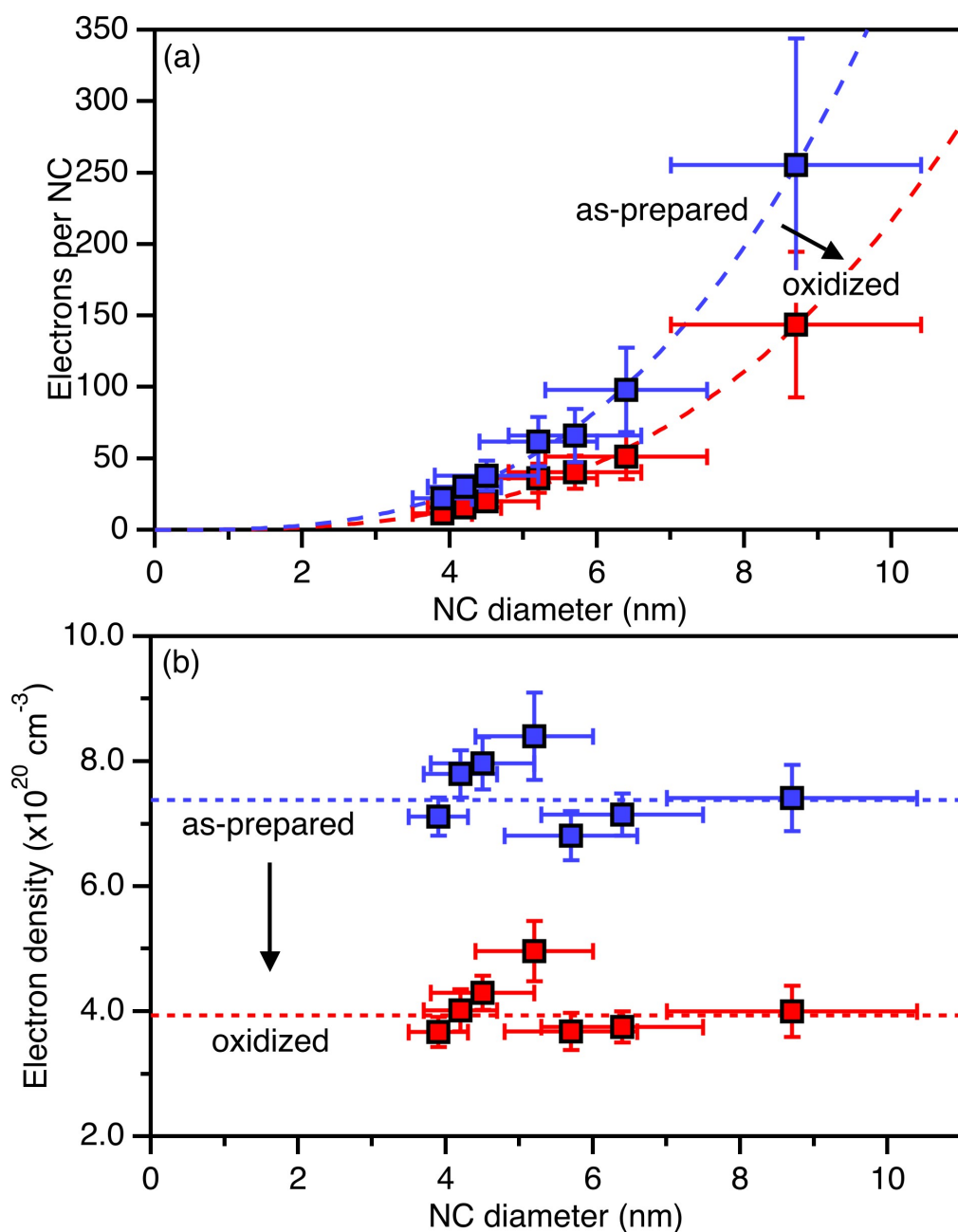


Figure 3.3. Size dependence of the free carrier density in InN NCs. (a) Number of electrons per NC for different NC sizes extracted from titration analyses, in as-prepared samples (blue squares) and maximally oxidized (red squares) samples. Dashed lines show the cubic dependence of the data on NC diameter. (b) Same data as in panel (a), but scaled to the NC volume, yielding the carrier density (N_e) vs diameter (d). $\langle N_e \rangle = (7.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$ (as-prepared) and $(3.9 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$ (oxidized).

3.5 Conclusions

We provided a direct, model-independent quantification of the carrier density of InN NCs by analyzing the IR absorption spectra with an one-electron acceptor, NO^+ . The free electron density of InN NCs was evaluated to be $\langle N_e \rangle \sim 7.4 \times 10^{20} \text{ cm}^{-3}$ and appears to be size-independent, implying that single InN NCs can hold up dozens to hundreds of delocalized charge carriers depending on their size.

APPENDIX

SI 3.1. Saturated Solution of NOBF₄ in Acetonitrile.

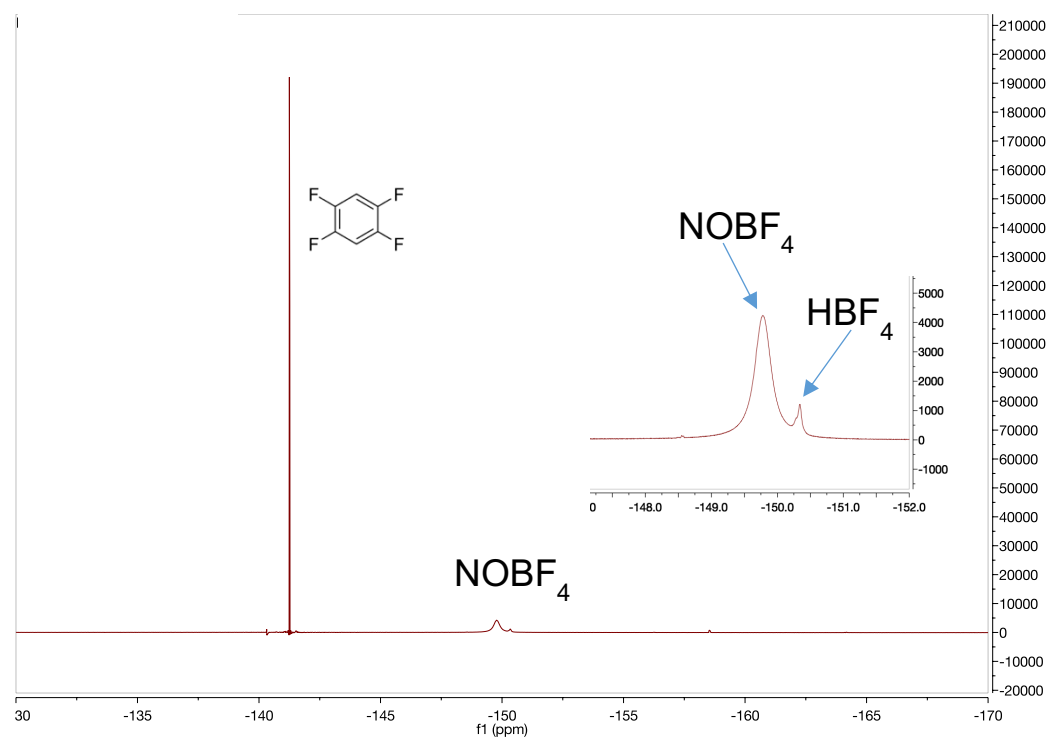


Figure SI 3.1. Fluorine-19 NMR of NOBF₄ and 1,2,4,5-tetrafluorobenzene. A saturated solution of NOBF₄ in ACN was prepared and diluted to desired concentration. The solubility of NOBF₄ was measured using fluorine-19 NMR. 1,2,4,5-tetrafluorobenzene (Fluorochem, 98%) was used as an internal standard. With the ratio of the integration of standard molecule to NOBF₄, the saturated concentration of NOBF₄ was calculated to be 33.7 ± 1.3 mM. 8 samples were prepared and measured independently; the results are given in Table SI 3.1

Table SI 3.1. Concentrations of NOBF₄ of eight independently prepared solutions.

sample	1	2	3	4	5	6	7	8	average	S.D.
concentration (mM)	34.0	31.3	34.3	34.4	32.5	33.3	34.6	35.3	33.7	1.3

SI 3.2. Calculation of the Free Carrier Density.

The free electron density of InN NCs (N_e), expressed in cm^{-3} in the text, can be obtained by dividing the total number of electrons by the total InN volume (in cm^3) in a sample. As described in the main text, the total number of electrons is obtained from chemical titrations with NOBF_4 , by extrapolating the linear decrease in the LSPR intensity to zero. The amount of oxidant added to reach that point is $n_{\text{NO}^+}N_A$, where n_{NO^+} is the extrapolated number of moles of NOBF_4 required to extinguish the LSPR and N_A is Avogadro's number:

$$n_e = n_{\text{NO}^+}N_A \quad (\text{S1})$$

The total volume of InN in a sample can be obtained independently from the NC volume, which allows to limit the uncertainty associated with size inhomogeneity in these samples. The total number of moles of In^{3+} in a given NC suspension can be obtained from ICP measurements, as described below; this quantity is then directly converted to volume by using the molar mass ($M_{\text{InN}} = 128.8 \text{ g} \cdot \text{mol}^{-1}$) and the density of InN ($\rho_{\text{InN}} = 6.92 \text{ g} \cdot \text{cm}^{-3}$):

$$V_{\text{InN}} = n_{\text{InN}} \frac{M_{\text{InN}}}{\rho_{\text{InN}}} = [\text{In}^{3+}] V_{\text{tot}} \frac{M_{\text{InN}}}{\rho_{\text{InN}}} \quad (\text{S2})$$

where $[\text{In}^{3+}]$ is the analytical concentration of In^{3+} measured by ICP and V_{tot} is the total solution volume. The free carrier density is then obtained from:

$$\langle N_e \rangle = \frac{n_e}{V_{\text{InN}}} = \frac{n_{\text{NO}^+} N_A}{[\text{In}^{3+}] V_{\text{tot}} M_{\text{InN}} \rho_{\text{InN}}^{-1}} \quad (\text{S3})$$

The average number of electrons per NC is obtained by multiplying the average carrier density by the average NC volume (which is not strictly identical to the volume of the average NC in a diameter distribution).

SI 3.3 TEM Images and Size Distribution Analyses

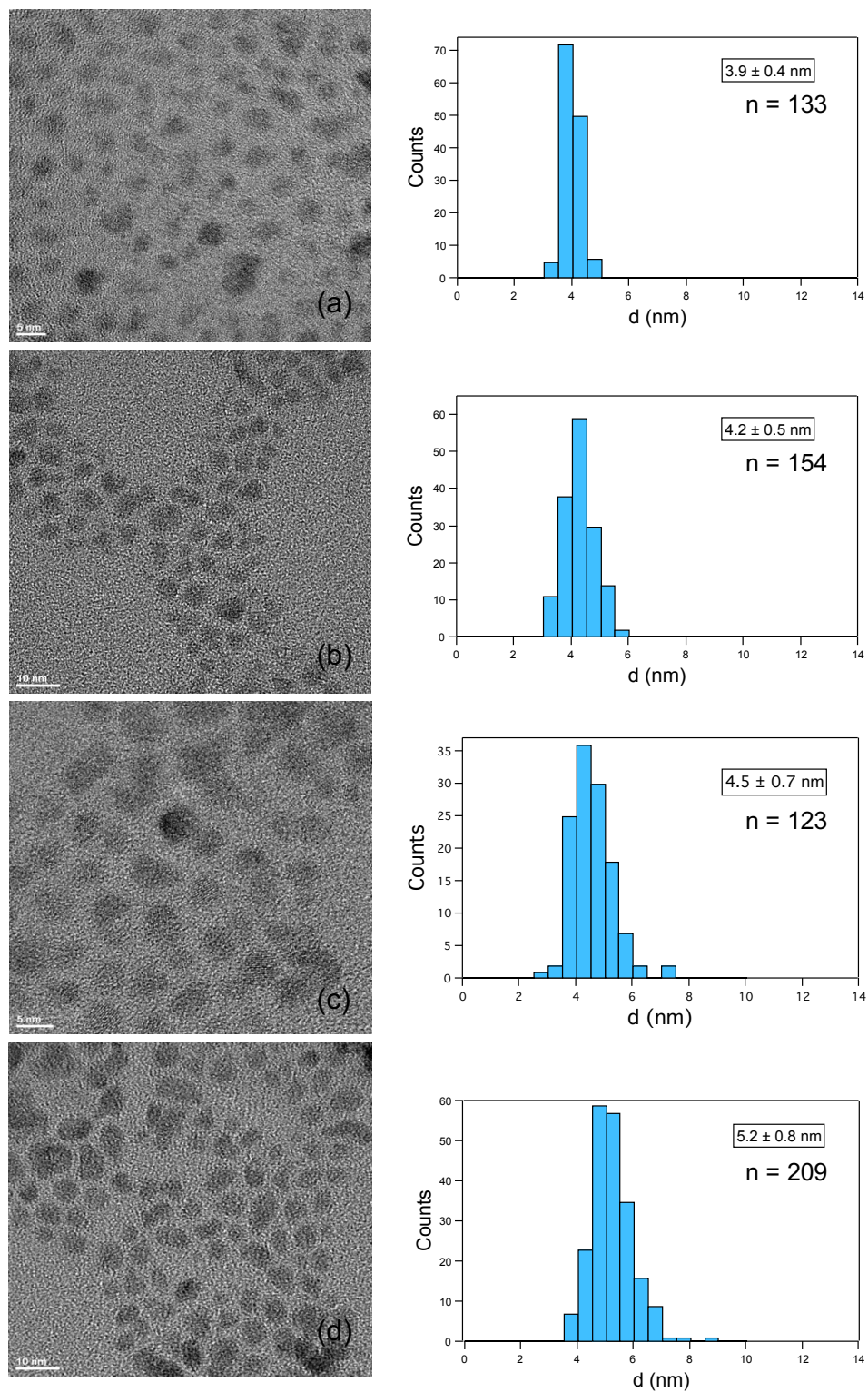
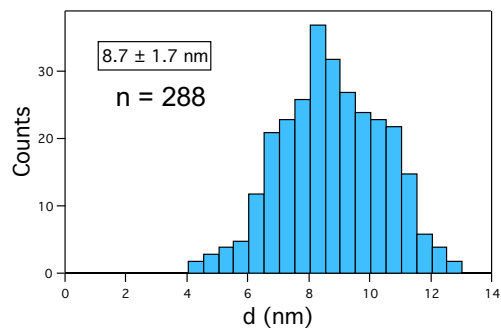
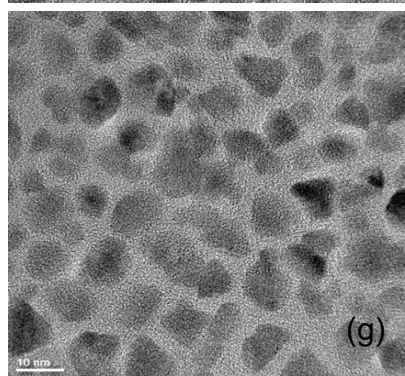
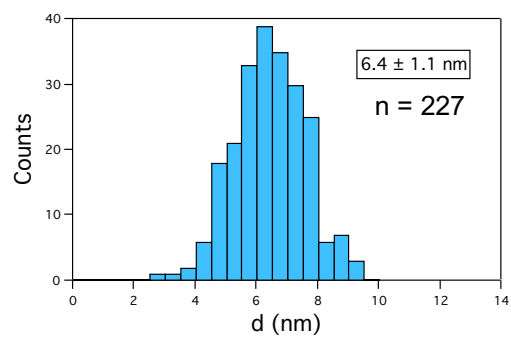
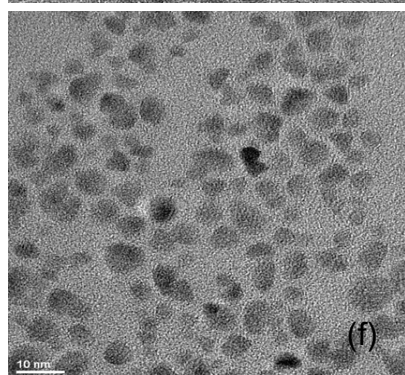
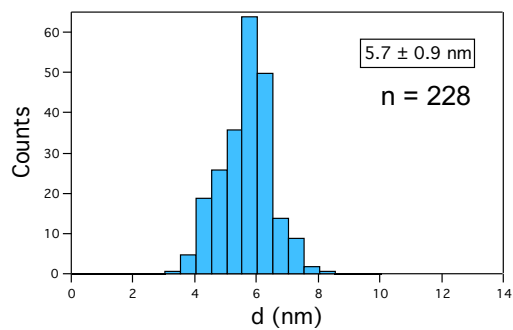
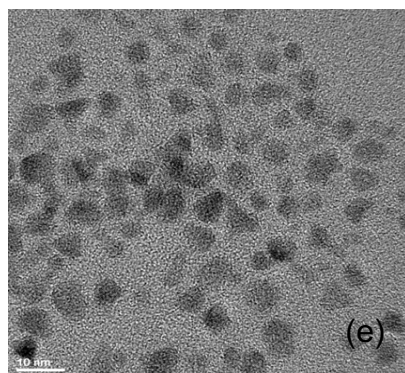


Figure SI 3.2. TEM images and histograms of different sizes InN NCs. (a) 3.9 nm, (b) 4.2 nm, (c) 4.5 nm, (d) 5.2 nm, (e) 5.7 nm, (f) 6.4 nm, (g) 8.7 nm InN NC.

Figure SI 3.2 (cont'd).



SI 3.4 Chemical Titration of InN NCs of Different Sizes

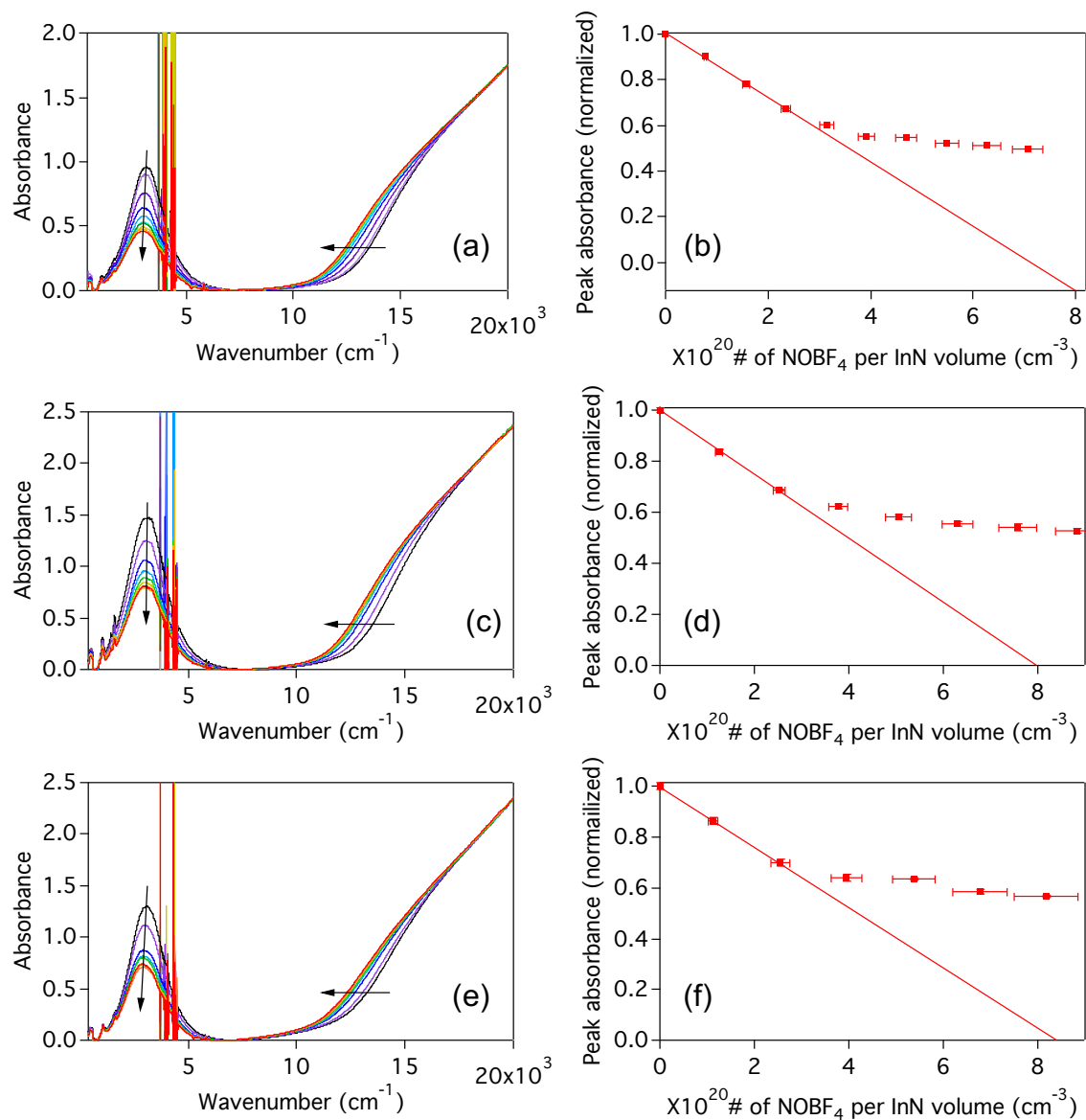
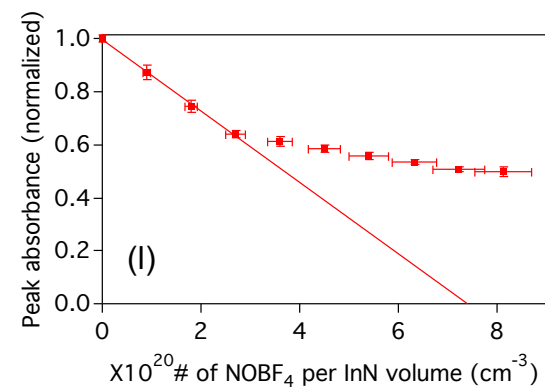
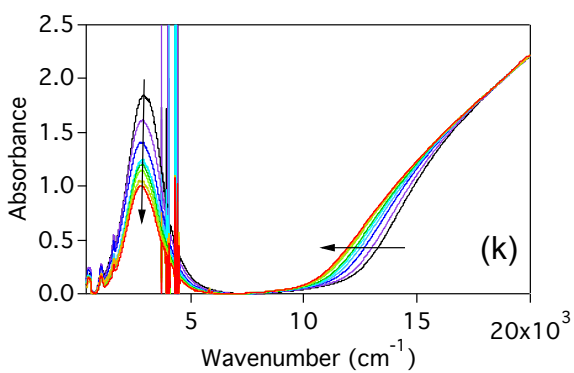
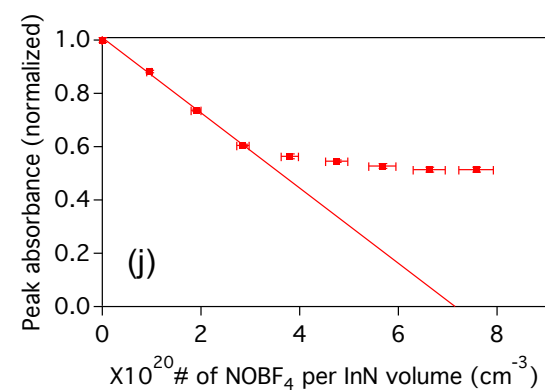
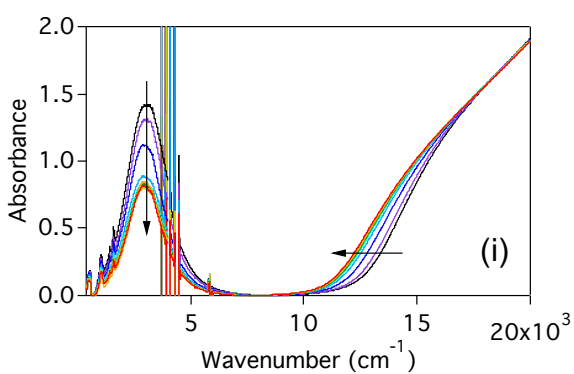
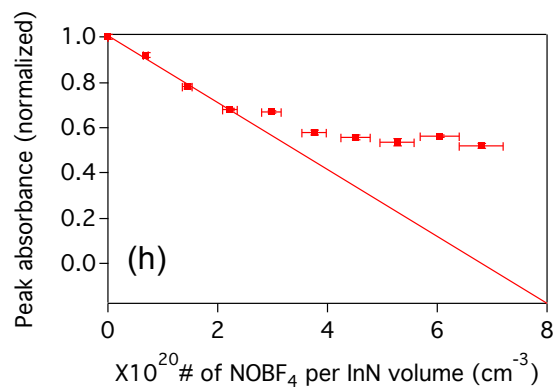
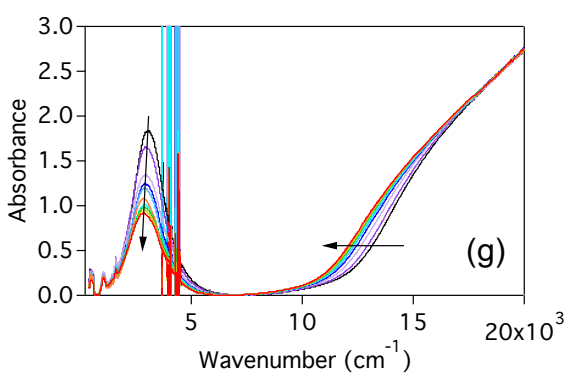


Figure SI 3.3. Chemical titration of *i*-InN NCs of different sizes. Absorption spectra and number of electrons per NC: (a)(b) 3.9 nm, (c)(d) 4.5 nm, (e)(f) 5.2 nm, (g)(h) 5.7 nm, (i)(j) 6.4 nm, (k)(l) 8.7 nm InN NC.

Figure SI 3.3 (cont'd).



SI 3.5 ICP Data

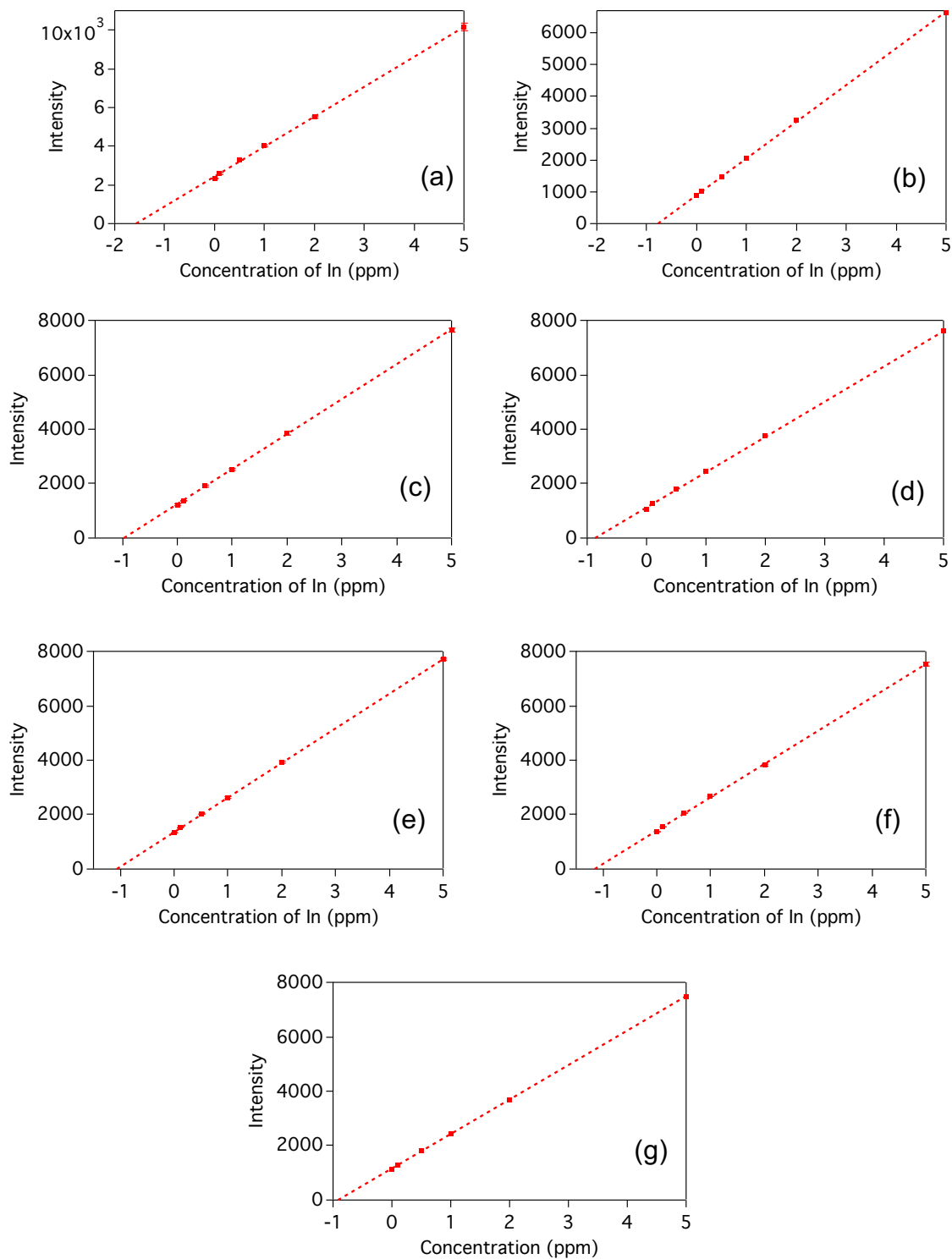


Figure SI 3.4. ICP of different sizes InN NCs. (a) 3.9 nm, (b) 4.2 nm, (c) 4.5 nm, (d) 5.2 nm, (e) 5.7 nm, (f) 6.4 nm, (g) 8.7 nm InN NC.

Table SI 3.2. Concentrations of In^{3+} of different sizes InN NCs from Figure SI 3.4.

Sizes (nm)	3.9	4.2	4.5	5.2	5.7	6.4	8.7
$[\text{In}^{3+}]$ (ppm)	1.57	0.77	0.98	0.87	1.07	1.16	0.91

SI 3.6 Kinetics of Addition of NOBF₄ Solution to InN-BF₄⁻ Suspension

A. InN NCs with limited equivalent of NOBF₄ (linear region)

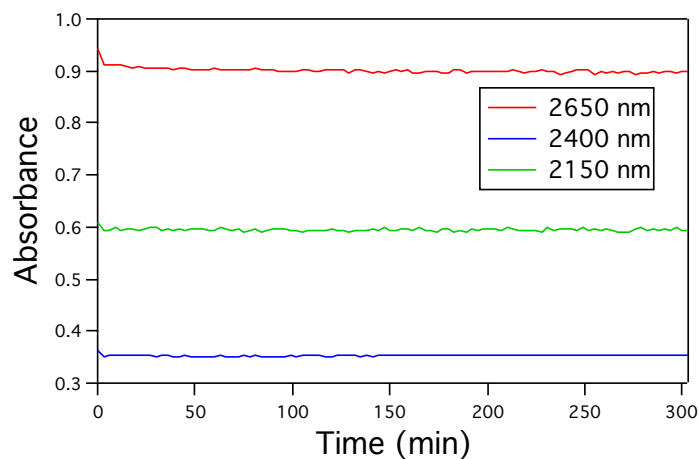


Figure SI 3.5 Absorbance of 4.5 nm *i*-InN with 1 equivalent NOBF₄ at 2650 nm, 2400 nm and 2150 nm as a function of time.

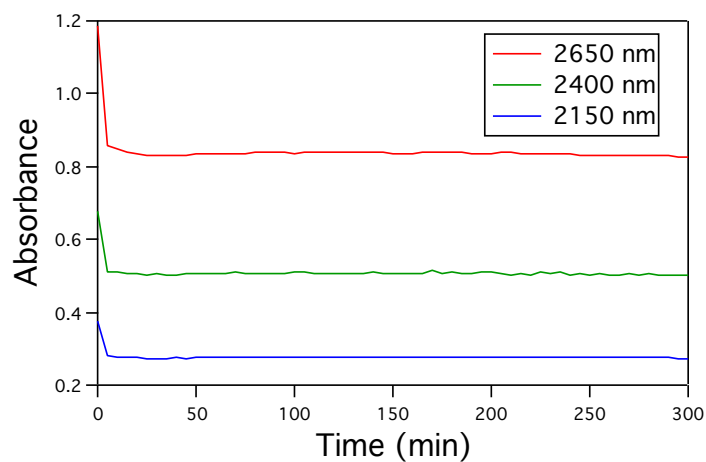


Figure SI 3.6. Absorbance of 8.7 nm *i*-InN with 20 equivalent NOBF₄ at 2650 nm, 2400 nm and 2150 nm as a function of time.

B. InN NCs with excess equivalent of NOBF₄ (plateau region)

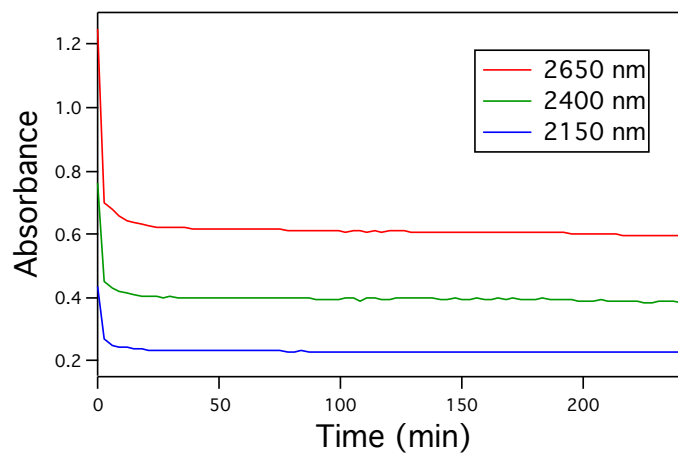


Figure SI 3.7. Absorbance of 5.7 nm *i*-InN with 40 equivalent NOBF₄ at 2650 nm, 2400 nm and 2150 nm as a function of time.

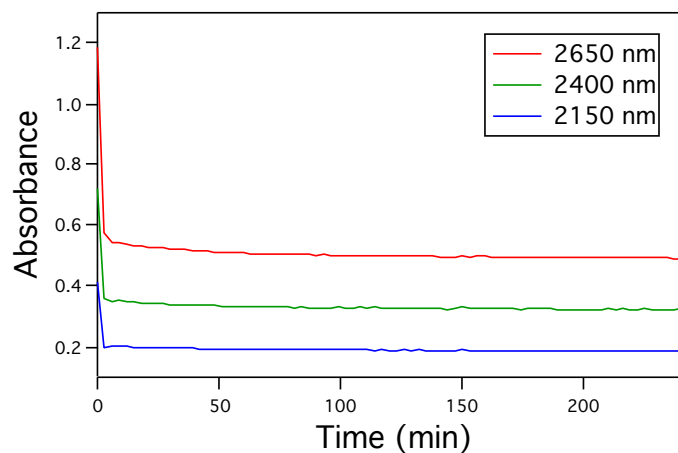


Figure SI 3.8. Absorbance of 5.7 nm *i*-InN with 160 equivalent NOBF₄ at 2650 nm, 2400 nm and 2150 nm as a function of time.

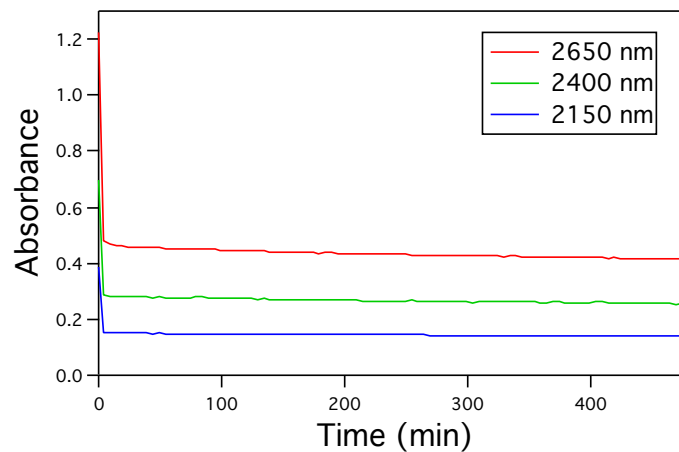


Figure SI 3.9. Absorbance of 8.7 nm *i*-InN with 200 equivalent NOBF₄ at 2650 nm, 2400 nm and 2150 nm as a function of time.

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REFERENCES

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Chapter 4: Nonparabolicity Effects on the Plasmonic Behavior of Doped Semiconductor Nanomaterials

4.1 Overview

Unlike degenerately doped oxides NCs system, the energy of the LSPR in InN NCs is nearly independent of the carrier density, which premises that simple classical models that are often used to describe metallic systems inadequately describe the plasmonic response of InN nanoparticles. Here, we show that the unusual plasmonic signatures of colloidal InN nanocrystals arise from the nonparabolicity of the conduction band dispersion, which explains the nearly invariant LSPR energy as a function of carrier density as well as the size dependence of the LSPR energy. The results and discussion presented in this chapter have been reported in the literature.¹

4.2 Introduction

In theory, heavily-charged (or “doped”) semiconductor NCs can behave like metallic NCs, but with a tunable doping level and a LSPR in the NIR region, which makes them attractive for plasmonics applications such as biosensing,^{2, 3} surface enhanced spectroscopy,⁴ smart windows,⁵ or for transparent conductors. Efforts have been taken to modulate the LSPR energy by chemical, photochemical or electrochemical external stimuli. In photodoped ZnO NCs, the LSPR energy can be tuned over 2000 cm^{-1} with progressively greater photoexcitation and the various identity of hole quencher.⁶ In Sn^{4+} -doped In_2O_3 NC films, over 2200 cm^{-1} shift in the LSPR could be achieved with external potential.⁷

As discussed in Chapter 2 and Chapter 3, as-prepared colloidal InN NCs are natively

degenerately-doped. The exact origin of the donor defects responsible for the native doping of InN NCs is still unknown but reflects the instability of intrinsic InN and the strong tendency of native defects to be donors, consistent with the behavior of the bulk material.⁸

⁹ The average free electron density of InN NCs was evaluated to be $\langle N_e \rangle \sim 7.4 \times 10^{20} \text{ cm}^{-3}$ and appears to be size-independent.¹ However, the LSPR energy barely changes with electron density, starkly contrasting with doped oxides NCs. Palomaki *et al.* have previously indirectly estimated the electron density of InN NCs with the classical model described in section 4.4, and the value they obtained ($2.89 \times 10^{20} \text{ cm}^{-3}$) was only half the value we obtained experimentally in Chapter 3.¹⁰ These observations underline the uniqueness of InN NCs and, on the other hand, the shortcomings of the classical models. The purpose of this chapter is: 1) demonstrate the inability of the simplest classical (Drude) models to properly describe the plasmonic behavior of InN NCs and consequently to correctly quantify carrier densities; 2) show that the small bandgap of InN directly impacts the behavior of the delocalized, but confined, charge carriers, suggesting that the plasmonic behavior of InN NCs directly reflects the non-parabolic dispersion of CB.

4.3 Experimental Methods

4.3.1 InN NC Synthesis

The synthesis, purification and ligand exchange of InN NCs were described in Chapter 2, Section 2.3.1.

4.3.2 Physical & Sample Characterization Methods

Instrumentation and measurements were described in detail in Chapter 2, Section 2.3.2.

4.4 Results and Discussion

The addition of oxidant to colloidal suspensions of InN reduces the intensity of the LSPR absorption and redshifts the interband transitions energy,¹⁰ as discussed in Chapter 3. An important observation is that the LSPR peak position does not shift appreciably upon oxidation of the InN NCs (Figure 4.1), a behavior strikingly at odds with that observed for other semiconducting plasmonic systems, which typically follow the classical Drude behavior of a free-electron gas:

$$\omega_{Drude} = \sqrt{\frac{\omega_p^2}{m_e(\epsilon_\infty + 2\epsilon_m)} - \gamma^2} \quad \text{eq. 4.1}$$

where m_e is the carrier effective mass (in units of the free electron mass, m_0), ϵ_∞ and ϵ_m are the optical dielectric constants of the material (of spherical symmetry here) and of the surrounding medium, respectively, γ is the damping constant of the free electron oscillation mode, and ω_p is the bulk undamped plasma frequency:

$$\omega_p = \sqrt{\frac{N_e e^2}{m_0 \epsilon_0}} \quad \text{eq. 4.2}$$

which depends on the free carrier density, N_e (the constants e , m_0 , and ϵ_0 are the elementary charge, the free electron mass, and the permittivity of vacuum constants, respectively; all equations and constants are expressed in SI units.). LSPR modes in

doped oxides exhibit large shifts upon doping level variations that are generally attributed to the $N_e^{1/2}$ dependence of the bulk plasma frequency (although more detailed analyses indicate the importance of considering the intricate roles of confinement effects^{11, 12} and of damping mechanisms¹³⁻¹⁵). The fact that the IR band of InN NCs does not shift contrasts sharply with the behavior of these other systems, and suggests either that the IR band is not appropriately characterized as a LSPR feature, or, as we demonstrate later, that the classical Drude model given by eq. 4.1 does not properly describe the LSPR behavior of InN NCs in ways that go beyond contributions due to quantum confinement and/or damping effects.

The recognition that eq. 4.1 cannot describe the physics of the spectroscopic transitions of InN NCs implies directly that a straightforward Drude analysis cannot be used to estimate the free carrier density; doing so would of course imply that the carrier density remains constant despite the addition of large amounts of oxidant and of the observed Burstein-Moss shift of the interband transitions.

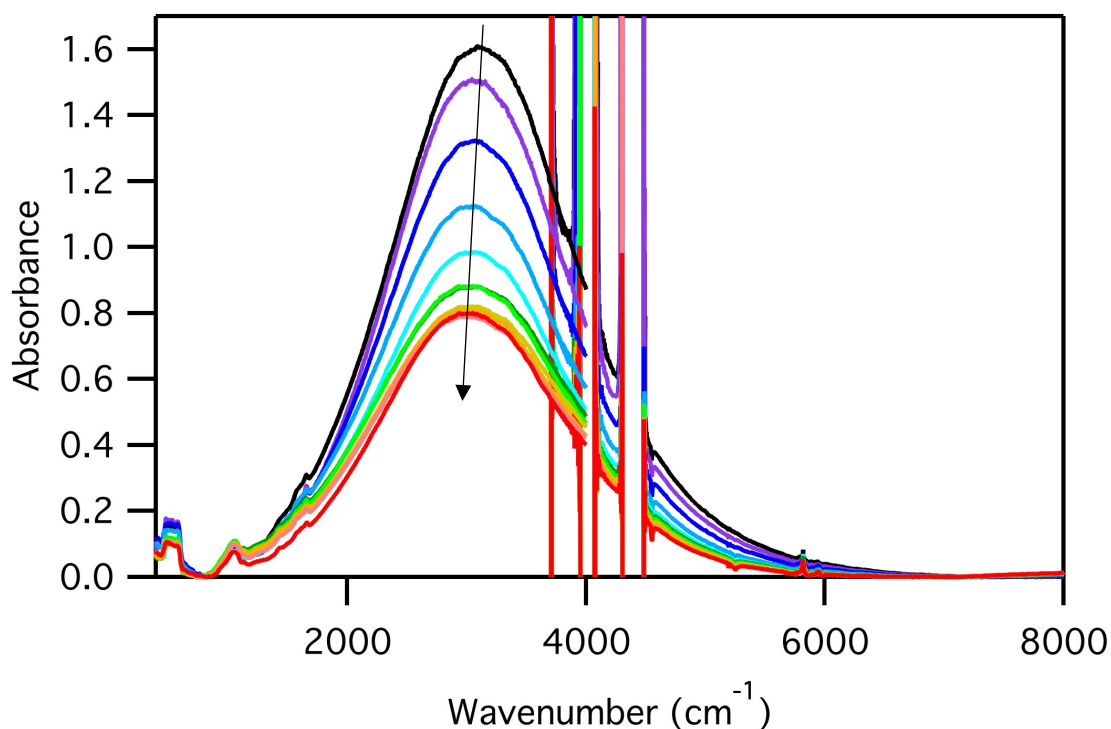


Figure 4.1. IR transition of *i*-InN NCs ($d = 4.2$ nm, $[\text{NC}] = 1.8 \mu\text{M}$), with various amounts of NOBF_4 oxidant added (0 – 30 equivalents per NC). The arrows indicate the direction of the shifts upon oxidation. The sharp features between $3,800$ and $4,500 \text{ cm}^{-1}$ are due to solvent overtone modes.

A quantitative estimate of the electron density was obtained in Chapter 3, yielding a size-independent carrier density average value of $(7.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$ and the carrier density in InN nanocrystals can be reduced to $(3.9 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$. However, for the $d = 4.2$ nm sample shown in Figure 4.1, the overall shift is about 100 cm^{-1} to the red (similar shifts are observed for all sizes) for a decrease of the electron density of nearly 50% the original value. As shown in Figure 4.2, this is clearly at odds with the Drude behavior, eq. 4.1, if one uses the established parameters of bulk InN ($m_e = 0.06$,^{16, 17} $\epsilon_\infty = 6.7$;¹⁸⁻²⁰ the dielectric constant of the medium is estimated here as $\epsilon_m = 5.3$).

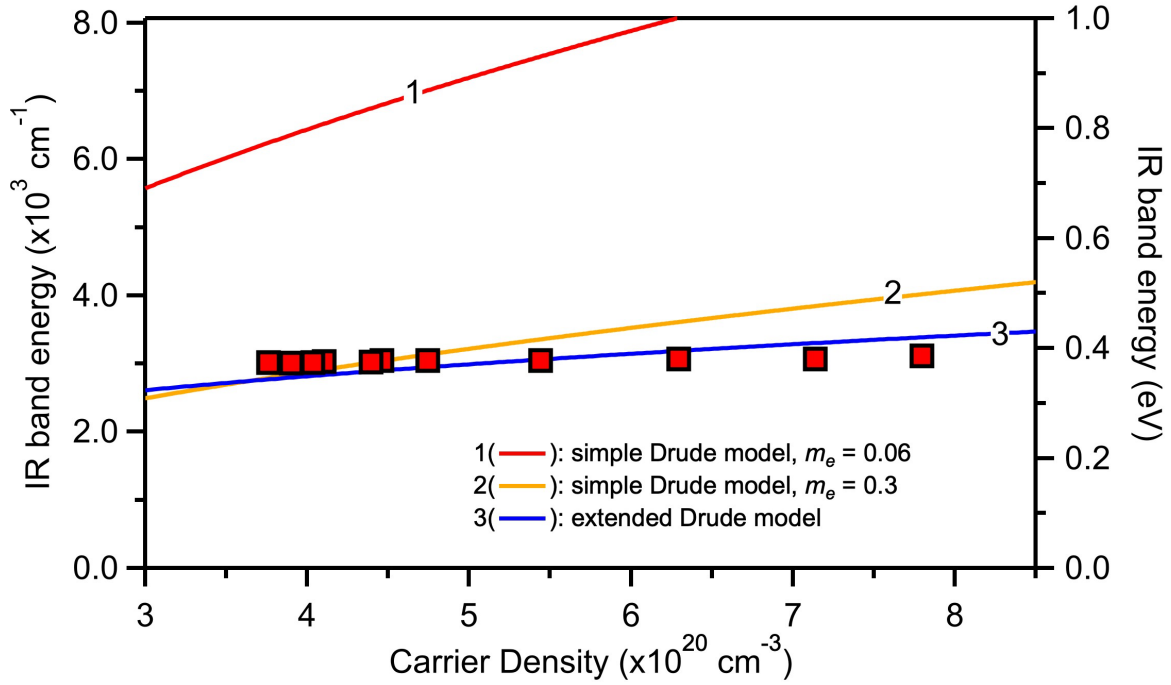


Figure 4.2. NIR absorption peak maxima of InN NCs ($d = 4.2 \text{ nm}$) as a function of electron density, emphasizing the near-invariance of the transition energy against carrier density, which is strikingly at odds with the classical plasmonic behavior (curve 1 and 2). A model that takes into account the non-parabolicity of the conduction band (curve 3) captures well this behavior.

The very small electron effective mass of InN leads to predicted resonance energies that are clearly much larger than the LSPR energies observed experimentally here, and which shift by over $3,000 \text{ cm}^{-1}$ for the whole range of carrier densities covered experimentally. The discrepancy cannot be resolved by taking into account the effect of damping in eq. 4.1, as the damping values necessary to redshift the $m_e = 0.06$ curve by $\sim 4,000 \text{ cm}^{-1}$ would lead to larger-than-observed bandwidths (in excess of $10,000 \text{ cm}^{-1}$). Better agreement between the classical model and experiment can be obtained by using significantly larger values of the effective mass, $m_e = 0.3$ shown in Figure 4.2: the average

LSPR energy matches better with experiment, but the calculated curve still strongly overestimates the LSPR shift with carrier density. This suggests that the LSPR behavior in InN NCs is not appropriately described by the dispersion at the bottom of the CB. The band structure of *w*-InN was previously calculated by Carrier and Wei,²¹ and is reproduced here in Figure 4.3 in the region of the CB. As can be seen from the comparison with the parabolic dispersion associated with the region close to the Γ point, the CB in InN exhibits a strongly non-parabolic dispersion at relatively small wavevectors, which reflects sizeable interband coupling due to the small bandgap ($E_g < 0.8$ eV).^{8, 22, 23} Importantly, in the case that concerns us here, carriers that are responsible for the plasmonic behavior of InN (that is, those close in energy to the Fermi level) lie in linear regions of the dispersion, which impacts their behavior in several ways. First, the effective mass of carriers is no longer well described by a unique value; rather, the effective mass depends strongly on the value of the wavevector (k) associated with each carrier:

$$m_e(k) = \frac{\hbar^2 k}{dE_{CB}/dk} = \frac{\hbar k}{v_g} \quad \text{eq. 4.3}$$

For linear dispersion regimes, the electron group velocity (v_g) is by definition constant ($v_g \sim 7 \times 10^5$ m·s⁻¹ from the calculated band structure of InN),²¹ and the effective mass then varies linearly with k . Because the high carrier densities observed here correspond to high Fermi energies (and thus large k values), the effective masses associated with carriers close to the Fermi level are significantly larger (up to an order of magnitude) than

the effective mass at the bottom of the CB ($k = 0$ for InN). This explains why the use of a large effective mass in the simple Drude model leads to a better estimate of the LSPR energy, as shown in Figure 4.2. The oxidation of NCs lowers the E_F energy and consequently reduces the wavevector magnitude of the free carriers near the Fermi level, which impacts their behavior by decreasing their effective mass as described by eq. 4.3.

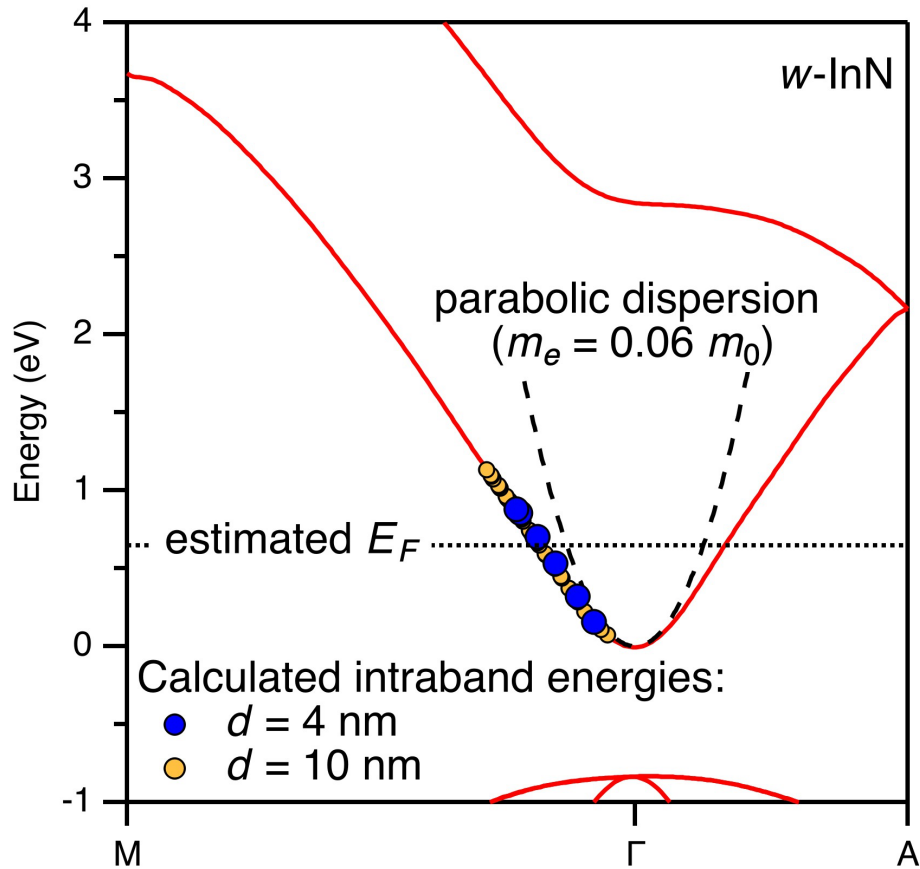


Figure 4.3. Band structure of $w\text{-InN}$. (Calculations from ref. 21) The region around the lowest conduction band (CB) is emphasized here. The parabolic dispersion associated with the effective mass of bulk InN ($m_e = 0.06 m_0$) is also shown (dashed line), emphasizing the non-parabolicity of the CB. The estimated average Fermi energy (E_F) is also shown, along with calculated particle-in-spherical-box levels for two diameters. The bottom of the CB defines the zero of the energy scale.

The concomitant reduction of both N_e and m_e upon oxidation mitigates the shift of the LSPR energy (see eq. 4.1 and 4.2) compared to the behavior of free carriers with a parabolic dispersion (for which m_e should be independent of N_e). A better agreement with experiment is thus obtained by explicitly taking into account this variation of the effective mass, using the effective mass vs carrier density relationship calculated by Carrier and Wei,²¹ which predicts a ~20% variation ($m_e \sim 0.5$ to 0.4) for the range of carrier densities covered here. Inserting this explicit variation of the effective mass with carrier density into eq. 4.1 (and further correcting for the relatively minor damping and quantum-size effects as discussed below) reproduces well the quasi-invariance of the LSPR energy upon oxidation and illustrates the importance of the nonparabolic dispersion of the CB in modulating the LSPR response in InN NCs. Nonparabolic effects play an important role in bulk semiconductors,²⁴⁻²⁷ and have been invoked recently to accurately describe the ultrafast response of LSPR in indium tin oxide nanorods.²⁸ The non-parabolicity of the CB of InN has also been shown to impact resonance Raman scattering of InN films.²⁹

Another intriguing feature of the plasmonic behavior of InN NCs is the size dependence of the resonance, as reported in Figure 4.4. A clear blueshift of the resonance is observed when the average diameter is decreased from about 9 nm to 4 nm. This trend is qualitatively similar than the LSPR shifts observed for other quantum-confined NCs.^{11, 30,}

³¹ Significantly though, the overall LSPR shift effect observed from InN (about 170 cm^{-1} , or 20 meV) is 1 order of magnitude smaller than for ZnO (about $1,200 \text{ cm}^{-1}$, or 150 meV)

for the same size range (*vide infra*).¹¹

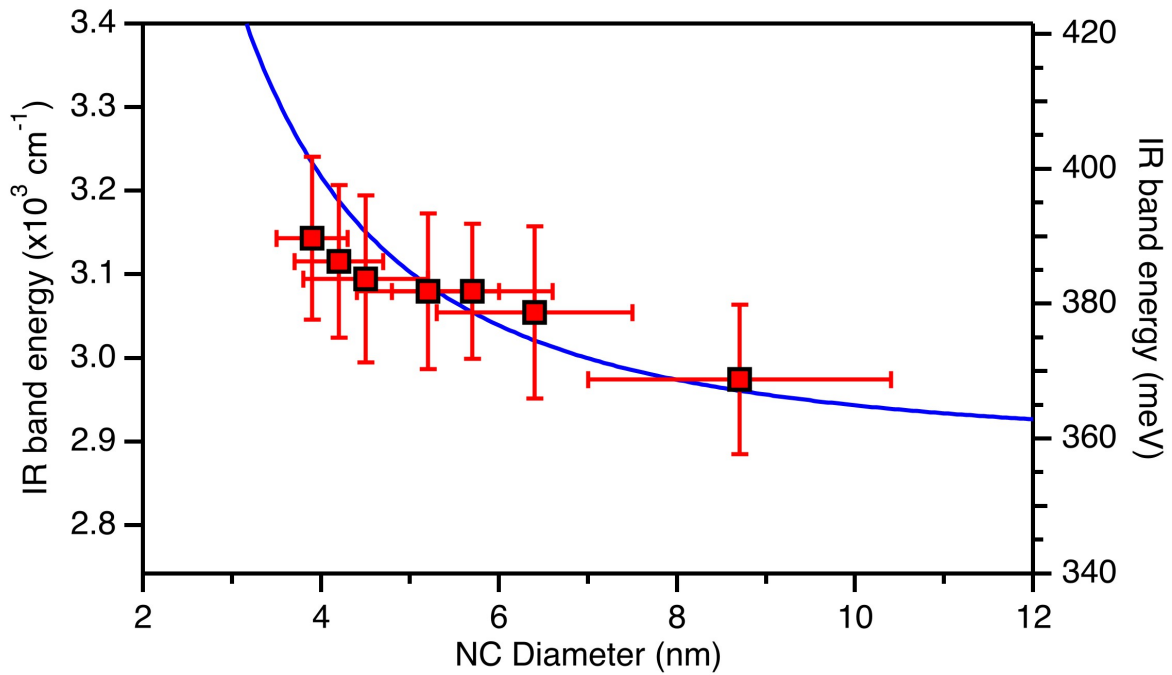


Figure 4.4. The NIR transition observed for InN NCs of varying sizes. The size dependence predicted by a nonparabolic Drude model, eq. 4.5, is also shown in blue.

As pointed out by Schimpf *et al.*,¹¹ the LSPR blueshift with decreasing NC size cannot be reconciled with the simplified model of eq. 4.1, which predicts the opposite energy shift with decreasing sizes if the damping constant is treated to account for size-dependent surface-scattering processes:^{32, 33}

$$\gamma = \gamma_0 + \frac{2Av_F}{d} \quad \text{eq. 4.4}$$

where γ_0 is the damping constant for bulk InN ($\gamma_0 \sim 100 \text{ cm}^{-1}$ for InN,^{23, 34} about 1 order of magnitude smaller than the surface term in eq. 4.4), v_F is the Fermi velocity (on the order of $10^6 \text{ m}\cdot\text{s}^{-1}$, see Appendix), and A is a constant on the order of unity.³² As all NC sizes

investigated here have similar electron densities (Chapter 3), the Fermi velocity associated with these NCs is not expected to vary appreciably, and hence the observed LSPR blueshift with decreasing NC size likely arises from effects that go beyond the extended Drude model of eq. 4.1. An important contribution to the LSPR arises from the finite dimensions of the NCs, which impose boundary conditions to the electronic motion.^{11, 12, 31, 33} We use here a simplified approach to include the effect of electronic confinement on the LSPR, which considers the contributions of intraband transitions in modulating the dielectric response of semiconductor NCs. Because these intraband transitions have a sharp dependence on NC dimensions for sizes comparable to (or smaller than) the excitonic Bohr radius, the behavior of “free” quantum-confined electrons diverges from the simple Drude model in that the restoring force no longer depends solely on the characteristics of the bulk dielectric environment but also on the discretization of the electronic motion; a reversed but equivalent picture is obtained by considering the motion of the confined “free” carriers as a local-field correction imposed over single-electron transitions. Although, strictly, all single-particle transition frequencies can in principle affect the LSPR, the excitation of carriers close to the Fermi level dominate strongly over all others, and we consequently limit the treatment to the use of a single frequency. A general expression for the resonance energy is then obtained as the quadratic mean of the single-electron transition (ω_0) and the classical LSPR (eq. 4.1) frequencies:^{11, 12, 31, 33, 35, 36}

$$\omega_{LSPR} = \sqrt{\omega_0^2 + \omega_{Drude}^2} \quad \text{eq. 4.5}$$

The approach used previously by a few groups has been to use particle-in-a-box energies to model the single-particle transition frequency in eq. 4.5,^{11, 12, 33} yielding single-particle transition energies varying as d^{-2} . This approach describes reasonably well the quantum confinement of electrons in parabolic bands (which have the same dispersion than free electrons but with different effective masses), but is likely not a good description for strongly nonparabolic bands, such as the CB of InN. Indeed, Figure 4.3 shows that the energy spacing between quantum confined levels (*i.e.* subjected to the boundary condition $\psi(r_{NC}) = 0$, where r_{NC} is the radius of the NC) leads to nearly constant energy spacings between adjacent levels (instead of the $2n + 1$ energy splittings obtained from classical particle-in-a-box models) that vary as d^{-1} ; a good approximation to the single-particle transition frequency is obtained from (SI for more details):

$$\omega_0 \approx \frac{1}{\hbar} \frac{dE_{CB}}{dk} \cdot \Delta k \approx v_s \frac{2C}{d} \quad \text{eq. 4.6}$$

where C is a constant which varies between 1 and 1.5. The key aspect of this treatment is that, in first approximation, the size-dependent contributions due to single-particle transitions, eq. 4.6, and the damping, eq. 4.4, vary directly proportionally to each other (that is, as d^{-1}), but with opposite signs, leading to the markedly reduced size dependence of the LSPR of InN compared to ZnO. Overall, as shown in Figure 4.4, the model (described in more detail in SI) yields very good agreement with the observed LSPR data.

A close analogue to the example presented here is the behavior of n-doped HgS NCs investigated by Shen and Guyot-Sionnest, who also invoked nonparabolicity of the CB to explain the reduced size dependence of the lowest intraband/LSPR energy³¹. More advanced treatments of the CB dispersions, which would include effects such as bandgap shrinkage and anisotropic contributions to the effective mass, would undoubtedly lead to better agreement with the experimental data but would also require better control on the homogeneity of the NC size, shape, and doping distributions than are afforded by current approaches to synthesize colloidal InN NCs^{10, 37-39}.

4.5 Conclusions

The plasmonic response of InN NCs is very complex and differs strikingly from that of other wide-bandgap semi- conducting materials such as oxides, pointing to the inadequacy of simpler models (based on Drude theory) to properly describe the plasmonic behavior of InN. The small bandgap of InN directly impacts the behavior of the delocalized, but confined, charge carriers, suggesting that the complex plasmonic behavior of InN nanocrystals arises from the nonparabolic dispersion of the conduction band. The model presented here should apply to other low-bandgap doped semiconductor NCs, or plasmonic materials for which large variations of the effective mass vs Fermi level in the relevant band are expected.

APPENDIX

SI 4.1. Model and Calculations

The particle-in-a-spherical-box (of radius a) problem imposes boundary conditions on the allowed values that the wavenumber value can take:

$$k_{n,l} = \frac{\beta_{n,l}}{a} \quad (\text{S1})$$

where $\beta_{n,l}$ is the n^{th} zero of the l^{th} order spherical Bessel function.

We consider the (n, l) to $(n, l + 1)$ transitions as being the dominant ones in terms of oscillator strength and neglect the other ones; in practice, only the excitations involving carriers close to the Fermi level contribute to the complex dielectric function and affect the LSPR of quantum confined systems. Solving numerically for the zeros of the Bessel functions shows that:

$$1 \leq (\beta_{n,l+1} - \beta_{n,l}) \leq 1.5$$

We define the following relationship:

$$\Delta k = k_{n,l+1} - k_{n,l} = \frac{\beta_{n,l+1} - \beta_{n,l}}{a} \approx \frac{C}{a} \quad (\text{S2})$$

where C is a constant between 1 and 1.5. This characterizes roughly, but reasonably well, the single-electron transitions involved in eq. 4.5 of the main text. The associated energies cannot be directly obtained from the traditional particle-in-a-box approach which rely on the dispersion of free electrons, subjected to appropriate boundary conditions.

The following remains valid for arbitrary dispersions:

$$\Delta E = \frac{\delta E}{\delta k} \cdot \Delta k = \hbar v_g \cdot \Delta k \quad (\text{S3})$$

which is equivalent to eq. 4.6 in the main text (v_g is the electron group velocity). We use

$C = 1.3$ in the calculations shown in the paper, the average value estimated for transitions close to the Fermi level.

The group velocity of InN in the linear region of the CB dispersion can be estimated from the calculated band structure by Carrier and Wei,²¹ from the average slope along both the M and A directions:

$$v_g = \frac{dE/dk}{\hbar} \approx \frac{4.5 \text{ eV} \cdot \text{\AA}}{\hbar} \approx 6.8 \times 10^5 \text{ m} \cdot \text{s}^{-1} \quad (\text{S7})$$

The Fermi velocity, which is used to estimate the surface scattering contribution to the damping factor (eq. 4.4 in the main text) is estimated by the following:⁴⁰

$$v_F = \frac{\hbar}{m_e m_0} (3\pi^2 N_e)^{1/3} \quad (\text{S8})$$

This quantity changes slightly as a function of the Fermi level position, as both N_e and m_e (in the non-parabolic region) depend on E_F . The variation of the effective mass with carrier concentration is plotted in the study by Carrier and Wei,²¹ and is approximated well in the carrier density range investigated here by the following equation:

$$m_e = 0.08 + 4.3375 \times 10^{-9} N_e^{0.38236} \quad (\text{S9})$$

if N_e is expressed in cm^{-3} units. The variation of m_e and v_F with N_e is plotted in Fig. S19(a-c).

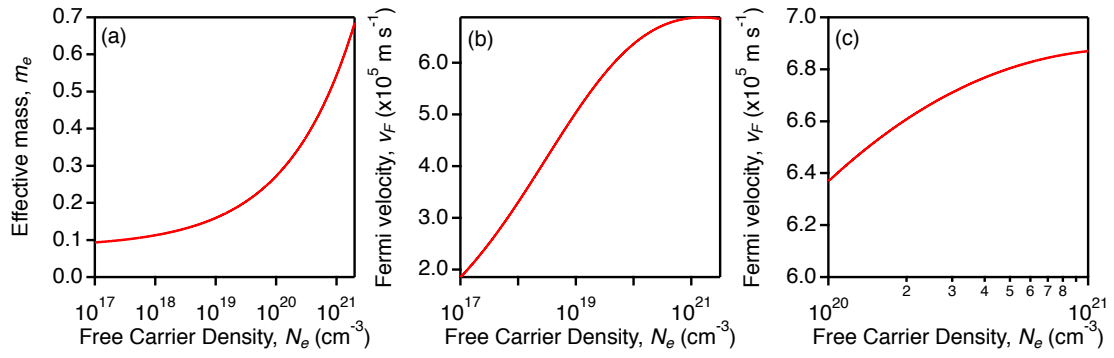


Figure SI 4.1. Calculated (a) effective mass and (b-c) Fermi velocity as a function of the free carrier density. Panel (a) reproduces Fig. 3(b) of ref.(21).²¹

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Chapter 5: Optical Oscillator Strength of Intraband Transition in Colloidal InN Nanocrystals

5.1 Overview

The plasmonic response of doped semiconductor NCs offers great potential for the development of new optoelectronic technologies. The LSPR oscillator strength is an important parameter to evaluate the strength of the light-matter interactions, yet remains undetermined for most semiconductor NC systems. In this chapter, we used InN NCs as a model system to quantify the optical oscillator strength of free electrons from their integrated IR absorbance. We find that the LSPR oscillator strength is $f = 0.3$ per electron per NC, independent of NC size.

5.2 Introduction

Optoelectronic devices operating in the IR regime attract great interest for bioimaging, sensing, and optical communication applications.^{1, 2} Conventional narrow-bandgap materials such as InSb,^{3, 4} HgTe⁵ and HgCdTe⁶ have been widely used for IR photodetection. However, achieving high photon absorption efficiency still remains a challenge with these materials. Another strategy relies on the intraband transition of doped semiconductor nanomaterials such as HgSe⁷⁻⁹ and SnTe.¹⁰ As discussed in Chapter 1, the free electrons in heavily doped semiconductor NCs can generate strong absorption features in the IR region which are attributed to intraband transitions or LSPR, depending on the number of free electrons introduced. Considerable effort in recent years has been devoted to the modulation of free carrier densities and LSPR.¹¹⁻¹³ However, the fundamental parameters that determine light-harvesting ability remain unknown.

InN NCs are promising candidates for IR technologies due to their strong LSPR response. As presented in Chapter 3, the free electron density in InN NCs has been quantified to be

$\langle N_e \rangle \sim 7.4 \times 10^{20} \text{ cm}^{-3}$ and size independent.¹⁴ This paves the way for the understanding of the LSPR of heavily doped semiconductor nanoparticles. In this chapter, we use InN NCs as a model system to discuss the optical oscillator strength of LSPR obtained from absorption spectroscopy.

5.3 Experimental Methods

5.3.1 InN NC Synthesis

The synthesis, purification and ligand exchange of InN NCs were described in Chapter 2, Section 2.3.1.

5.3.2 Physical & Sample Characterization Methods

Instrumentation and measurements were described in detail in Chapter 2, Section 2.3.2.

5.4 Results and Discussion

Figure 5.1(a) shows the two main spectroscopic signatures of colloidal 4.2 nm InN NCs: a bleach in the band edge transition and a strong IR absorption feature (LSPR), both due to the existence of free carriers in InN NCs. The LSPR peak lies between 1000 and 7000 cm^{-1} with the central plasmon energy at $\sim 3000 \text{ cm}^{-1}$. The region of intense solvent overtone modes ($\sim 3800\text{--}4500 \text{ cm}^{-1}$) has been interpolated for clarity (dotted lines); the weak absorbance baseline between 500 and 600 cm^{-1} arises partly from the BF_4^- ligands as well as the fundamental phonon spectrum of InN. For 4.2 nm InN NCs, the number of oscillators (i.e., free electrons) per NC was shown to be 30 (Chapter 3).

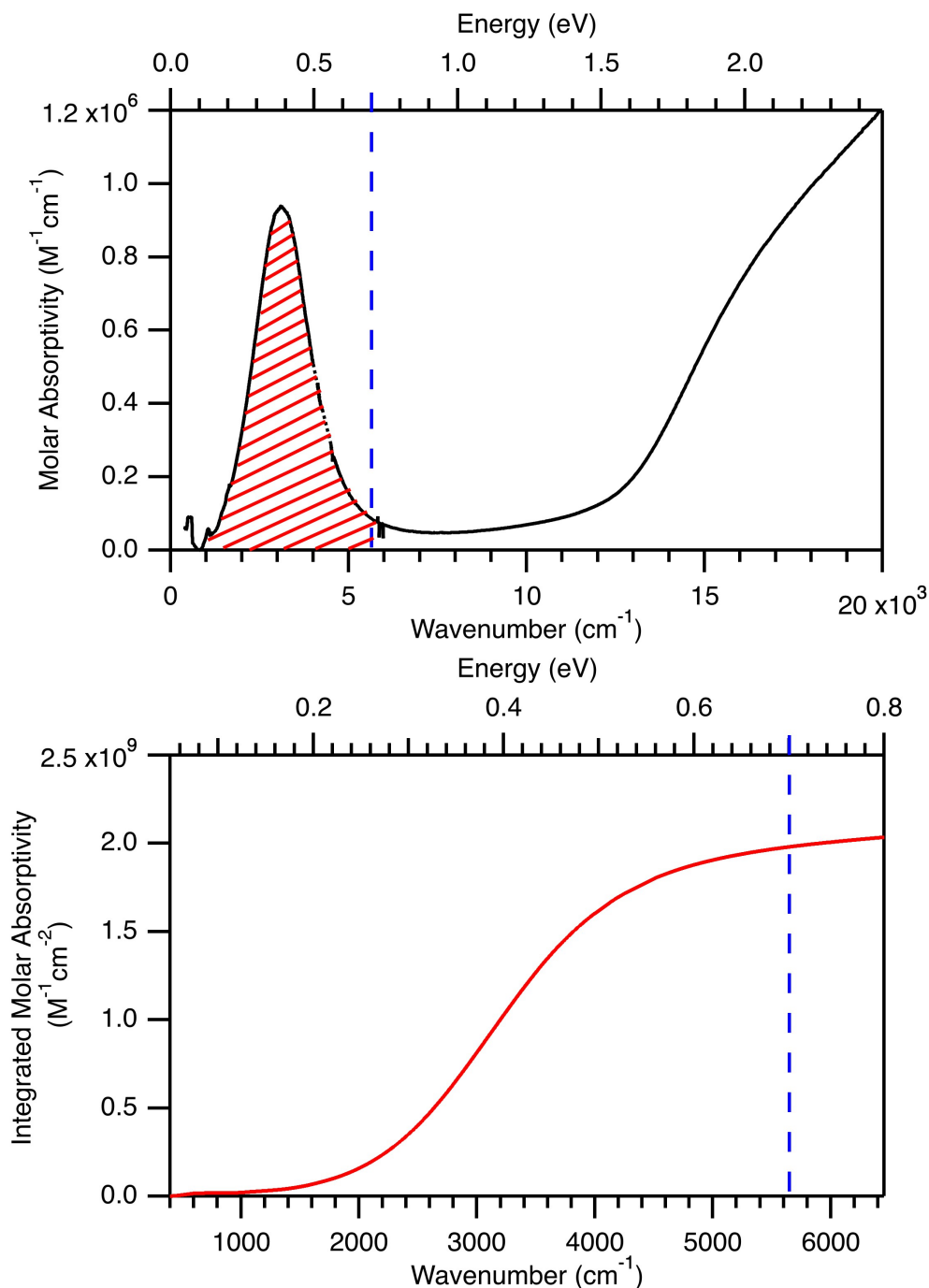


Figure 5.1. (a) Spectroscopic signatures of colloidal InN NCs ($d = 4.2 \text{ nm}$, $[\text{NC}] = 1.8 \text{ }\mu\text{M}$). The region of intense solvent overtone modes ($\sim 3800\text{--}4500 \text{ cm}^{-1}$) has been interpolated for clarity (dotted lines). The weak absorbance between 500 and 600 cm^{-1} arises partly from the BF_4^- ligands as well as the fundamental phonon spectrum of InN. The red area ($0\text{--}0.7 \text{ eV}$) was integrated in cm^{-1} in (b). The blue dashed line shows the end of integration.

Here, an estimate of the optical oscillator strength for 4.2 nm InN NCs can be obtained from the data in Figure 5.1 by integrating 0-0.7 eV which represents most of the intensity of the absorption cross-section. The optical oscillator strength, per electron, is obtained by:

$$f = \frac{1}{V \cdot N_e} \frac{4m_e \epsilon_0 c^2}{N_A \cdot e^2} 10 \ln 10 \int_0^\infty \epsilon(\bar{\nu}) d\bar{\nu} \quad (\text{eq. 5.1})$$

Where V is the volume of the sphere, N_e the free-charge density (i.e. the number of classical oscillators per unit volume), m_e the electron mass ($0.5 m_0$), ϵ_0 the permittivity of free space, c is the speed of light *in vacuo*, N_A Avogadro's number, e the elementary charge, ϵ the molar absorptivity and $\bar{\nu}$ the wavenumber. Note that all units are in SI, expect for ϵ in $\text{M}^{-1}\text{cm}^{-1}$ and $\bar{\nu}$ in cm^{-1} .

For the as-prepared 4.2 nm InN sample, the optical oscillator strength of LSPR is 0.14. As demonstrated in Chapter 2, the free electron density can be manipulated by the addition of redox species. In Figure 5.2(a), 4.2 nm InN NCs were treated with 0 - 12 equiv. NO^+ . The integrated IR transition is plotted as a function of the number of free electrons per NC in Figure 5.2(b). The slope of this line yields the integrated cross-section per electron per NC, which converts to an oscillator strength of 0.14, per electron, per NC.

Table 5.1 summarizes the optical oscillator strength of the IR absorbance of colloidal InN NCs with diameters range 4-9 nm. Interestingly, the LSPR oscillator strength is independent of size, with an average value of 0.14 ± 0.01 . Future work will attempt to simulate the LSPR in InN NCs to better understand the oscillator strength and its dependence on surrounding medium.

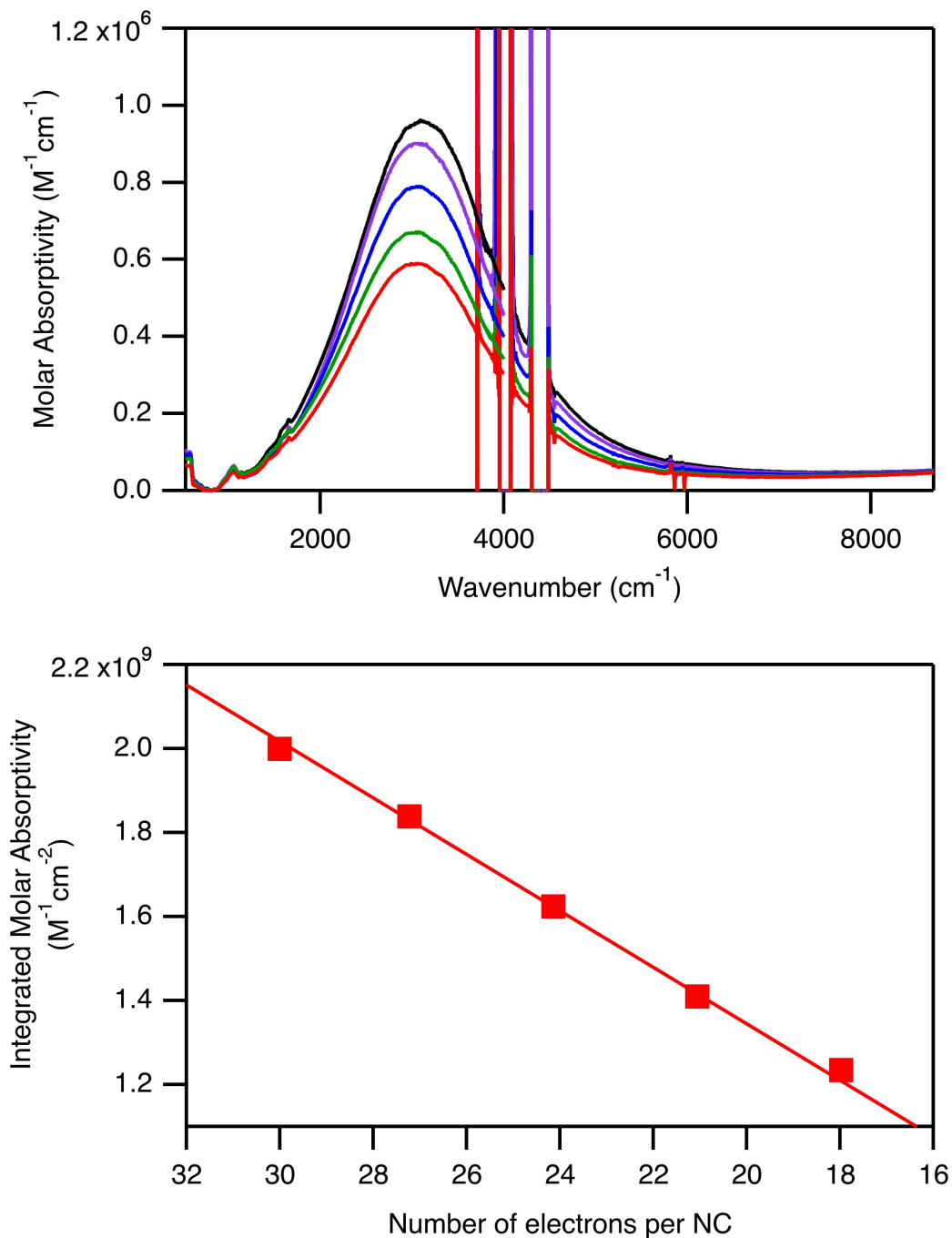


Figure 5.2. (a) Absorbance spectra of InN NCs ($d = 4.2$ nm, $[NC] = 1.8 \mu M$), with 0 – 12 equiv. NO^+ . (b) Integrated LSPR absorption (0-0.7 eV) as a function of the number of free electrons. The red line is a linear fitting $y = (6.72 \times 10^7 \pm 3.02 \times 10^5) x$. The slope yields the oscillator strength of free electrons to be 0.14.

Table 5.1. Optical oscillator strength of LSPR in colloidal InN NCs.

Size (nm)	3.9	4.2	4.5	5.2	5.7	6.4	8.7
Integration ($\times 10^9 \text{ M}^{-1}\text{cm}^{-2}$)	1.33	1.96	2.61	3.80	3.77	6.00	17.10
Number of free electrons per NC	22	30	38	62	66	98	255
Oscillator strength	0.13	0.14	0.15	0.13	0.12	0.13	0.14

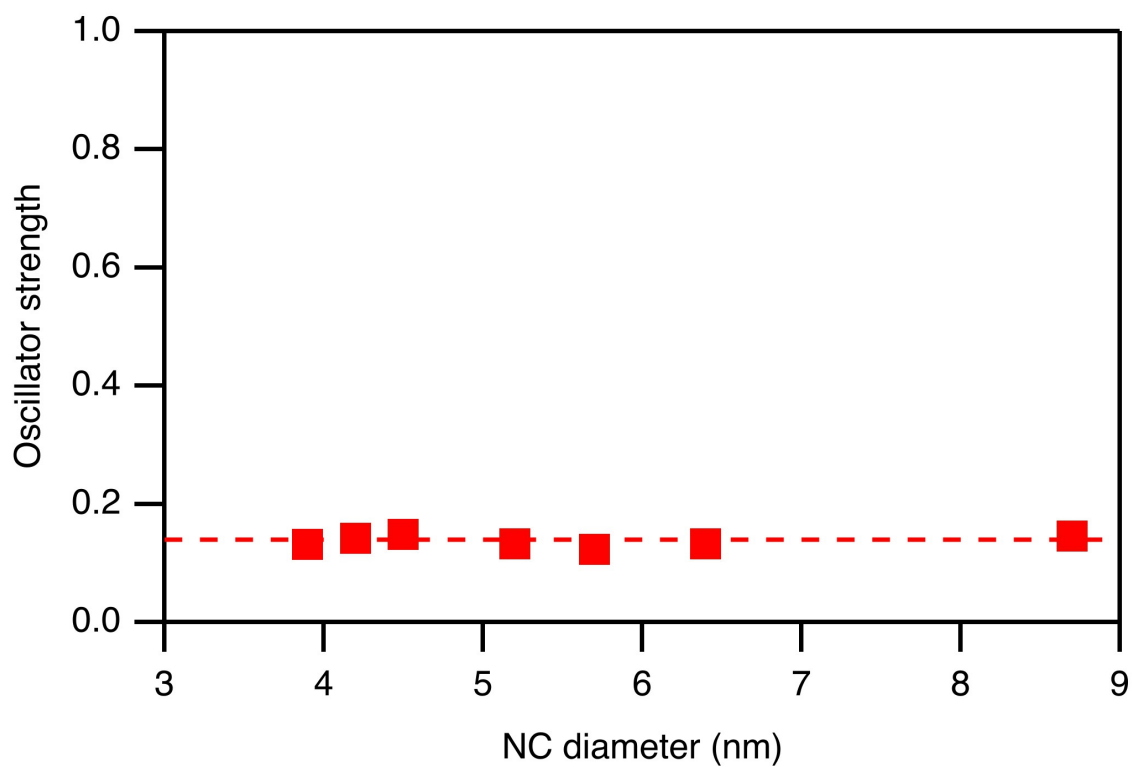


Figure 5.3. Size dependence of the oscillator strength of free carrier in colloidal InN NCs. The oscillator strength is 0.14 ± 0.01 .

5.5 Conclusions

We calculated the optical oscillator strength of the LSPR in InN NCs with the integrated cross-section. This value was evaluated to be 0.14 and appears to be size-independent. The value was underestimated due to the fact a part of LSPR overlaps with the interband transition. Work is in progress to simulate the LSPR feature which can better estimate the integrated cross-section. Future work to measure LSPR in various solvent can demonstrate the effect of surrounding medium on the optical oscillator strength and further understand the optical properties of heavily doped semiconductor NCs.

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Chapter 6: Charge Storage and Quantum Confinement Resilience in Colloidal InN Nanocrystals

6.1 Overview

Colloidal InN NCs are stable heavily-doped nanomaterials, with as-prepared electron densities around $\langle N_e \rangle \sim 7.4 \times 10^{20} \text{ cm}^{-3}$, independent of size, making these attractive candidates for charge storage applications at the nanoscale. Unfortunately, many fundamental quantities that inevitably control the behavior of charges in InN NCs, such as the band potentials or the energy of the Fermi Level, are currently unknown. Here, we report a direct and simple optical spectroscopic method that allows to quantify the charge storage capacity of colloidal InN nanocrystals. A size-independent, high volumetric capacitance $(69 \pm 4) \text{ F} \cdot \text{cm}^{-3}$ is found, underlying the potential of InN NCs as nanoscaled supercapacitors in energy harvesting and storage applications. Importantly, this study directly yields the band edge potentials and the charge-neutrality level of InN NCs as a function of NC size, positioning the conduction band potential of InN at about $(1.13 \pm 0.07) \text{ V vs. Fc}^{+/0}$ (ferrocenium/ferrocene), consistent with calculated estimates of bulk electron affinity values ($E_A \sim 6 \text{ eV}$), and the charge-neutrality level (i.e. the Fermi level of pristine InN NCs) at $(-0.59 \pm 0.03) \text{ V vs. Fc}^{+/0}$. The apparent lack of quantum confinement effect on the energy of the conduction band potential is discussed in terms of the nonparabolicity of the band dispersion and of confinement on size effect. The content in this chapter have been reported in the literature.¹

6.2 Introduction

Colloidal semiconductor NCs are often lauded for combining solid-state properties (small excitonic binding energies, electronic delocalization, large oscillator strengths, etc...) with the behavior typically associated with isolatable molecular species.²⁻⁴ This dual aspect of

NCs is most directly reflected in the much-celebrated quantum confinement behavior,^{2, 3} whereby many of the observables associated with the excited wavefunctions can be finely tuned by direct changes to the size and shape of the crystallite. But NCs also exhibit other properties that are not related, at least not directly, to size-dependent physics: for instance, their large surface-to-volume ratios make them attractive for heterogeneous applications relying on interfacial exchange or recognition processes.^{5, 6} Another very attractive characteristic unique to NCs is their ability to reversibly and substantially store electrical charge,⁷⁻²⁰ which stems from the large density of states coupled with the reduced Coulombic energetics (large dielectric constant) that are typical of inorganic semiconducting materials.

InN is an interesting material for charge storage purpose. In Chapter 3, we directly evaluated the free-carrier density of InN NCs and showed that this important quantity appears to be size-independent ($\langle N_e \rangle \sim 7.4 \times 10^{20} \text{ cm}^{-3}$),²¹ implying that single InN NCs can hold up dozens to hundreds of delocalized charge carriers depending on their size. We also demonstrated in Chapter 4 that the optical response of the delocalized carriers in InN NCs does not follow the classical (Drude) behavior often used to describe the localized surface plasmon resonance of NCs, which we attributed to the non-parabolic character of the conduction band dispersion of InN.²¹ However, other important fundamental quantities that necessarily control the charge storage behavior of InN NCs remain either ill-defined, or completely unknown. Here, we report on a simple and direct optical method that directly yields precise information on the Fermi level and on the chemical capacitance of InN NCs, which allows the conduction band edge potential of InN NCs to be quantitatively determined for the first time. Interestingly, we show that the

conduction band edge in InN hardly exhibits any sign of quantum confinement effects in spite of NC sizes that are clearly below the semiconductor Bohr radius. This resilience to quantum confinement is shown to be due to nonparabolic dispersion effects that force the effective mass of the conduction band electron to increase proportionally with decreasing NC size, which strongly mitigates the increase in kinetic energy typically observed in nanoscale semiconductors.

6.3 Experimental Methods

A. Chemicals

Dimethylferrocene (Me_2FeCp_2 , Sigma Aldrich, 97%), decamethylferrocene ($\text{Me}_{10}\text{FeCp}_2$, Sigma Aldrich, 97%), ferrocene (Sigma Aldrich, 98%), copper (II) triflate (CuTf_2 , Sigma Aldrich, 98%), Tetrabutylammonium hexafluorophosphate (TBAPF_6 , Sigma Aldrich, $\geq 99\%$), p-benzoquinone (Sigma Aldrich, $\geq 98\%$), diethyl ether (Sigma Aldrich, $\geq 99\%$), tetrafluoroboric acid diethyl ether complex ($\text{HBF}_4 \cdot \text{OEt}_2$, Sigma Aldrich, 51-57% HBF_4 in diethyl ether), diethyl ether (Sigma Aldrich, $\geq 99\%$) and acetone (Fisher Chemical) were used as received. Other chemicals were described in Chapter 2, Section 2.3.1.

B. InN NC Synthesis

The synthesis of InN NCs, the protocol of purification and ligand exchange were described in Chapter 2, section 2.3.1. The precursors were heated to the desired temperature for a certain amount of time to control the size of InN NCs as listed in Table 6.1.

Table 6.1. Average size of InN NCs at varying reaction temperatures and times.

Temperature (°C)	250	250	220
Time (h)	0.5	3	12
Diameter (nm)	3.9	6.0	8.7
Standard dev. (nm)	0.5	1.0	1.7

C. Synthesis of Substituted Ferrocenium Oxidants

Dimethylferrocenium tetrafluoroborate (Me_2FcBF_4) and decamethylferrocenium tetrafluoroborate ($\text{Me}_{10}\text{FcBF}_4$) were synthesized through a previously published method.²² $\text{HBF}_4 \cdot \text{OEt}_2$ (3.7 ml, 26.9 mmol) was added to a solution of *p*-benzoquinone (0.70 g, 6.5 mmol) in diethyl ether (20 ml) at room temperature, under stirring. A solution of Me_2FeCp_2 (2.78 g, 13 mmol) in diethyl ether (40 ml) was then mixed in the former solution, which led to the precipitation of a blue solid. The mixture was stirred for 10 min, and then allowed to stand for another 10 min. The blue solid was removed by filtration, washed with diethyl ether (2×10 ml), and dried in air. The crude product was purified by dissolution in acetone (100 ml), filtration, and recrystallization by addition of diethyl ether (150 ml) to give a fine blue powder. The final product was measured by UV-vis absorbance spectroscopy, H-NMR, F-NMR, CV for identification. The synthesis of decamethylferrocenium was done similarly but using $\text{Me}_{10}\text{FeCp}_2$ instead.

D. Characterization Methods

TEM, XRD, UV-vis-NIR spectra, FTIR and ICP-OES were all performed as in Chapter 2, section 2.3.2 and Chapter 3, section 3.3.2.

E. Absorption Spectra

i-InN NC suspension was added with desired volume of a solution of redox species in a

glass vial in glassbox. The vial is sealed and let to stand for overnight before measurement. 400 to 2700 nm was measured with *i*-InN suspension in a sealed quartz cuvette with UV-vis-NIR spectrometer. 4000 to 400 cm^{-1} was measured with FTIR. (More details in Chapter 2, section 2.3.2.) The UV-vis-NIR and FTIR spectra for one same sample were connected by matching the overlapping region (4000 – 3704 cm^{-1}).

F. Cyclic Voltammetry

Cyclic voltammograms (CV) of each oxidant was performed on a Wavedriver 20 Bipotentiostat/Galvanostat from Pine research instruments. The solution for each CV was as follows: 0.1 M TBAPF₆ with 1-10 mM oxidant (2 mM for Me₁₀FcBF₄, 1 mM for Me₂FcBF₄, 2 mM FcBF₄, 4mM for CuTf₂, and 10 mM for NOBF₄) in 5 ml ACN. All measurements were prepared in a N₂ glovebox and placed into a sealed cuvette. The CVs were measured using a three-electrode cell with a Pt wire (Sigma Alrdich, 0.5 mm diameter) working electrode with a surface area of 0.19 mm², a Pt wire as a counter electrode, and a Ag/AgCl (edag) reference electrode. The potentials were referenced to the ferrocene/ferrocenium redox couple. The scan rate of each CV was varied between 100-900 mV/s and was scanned from positive to negative potentials.

6.4 Results and Analysis

6.4.1. Oxidation of InN NCs

As described previously and shown in Figure 6.1, InN NCs are characterized by two main spectral features, both consistent with the presence of a large number of free carriers in the CB: a localized surface plasmon resonance (LSPR) peak in the infrared region and a Burstein-Moss shifted bandgap transition in the visible.^{21, 23} The chemical oxidation of the

NCs directly reduces both the LSPR intensity and the extent of the Burstein-Moss shift, as expected for decreases in the stored electron density. We previously showed that the extraction of these free carriers from InN NCs depends linearly on the concentration of added oxidant, which allowed for a direct quantification of the average carrier density, $\langle N_e \rangle = (7.4 \pm 0.4) \times 10^{20} \text{ cm}^{-3}$, a value which was found to be independent of NC size, at least in the 4-9 nm diameter range – that is, the total number of free electrons per NC scales directly with the cube of the NC radius.²¹

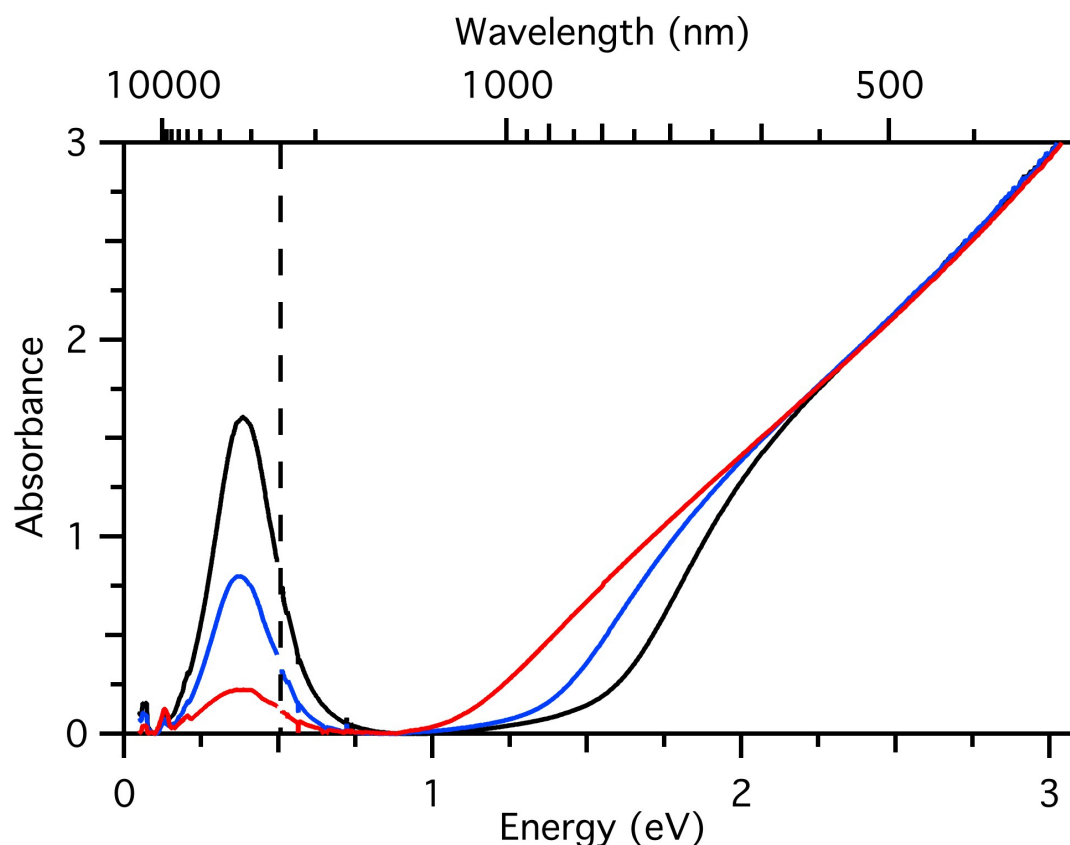


Figure 6.1. Absorbance spectra of InN NCs ($d = 6.0 \text{ nm}$; $[\text{NC}] = 0.7 \text{ }\mu\text{M}$ in ACN). As-prepared (black) and with 40 equivalents (blue) and 5000 equivalents (red) of NOBF_4 added per NC. The vertical dashed line shows the transition between the FTIR-acquired data (spin-coated on Si window) and the NIR-vis-UV data.

The oxidation of the NCs was also shown to diverge from linearity beyond extraction of about 40% of total number of charge carriers – for the 6.0 nm diameter InN NCs sample

shown in Figure 6.2, this occurs around 40 equivalents of NOBF_4 per NC. Although the data appears to plateau beyond that point, it is clear that InN NCs can still be further oxidized, albeit with a much-reduced efficiency, reaching an actual plateau around thousands of equivalents of oxidant per NC.

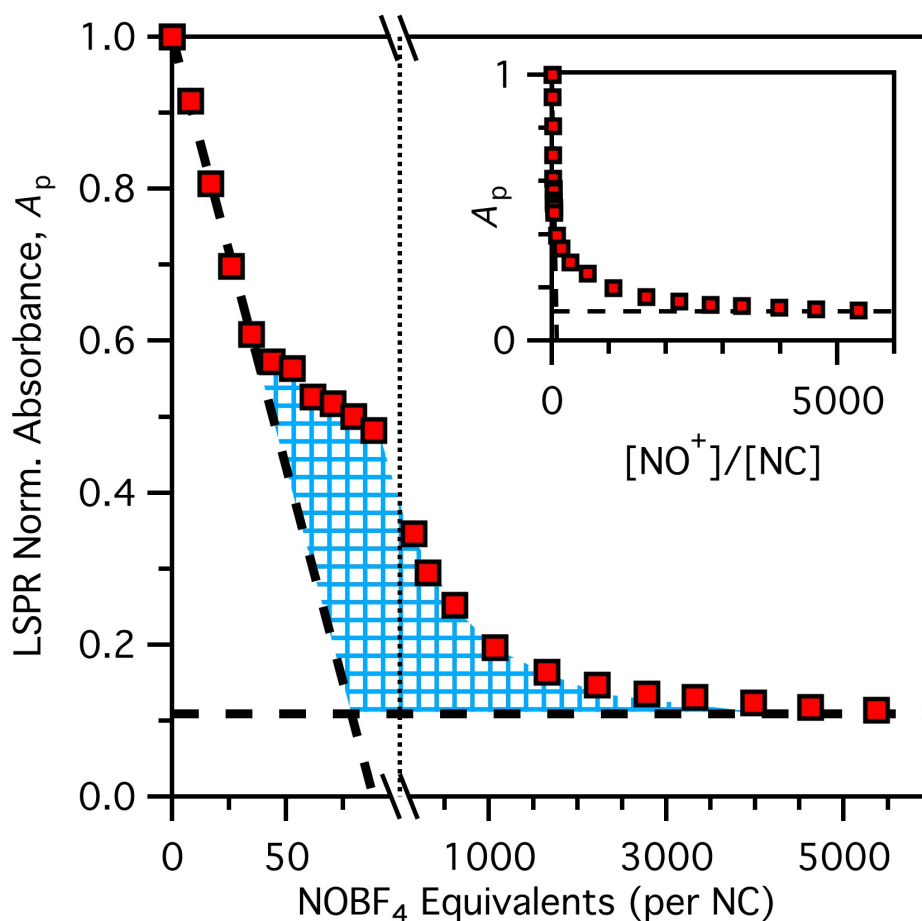


Figure 6.2. The reaction of InN NCs ($d = 6.0$ nm) with nitrosonium (NO^+) leads to a reduction of the LSPR peak absorbance (normalized to peak absorbance of as-prepared InN NCs here). The LSPR peak decreases linearly at first, extrapolating to ~ 84 e^-/NC . The non-linear behavior reaches a plateau around ~ 3000 NO^+ equivalents, corresponding to $A_{\text{plasmon}} \sim 0.1$. Note the change in scale of the horizontal axis, used to emphasize the behavior in the onset region. Inset: Same data as main panel, but without the change in scaling.

As we showed previously,²¹ the number of free carriers extracted from each InN NCs (Δn) by a given amount of added oxidant per NC (n_{ox}) can be obtained from the data presented in Figure 6.1 by:

$$\Delta n(n_{ox}) = [1 - A_p(n_{ox})] n_{tot} \quad \text{eq. 6.1}$$

where A_p is the plasmon absorbance, normalized so that $A_p(n_{ox} = 0) = 1$, and n_{tot} is the total number of carrier per NC, directly obtained from the product of the carrier density and the NC volume V_{NC} :

$$n_{tot} = \langle N_e \rangle V_{NC} \quad \text{eq. 6.2}$$

Following eq. 6.1, the observed plateau in the LSPR absorbance at high concentrations of oxidants can be interpreted directly as a “maximum” number of charge carriers that a given chemical oxidant can extract from each NC, which we label here as Δn_{max} . As we show below, under this definition, Δn_{max} is not a well-defined quantity (the observed plateau is only an apparent one), but in practice, the rate of change of the plasmon absorbance per equivalent of oxidant in this regime is small enough that Δn_{max} is still a useful metric to quantify the charge storage/extraction behavior. Independent of these considerations, the quantity Δn_{max} nevertheless exhibits two main features that will be discussed in further detail here: 1) Δn_{max} depends strongly on the nature of the chemical oxidant used, with stronger oxidants leading to larger values of Δn_{max} ; 2) for a given chemical oxidant, the ratio $\Delta n_{max}/n_{tot}$ is independent of NC size.

6.4.2. Chemical capacitance of InN NCs

The first point above can be directly seen in the data plotted in Figure 6.3, which shows the oxidation of a 6 nm InN NC sample using four different chemical oxidants of varying

redox potential. The data of the nitrosonium tetrafluoroborate (NO^+ , $E^0 = +0.84 \text{ V vs Fc}^{+/0}$) shown in Figure 6.2 is reported alongside that of 1,1'-dimethylferrocenium tetrafluoroborate (Me_2Fc^+ , $E^0 = -0.11 \text{ V vs Fc}^{+/0}$), ferrocenium tetrafluoroborate (Fc^+ , $E^0 = 0 \text{ V vs Fc}^{+/0}$), and copper(II) triflate (CuTf_2 , $E^0 = +0.67 \text{ V vs Fc}^{+/0}$), see SI for further details.

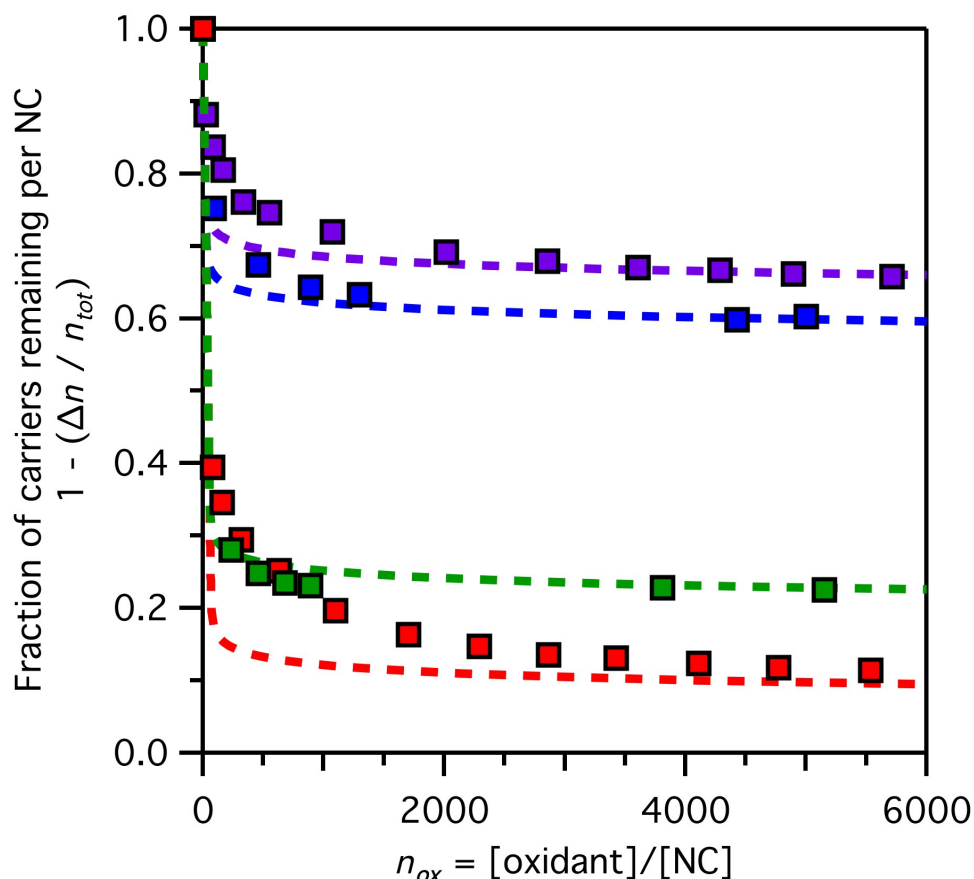


Figure 6.3. Change of the carrier density following the oxidation of InN NCs ($d = 6.0 \text{ nm}$), for four different chemical oxidants. Red: nitrosonium (NO^+); Green: copper(II) triflate (CuTf_2); Blue: ferrocenium (Fc^+); Purple: 1,1'-dimethylferrocenium (Me_2Fc^+). The dashed lines represent fits of the data using the equilibrium relationship given by eq. 6.7.

Whereas all four oxidants show the same general behavior arising from progressive charge carrier extraction, it is clear that stronger oxidants extract more carriers per NC before reaching the pseudo-plateau region, with $\Delta n_{max} \sim 0.3 n_{tot}$ for Me_2Fc^+ (the weakest

oxidant of the series), compared to $\Delta n_{max} \sim 0.9 n_{tot}$ for NO^+ (the strongest oxidant of the series).

The redox response shown in Figure 6.3 can be modeled assuming direct equilibration between the charge carriers stored in the InN NCs and the added oxidant, whereby the Fermi level of the NCs is matched to the chemical potential of the redox couple:

$$E_F(\Delta n) = E_{\text{ox/red}} \quad \text{eq. 6.3}$$

where the labels ox/red refer to the oxidized /reduced forms of the redox couple used; the solution potential $E_{\text{ox/red}}$ is directly obtained from Nernst equation:

$$E_{\text{ox/red}} = E_{\text{ox/red}}^0 + \frac{RT}{zF} \ln \frac{[\text{ox}]}{[\text{red}]} \quad \text{eq. 6.4}$$

with T the temperature, R the ideal gas constant, z the number of electrons involved in the redox process ($z = 1$ for each of the oxidants employed here) and F is Faraday's constant. The NCs Fermi level is related to the intrinsic capacitance, C_{InN} , of these nanostructures:

$$E_F(\Delta n) = E_F(0) + \frac{\Delta n \cdot e}{C_{\text{InN}}} \quad \text{eq. 6.5}$$

where $E_F(0)$ is the Fermi level of unoxidized InN NCs and e is the elementary charge. With each addition of oxidants, the solution potential is made progressively more positive – i.e., the ratio $[\text{ox}]/[\text{red}]$, initially much smaller than one due to quantitative conversion of each equivalent of oxidant to its reduced form, progressively increases to larger values. Pushing the solution potential beyond the standard potential value of the redox couple (that is, for ratios $[\text{ox}]/[\text{red}] > 1$) evidently requires large amounts of oxidants for progressively smaller gains in potential (the Nernst behavior of one-electron redox processes leads to increases in the solution of potential of 59 mV for every factor of 10

increase of the ratio [ox]/[red]), which is the origin of the observed pseudo-plateau. The ratio [ox]/[red] can be related to the titrated amount of oxidants (n_{ox} , the number of equivalents of oxidants added per NC) and the number of equivalents of electrons extracted per NC (Δn) by:

$$\frac{[\text{ox}]}{[\text{red}]} = \frac{z \cdot n_{ox} - \Delta n}{\Delta n} \quad \text{eq. 6.6}$$

Combining eqs. (6.3)-(6.5) yields

$$n_{ox} = \frac{\Delta n}{z} \left\{ 1 + e^{\left(E_F(0) - E_{ox/red}^0 + \frac{\Delta n \cdot e}{C_{InN}} \right) \frac{zF}{RT}} \right\} \quad \text{eq. 6.7}$$

which relates the number of electron extracted and the amount of oxidant added per NC. Eq. (6.7) can be used to model the data shown in Figure 6.3, under the assumption that the capacitance of InN NCs remains constant throughout the whole oxidation range. The four oxidative titration curves shown in Figure 6.3 were global-fitted to eq. (6.7), leaving only C_{InN} and $E_F(0)$ as floating parameters (but fixed to a unique value for all four datasets), and the known values for n_{tot} (Table 6.2) and $E_{ox/red}^0$ for each oxidant (see Appendix). Generally, the model agrees very well with the observed data: the initial drop of the absorbance vs. added oxidant and the plateau region are very well reproduced for $E_F = (-0.58 \pm 0.03) \text{ V vs Fc}^{+/0}$ and $C_{InN} = (7.6 \pm 0.5) \text{ aF}$, a capacitance value which corresponds to a charging potential of about 21 mV per carrier stored in the CB. Importantly, this analysis readily supports the *a priori* assumption that the capacitance of InN NC is independent of the degree of oxidation of the NCs (i.e., C_{InN} is a constant that does not depend on the number of charge carriers stored in a specific NC size); as we show below, this conclusion leads to significant implications regarding the energetics of the charge storage in InN NCs (vide infra). The intermediate regime observed most notably for the

NO⁺ oxidation data (Figs. 6.2 and 6.3) is notably not reproduced by the model. This behavior could indicate the presence of a reservoir of localized charges which are at equilibrium with the delocalized carriers probed here, although the fact that the effect is not commensurate for the different oxidants clearly indicates that other factors must also play a role. For instance, the oxidation data with CuTf₂ shows little to no deviation from the model, even though its saturation level is clearly below the point where the NO⁺ deviates from the model, suggesting that kinetic effects likely also determine the behavior of each oxidant. A full characterization of such effects is clearly beyond the scope of this study, although it is important to note here that the entire analysis relies solely on the saturation ratios ($\Delta n_{max}/n_{tot}$), which are independent of the degree of adequation between the model and the data in the intermediate regime. In fact, with this analysis in hand, the quantity Δn_{max} can actually be redefined as the number of charge carriers extracted required to bring the NC Fermi level at the standard potential of the chemical oxidant used:

$$E_F(\Delta n_{max}) = E_{ox/red}^0 \quad \text{eq. 6.8}$$

which is in effect analogous to the definition of the equivalent point in a potentiometric titration; this definition has the advantage that the quantity Δn_{max} is now firmly rooted in the thermodynamic equilibrium of charge storage/extraction of InN NCs, and will be used in the remainder of this study.

6.4.3 Band potentials and size effects in InN NCs

A second important feature exhibited by the quantity Δn_{max} is its dependence on the NC size, which is reported in Figure 6.4.

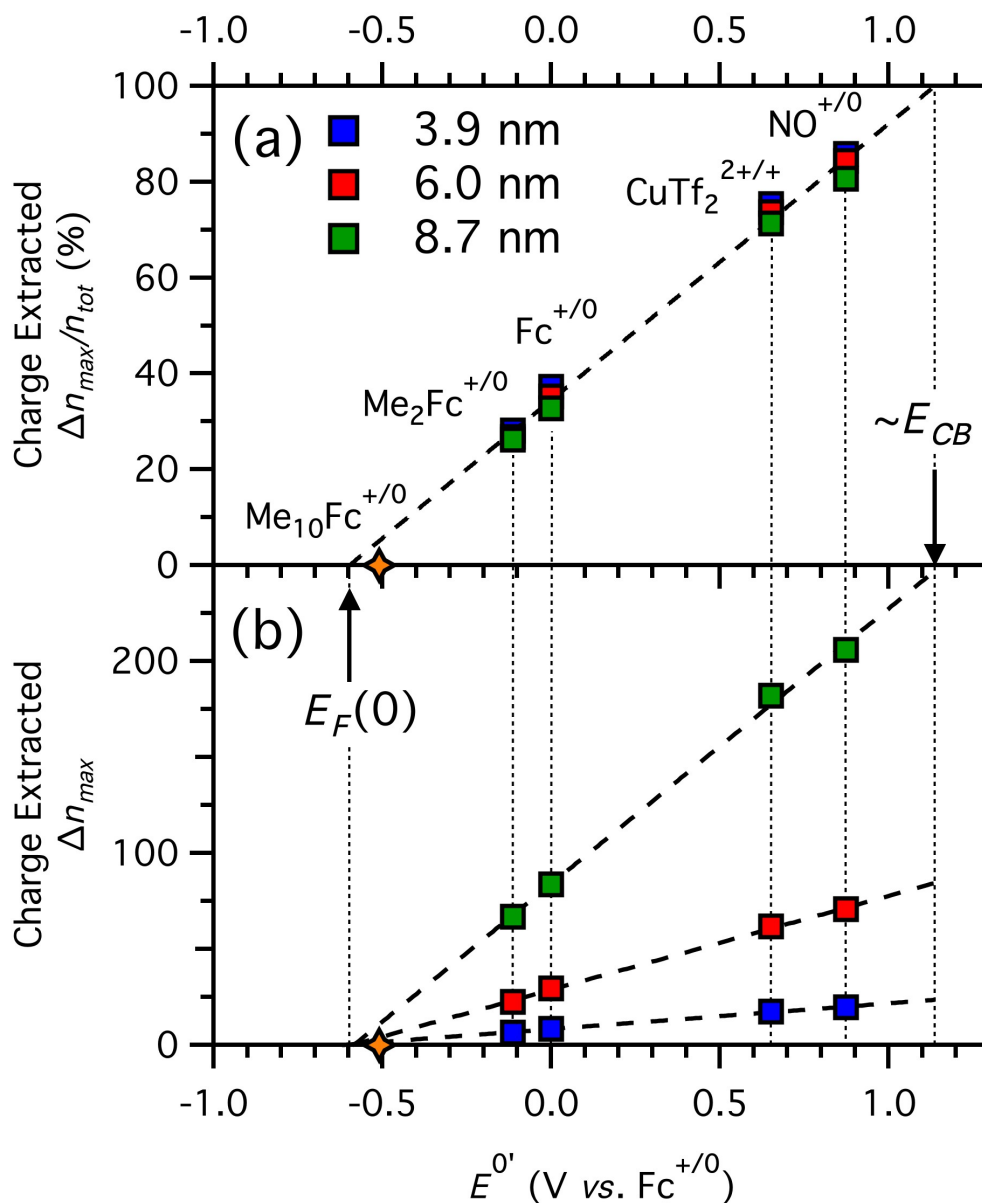


Figure 6.4. Oxidation of InN NCs using different chemical oxidants. (a) Maximum number of charge carriers extracted for 3.9 nm (blue squares), 6.0 nm (green squares) and 8.7 nm (red squares) InN NCs, as a fraction of the total number of free carriers per NC. The oxidation of InN NCs exhibits a size-independent linear variation of the electron density vs oxidation potential ($\sim 0.05\%$ density change per mV) over the potential range studied. (b) Same data as above, but expressed in total number of free carriers extracted, yielding a volumetrically-scaled capacitance. The data point for $\text{Me}_{10}\text{Fc}^+$ is indicated for reference only and was not included in the global fit to extrapolate the position of the charge-neutrality level, $E_F(0)$.

A striking observation is that $\Delta n_{max}/n_{tot}$, the number of carriers that each oxidant can extract, expressed as a fraction of the total number of free carriers stored per NC, is independent of size (see Figure 6.4(a)). Given that the total number of charge carrier per NC is directly proportional to the NC volume (that is, the charge density of InN NCs is a size-independent quantity), this observation implies a constant volumetric capacitance for InN, that is, a fixed amount of potential energy required to store a unit charge per unit volume. From the data presented in Figure 6.4(a), the volumetric capacitance of InN NCs (averaged over all three sizes) is $(69 \pm 4) \text{ F}\cdot\text{cm}^{-3}$. Such large capacitance values are typically associated with supercapacitors,^{19, 24, 25} although it is important to note here that the potential energy is not stored in the electric field of a dielectric (classical capacitive storage), but rather as electrochemical potential (pseudocapacitance).

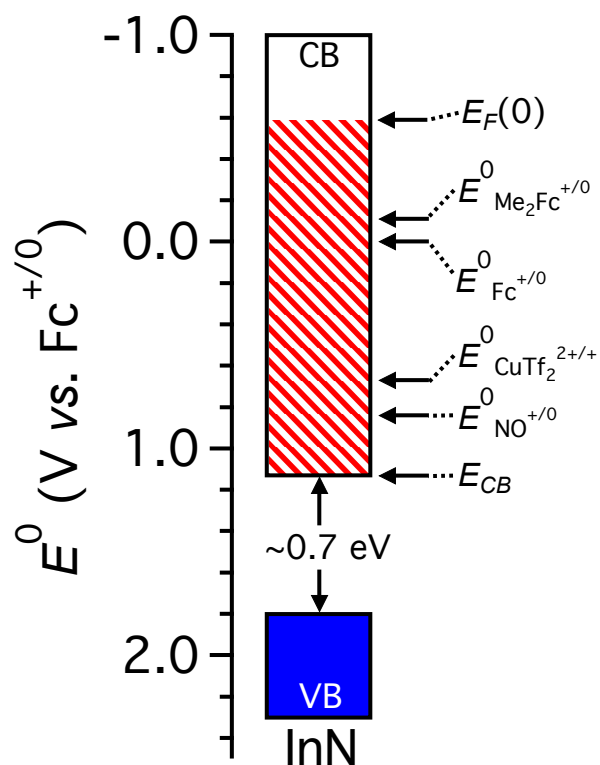
Table 6.2. Capacitance values of InN NCs.

NC diameter (nm)	n_{tot}	$E_F(0)$ (V vs $\text{Fc}^{+/0}$)	C_{InN} ($\text{F}\cdot\text{cm}^{-3}$)	C_{InN} (aF)	C_{InN} (e^-/V)
3.9 ± 0.6	22 ± 7	-0.61 ± 0.04	69 ± 4	2.1 ± 0.3	13 ± 2
6.0 ± 0.9	70 ± 40	-0.58 ± 0.03	69 ± 4	7.6 ± 0.5	47 ± 3
8.7 ± 1.7	220 ± 80	-0.58 ± 0.03	66 ± 4	19.8 ± 0.3	124 ± 2

Table 6.2 summarizes the data obtained from the analysis of Figure 6.4, and shows that the position of the Fermi level of as-prepared InN NCs is also independent of size, $E_F(0) = (-0.60 \pm 0.03) \text{ V vs Fc}^{+/0}$. To verify this value, we investigated the oxidative behavior of decamethylferrocenium ($\text{Me}_{10}\text{Fc}^+$, $E^0 = -0.51 \text{ V vs Fc}^{+/0}$); we could not detect any change to the LSPR intensity, even for ratios of $\text{Me}_{10}\text{Fc}^+:\text{NC}$ as high as 6400:1 (SI), which is consistent with the value of $E_F(0)$. We note here that the estimate of $E_F(0)$ is predicated

upon the assumption that the linear (constant capacitance) behavior observed in Figure 6.4 applies all the way to the charge-neutrality level and as such should be taken as an upper-bound value.

Importantly, if we assume that the charge storage obeys the same general behavior described above over the whole CB, then an estimate for the CB potential can also be made by extrapolating the charge extraction to completion ($\Delta n/n_{tot} = 1$), which yields $E_{CB} = (1.13 \pm 0.07) \text{ V vs Fc}^{+/0}$. This value is about half a volt more positive than the calculated bulk CB potential,²⁶ $E_{CB} = 5.7 \text{ V vs vacuum} \sim 1.2 \text{ vs SHE} \sim 0.6 \text{ vs Fc}^{+/0}$, although it is important to note that such calculated values do not account for surface effects that can modulate the absolute band potentials by as much as 1 V.²⁷



Scheme 6.1. Fermi level and band edge potentials of InN NCs.

It is interesting to note that this analysis does not reveal any sign of quantum confinement effects on the energy of the CB: within the accuracy of the analysis presented above, all three sizes all converge to the same E_{CB} value in Figure 6.4(a) and Table 6.1. Assuming that the valence band (VB) is equally unperturbed by size-dependent effects, we can estimate its position at around 1.8 V vs $\text{Fc}^{+/0}$, using the bulk bandgap value of 0.7 eV. The energetics of InN are reported in Scheme 1; to the best of our knowledge, these are the first direct measurements of these fundamental values for InN NCs.

6.4.4 Delocalization without Confinement: Quantum Confinement Resilience

The fact that we could not observe size-dependent shifts of the energy of the band is perhaps suprising on first sight. Indeed, the relatively small effective masses associated with the carriers of InN (Table 6.3), along with dielectric constants that are practically identical to those observed for II-VI materials, would be expected to give rise to rather strong quantum confinement effects.

Table 6.3. Bulk Optical and Electronic Properties of InN.

Parameter	Value	Ref
bulk bandgap, $E_g(\infty)$	0.69 eV	28-30
static dielectric constant, ϵ_s	10.5	31, 32
optical dielectric constant, ϵ_∞	6.7	31-33
electron effective mass, m_e ^a	$(0.055 \pm 0.002) m_0$	30, 34-36
heavy-hole effective mass, m_h	$(0.59 \pm 0.06) m_0$	30, 37, 38
excitonic reduced mass, m_{exc}	$(0.05 \pm 0.01) m_0$	—
Electron group velocity	$7.7 \times 10^5 \text{ m s}^{-1}$	39

^a at the Γ -point; the electron effective mass varies strongly across the CB.

Quantum confinement effects generally occur for NC sizes that are on the same order of magnitude (or smaller) than the dimension of the excitonic Bohr radius, a_{exc} , given by:⁴⁰

$$a_{exc} = \frac{\varepsilon^*}{m_{exc}/m_0} a_0 \quad \text{eq. 6.9}$$

where ε^* is an effective dielectric constant typically taken as the optical dielectric constant,⁴⁰ m_{exc} is the excitonic reduced mass (Table 6.2), m_0 is the mass of the free electron, and a_0 is the hydrogenic Bohr radius. Using the data in Table 6.2, the InN excitonic Bohr radius is around 7 nm – clearly larger than every sample studied here (NC radii between 2.0 and 4.4 nm). Strictly speaking the excitonic Bohr radius reports on confinement effects arising from both the valence-band hole and conduction-band electron, but given that the effective electron mass is almost one order of magnitude smaller than that of the hole in InN (Table 6.2), most of the confinement should arise as kinetic energy of the electron.

In the simplest approximation, the kinetic energy of the CB for a given NC radius r_{NC} is given by:⁴¹

$$E_{CB} = \frac{\hbar^2 k_{NC}^2}{2m_e} \quad \text{eq. 6.10}$$

where m_e is the CB-electron effective mass and k_{NC} is the effective wavenumber of the lowest-energy electron level. In the “infinite potential well” limit where the electronic wavefunction goes strictly to zero at the NC surface, the wavenumber is related to the NC radius (r_{NC}) by:

$$k_{NC} = \frac{\pi}{r_{NC}} \quad \text{eq. 6.11}$$

Using the known effective mass for the CB in eq. 6.9 yields confinement-induced shifts

larger than 1.3 eV over the size range studied here ($4.0 \text{ nm} < 2r_{\text{NC}} < 8.7 \text{ nm}$), as represented in Figure 6.5. This simple confinement model is well known to strongly overestimate confinement energies for the smallest NC radii, and a fairer approximation for the quantum-confinement is obtained by allowing the charge to tunnel outside the radius of the NC, which is obtained in Fig. 6.5 by putting a reasonable potential barrier of $V_0 = 5 \text{ eV}$ (see Appendix for further details). This reduces the size-dependence of the CB energy, although far from within the empirically-observed range, indicated by the shaded box in Fig. 6.5. The large effect observed from reducing the barrier height at the surface is due to the very small effective mass of the CB electron (Table 6.3), which induces strong tunnelling outside the surface, and subsequently lowers the kinetic energy of confinement.

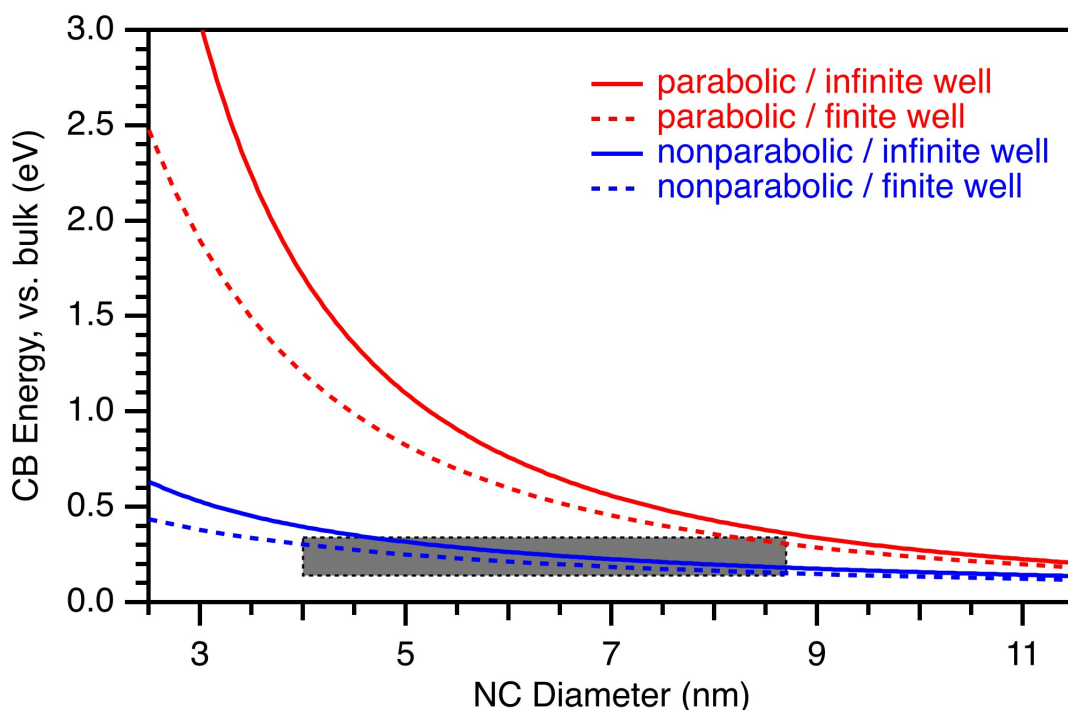


Figure 6.5. Quantum confinement effects on the energy of the conduction band (CB), calculated for both parabolic (red) and non-parabolic (blue) dispersions, using the electronic parameters of bulk InN listed in Table 6.3. Straight lines: infinite spherical potential well, dashed lines: finite spherical potential well ($V_0 = 5 \text{ eV}$). The shaded box represents the range of NC sizes studied here (4.0-8.7 nm) and the accuracy of the experimental value of E_{CB} ($\pm 0.1 \text{ eV}$).

Clearly, the behavior of InN NCs is not well-described by the conventional behavior that has proven successful at describing quantum confinement of II-VI semiconductors. This peculiar feature of InN can be assigned to the dispersion of the CB, which we previously showed to be responsible for the unusual frequency response of the LSPR of InN NCs.²¹ The CB of InN is strongly non-parabolic over a large range of the reduced Brillouin zone;^{21, 30, 39, 42} an important consequence of this property is that the effective mass can not be described by its value at the band-edge (which is the value listed in Table 6.2 and used in Figure 6.5), but rather varies strongly and continuously across the CB:

$$m_e(k) = \frac{\hbar k}{v_g} \quad \text{eq. 6.12}$$

where k is a specific wavevector in the reduced Brillouin zone and v_g is the CB electron group velocity:

$$v_g = \frac{1}{\hbar} \frac{dE_{CB}}{dk} \quad \text{eq. 6.13}$$

Because of the linear dispersion of its CB, the group velocity is nearly constant over much of the CB in InN; from the band structure calculated by Carrier and Wei, $v_g = 7.7 \times 10^5 \text{ m}\cdot\text{s}^{-1}$.³⁹ As described by eq. (6.10), the electronic wavefunctions associated with smaller NCs can be conceived as wavepackets of different k values, with the smallest k values allowed being defined by the reciprocal of the NC radius. The effective mass of the CB electron thus gets progressively larger the smaller the volume of confinement, with the direct consequence that the kinetic energy term associated with the motion of the CB electron in InN does not directly scale with the inverse square of the NC radius as suggested by eq. (6.9), but rather as:

$$E_{CB}(r_{NC}) = \frac{\hbar\pi v_g}{2r_{NC}} \quad \text{eq. 6.14}$$

This behavior is represented in Figure 6.5, showing that in effect, size effects in InN NCs are mitigated compared to systems where the constant effective-mass approximation holds well. This peculiar feature distinguishes InN from other traditional materials, but it is important to note here that the reduced impact of confinement does not imply that charge carriers in InN are localized: electrons are strongly delocalized over the whole volume of the NC (giving rise, among other things, to the strong LSPR signature seen in the infrared), but any increase in electronic quasimomentum due to spatial confinement is compensated, nearly equally, by a concomittent increase in effective mass, so that overall the kinetic energy associated with confinement remains largely unaffected. Although the model presented here is necessarily too simple to account precisely for the details of the electronic structure of NCs, it likely captures well the essence of this “resilience against confinement” effect, which constitutes an interesting manifestation of the impact that nonparabolic dispersions can have on electronic properties at the nanoscale.

6.5 Conclusions

We have shown that the free carrier density of InN NCs can be modulated directly and specifically by proper choice of the redox potential of the chemical oxidant. The volumetric capacitance of colloidal InN NCs was determined to be $(69 \pm 4) \text{ F}\cdot\text{cm}^{-3}$, independent of size, illustrating the stability of delocalized charges in InN. For the first time, the Fermi level and CB potential of InN NCs were estimated. Furthermore, it was seen that the position of the CB does not exhibit the size-dependent expected from the dimension of

the excitonic Bohr radius. This “quantum confinement resilience” is attributed to the nonparabolic CB dispersion, which results in a continuous change in the effective mass of the electrons in the CB, mitigating quantum confinement effects. This quantum confinement resilience, which should apply to other semiconductor nanomaterials with strongly nonparabolic dispersions, adds a new dimension to the physics and chemistry of semiconductor NCs that has not been exploited up to this point.

APPENDIX

SI 6.1. Synthesis of Dimethylferrocenium Tetrafluoroborate

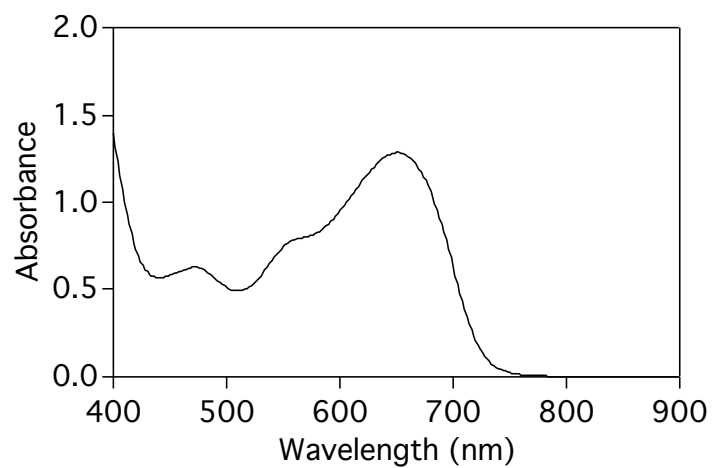


Figure SI 6.1. Absorbance spectra of 4mM Me_2FcBF_4 in ACN. The absorbance feature is consistent with published result.⁴³

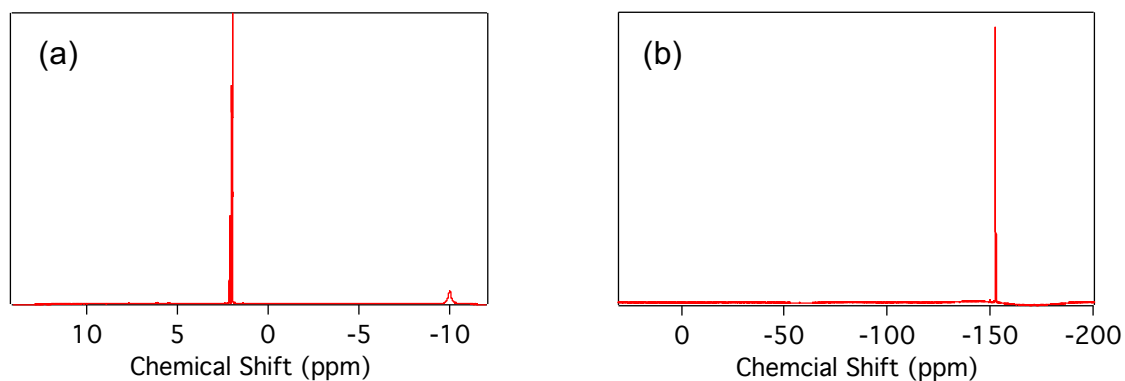


Figure SI 6.2. (a) ^1H NMR spectra (b) ^{19}F NMR spectra of Me_2FcBF_4 in *d*-acetonitrile.

SI 6.2. Synthesis of Decamethylferrocenium Tetrafluoroborate

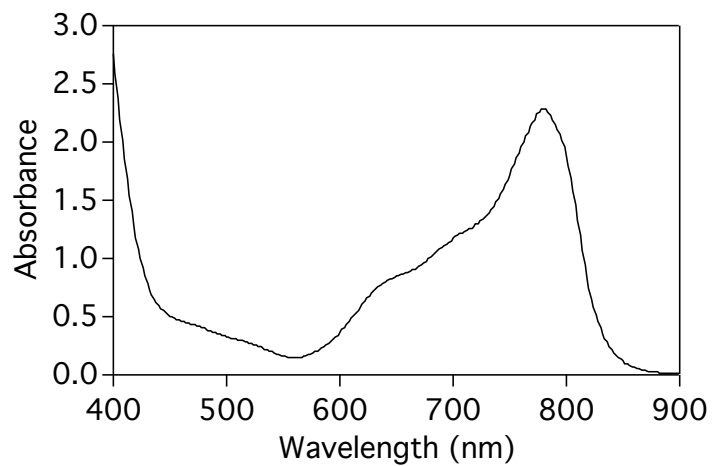


Figure SI 6.3. Absorbance spectra of 4mM $\text{Me}_{10}\text{FcBF}_4$ in ACN. The absorbance feature is consistent with published result.⁴⁴

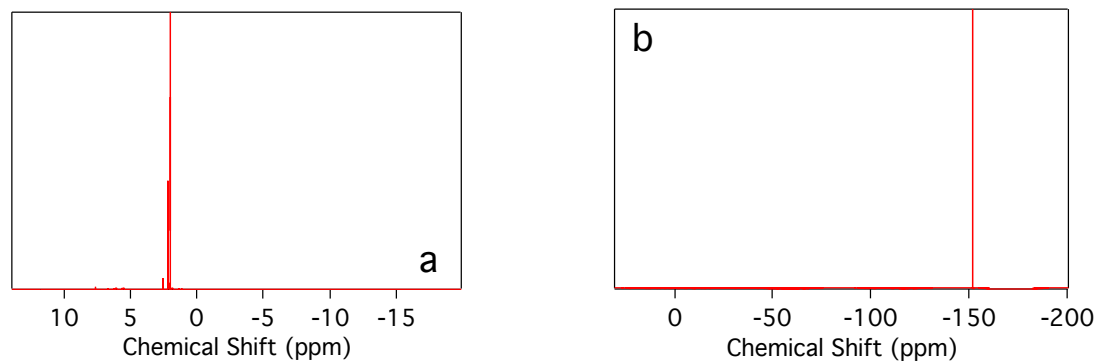


Figure SI 6.4. (a) ^1H NMR spectra (b) ^{19}F NMR spectra of $\text{Me}_{10}\text{FcBF}_4$ in *d*-acetonitrile.

SI 6.3. TEM Images and Size Distribution Analyses

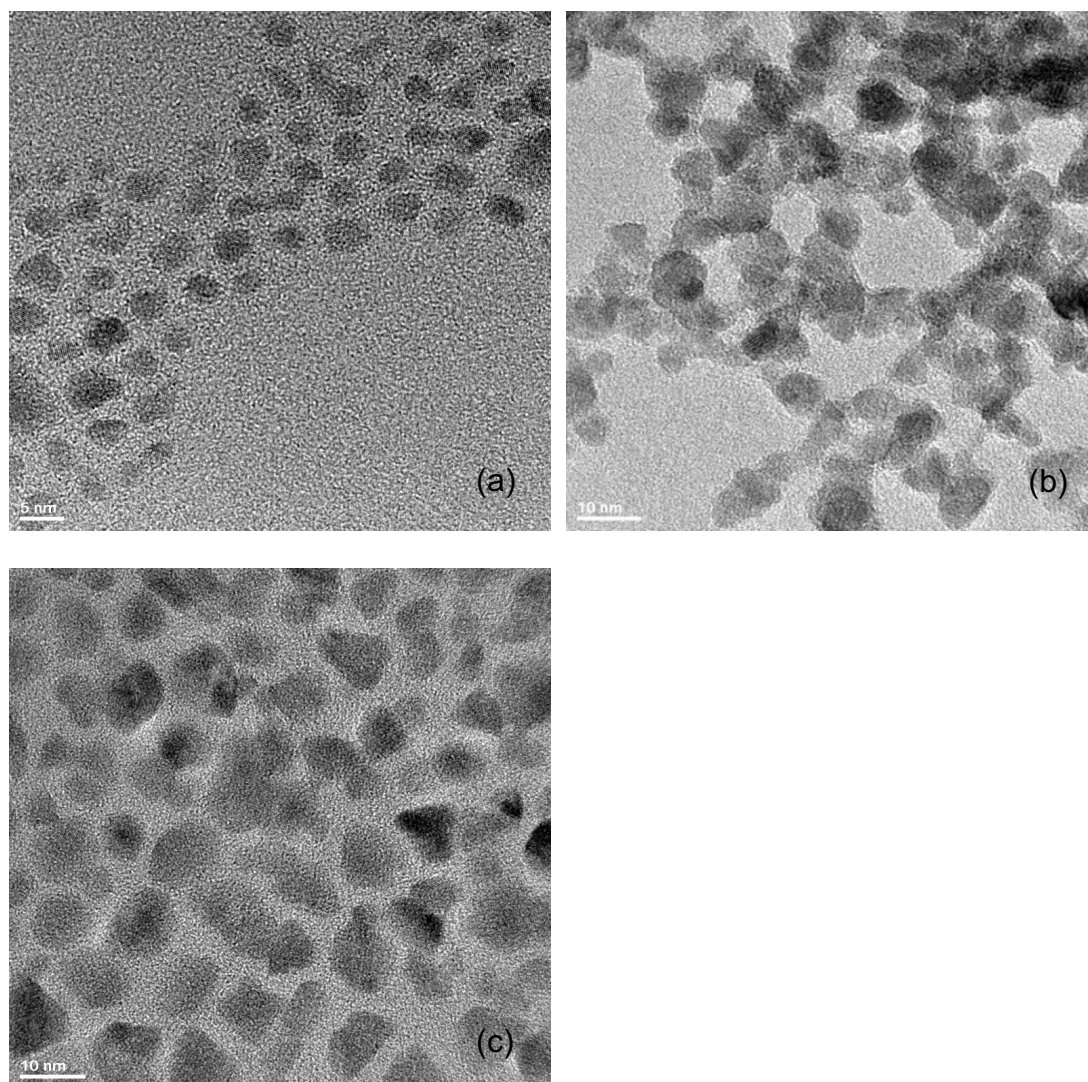


Figure SI 6.5. TEM images of different sizes InN NCs. (a) 3.9 nm, (b) 6nm, (c) 8.7 nm.

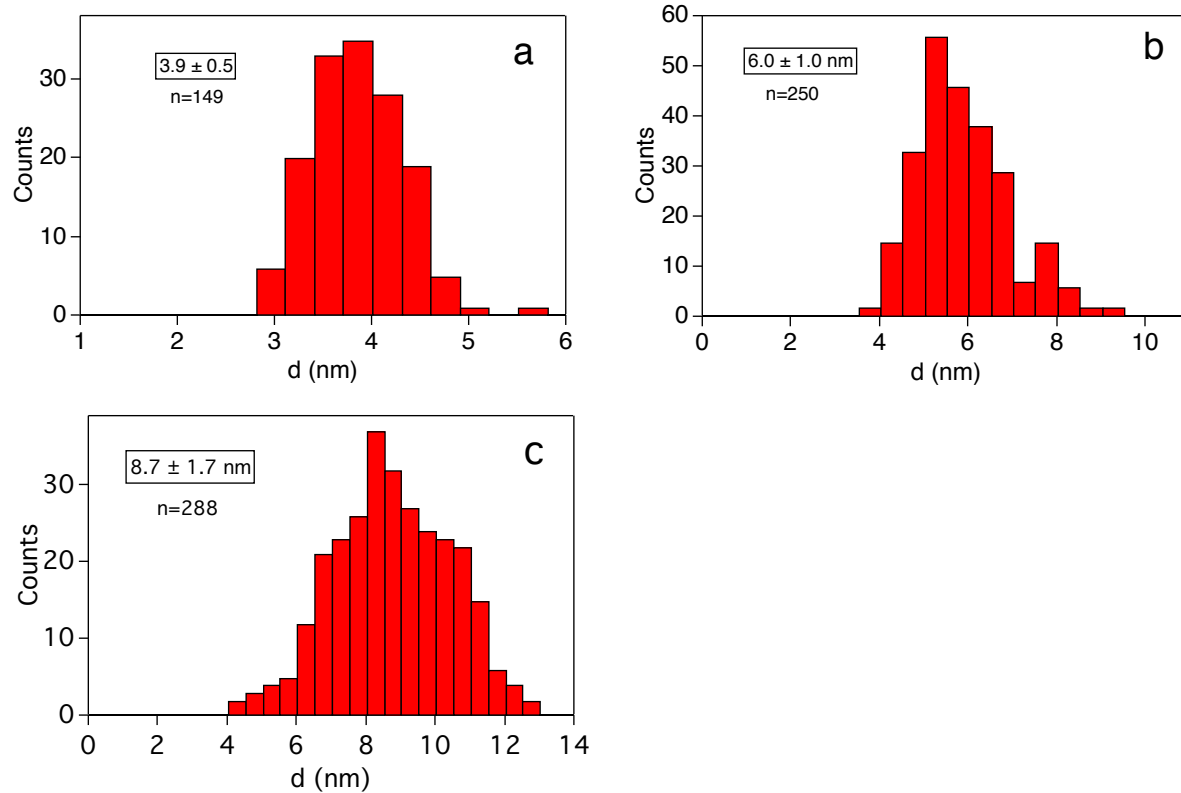


Figure SI 6.6. Histograms of different sizes InN NCs. (a) 3.9 nm, (b) 6 nm, (d) 8.7 nm.

SI.6.4. XRD Data

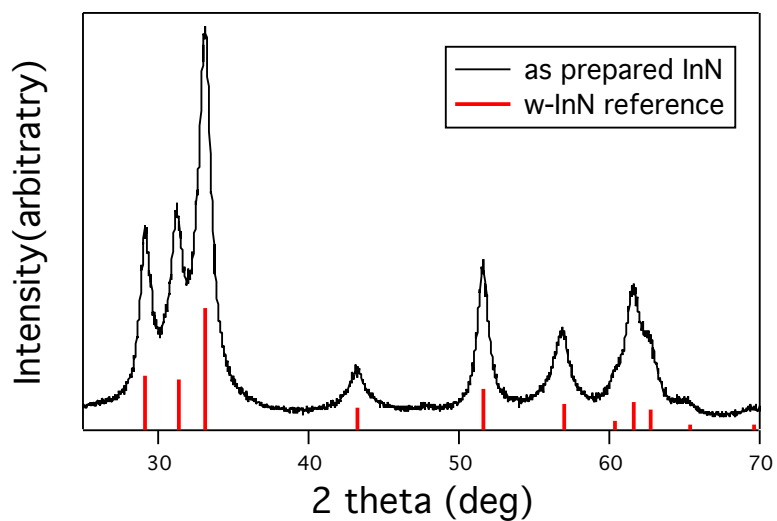


Figure SI 6.7. X-ray powder diffraction of 6 nm Et_3OBF_4 -treated InN NCs. Reference diffraction angles for bulk wurtzite InN are given as red bars.⁴⁵

SI 6.5. ICP Data

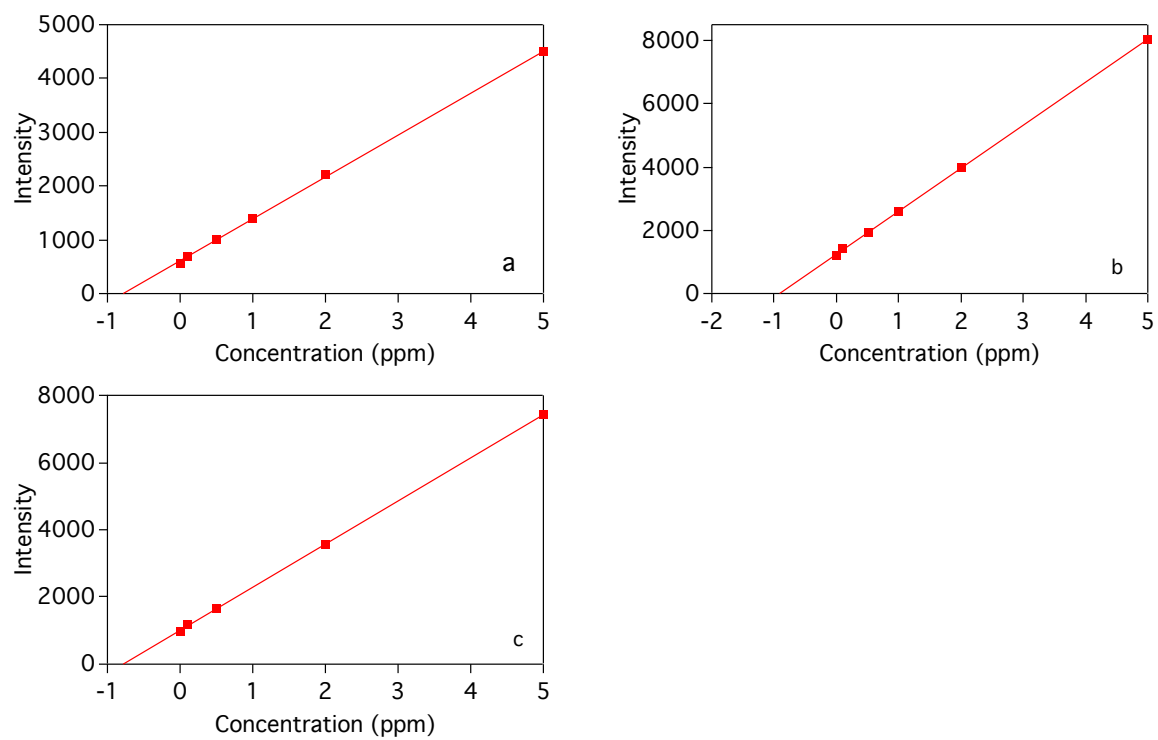


Figure SI 6.8. ICP of different sizes InN NCs. (a) 3.9 nm, (b) 6 nm, (c) 8.7 nm.

SI.6.6. Standard Potential of Oxidants

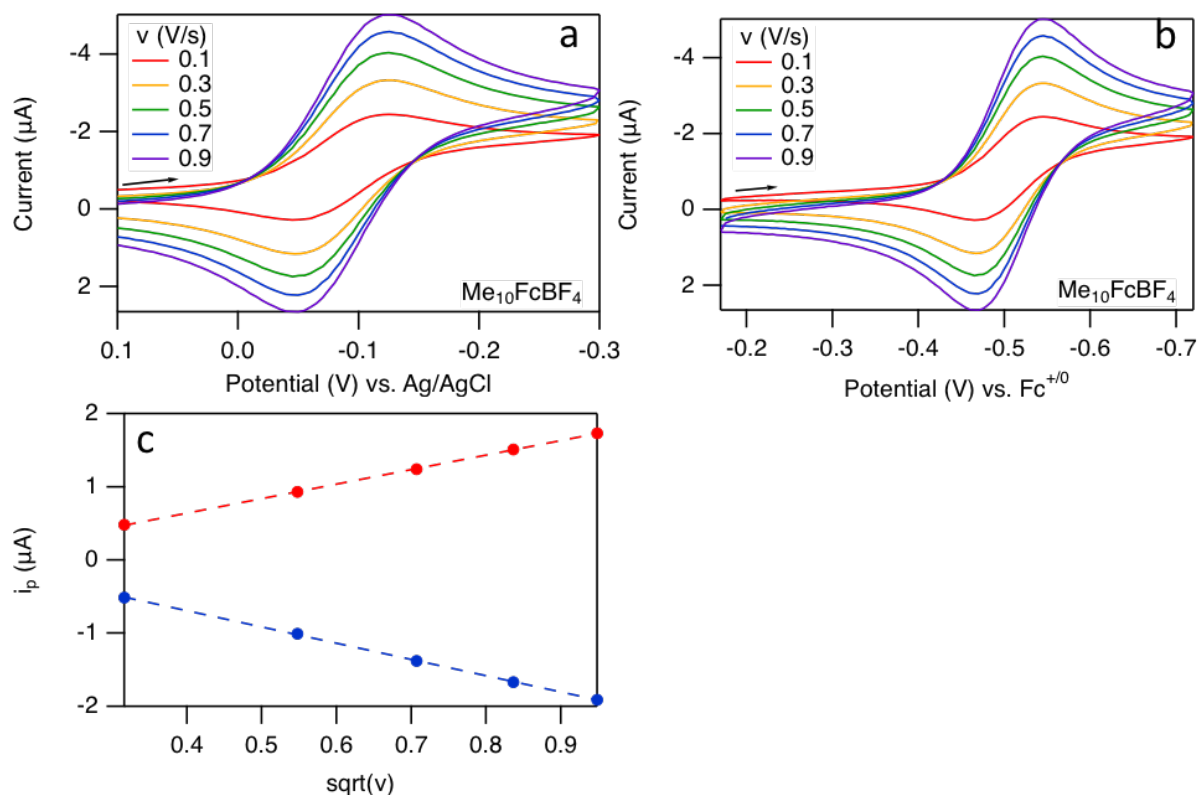


Figure SI.6.9. CVs of $\text{Me}_{10}\text{FcBF}_4$ (2 mM in ACN w/ TBAPF_6 as supporting electrolyte). (a) CV vs. Ag/AgCl at various scan rates. (b) CV vs. $\text{Fc}^{+/0}$ at various scan rates. (c) Behavior of the peak anodic and cathodic current at different scan rates.

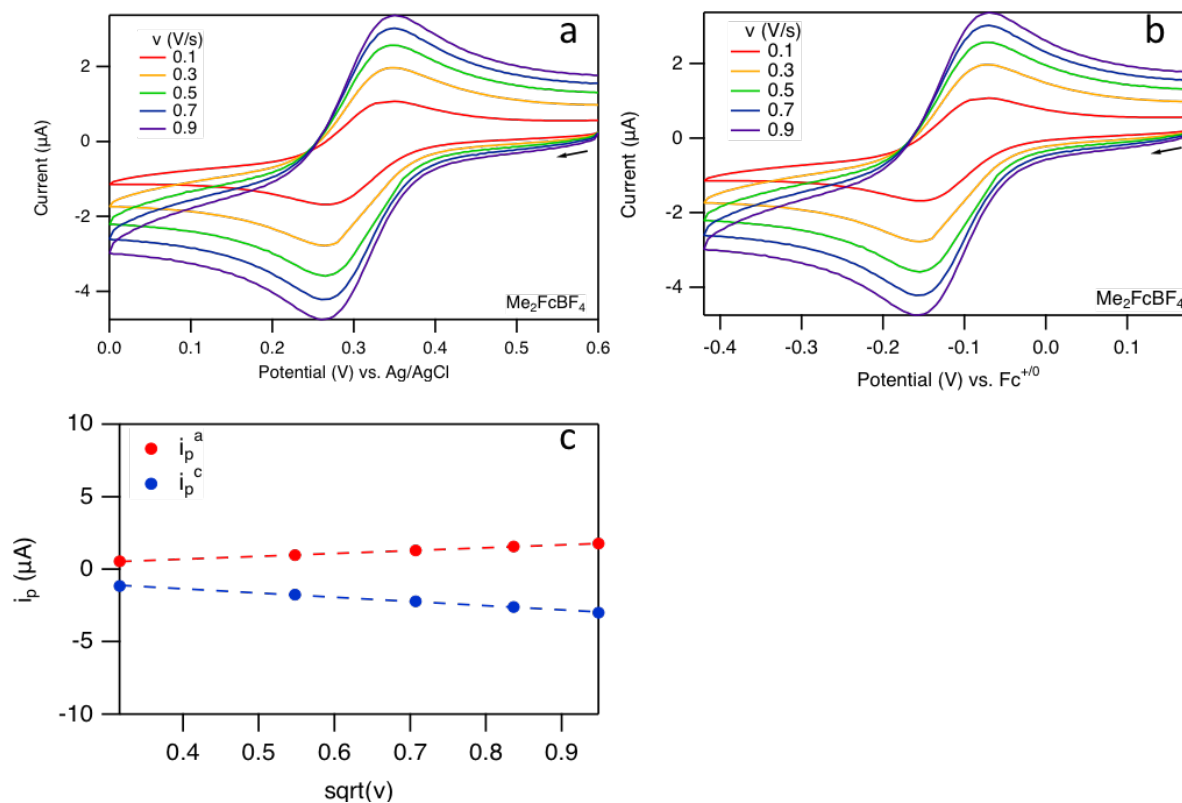


Figure SI 6.10. CVs of Me_2FcBF_4 (1 mM in ACN w/ TBAPF_6 as supporting electrolyte). (a) CV vs. Ag/AgCl at various scan rates. (b) CV vs. $\text{Fc}^{+/0}$ at various scan rates. (c) Behavior of the peak anodic and cathodic current at different scan rates.

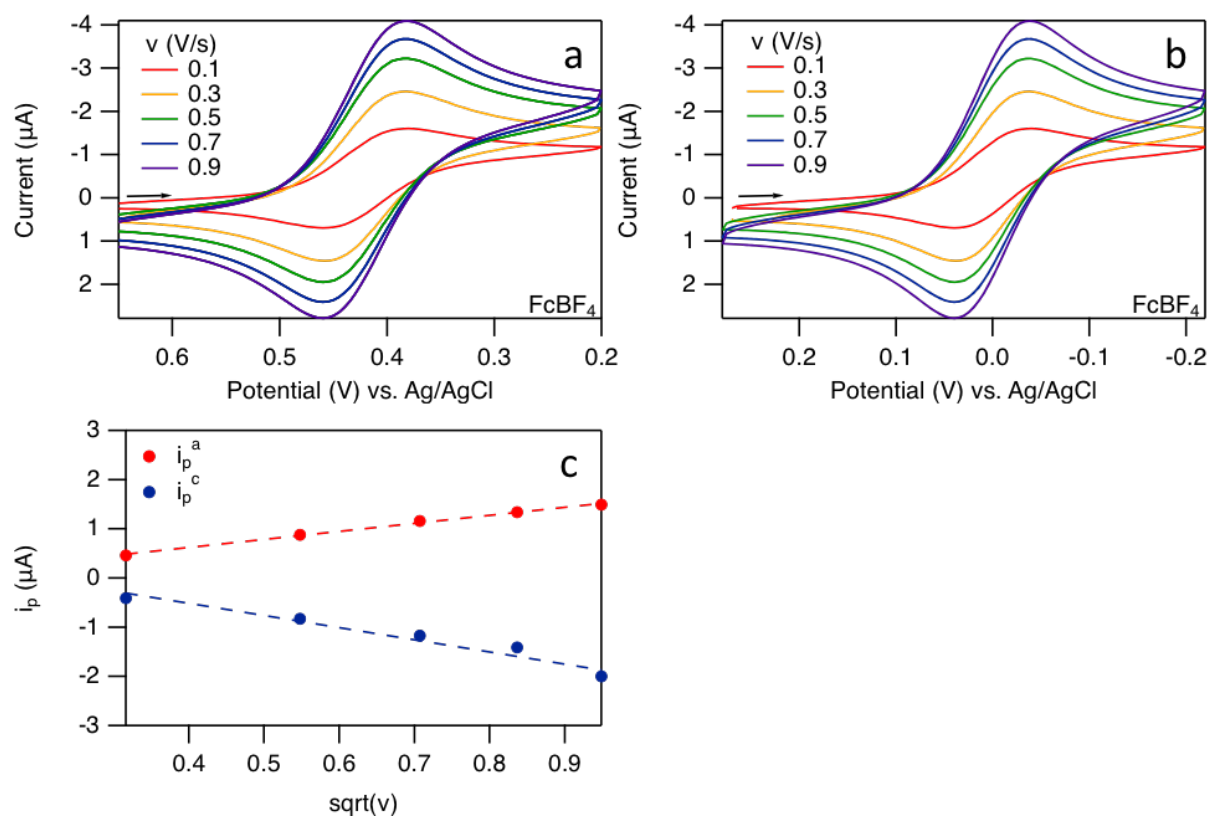


Figure SI 6.11. CVs of FcBF_4 (2 mM in ACN w/ TBAPF_6 as supporting electrolyte). (a) CV vs. Ag/AgCl at various scan rates. (b) CV vs. $\text{Fc}^{+/0}$ at various scan rates. (c) Behavior of the peak anodic and cathodic current at different scan rates.

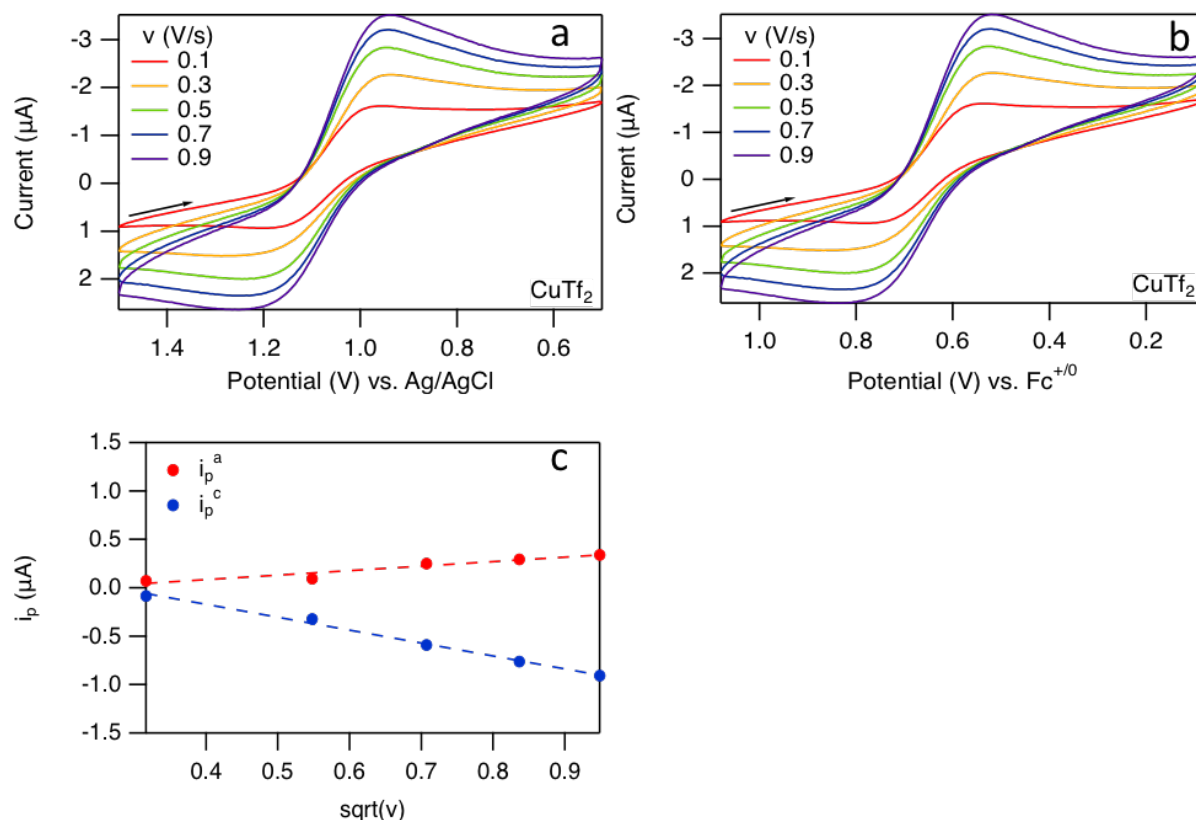


Figure SI 6.12. CVs of CuTf_2 (4 mM in ACN w/ TBAPF_6 as supporting electrolyte). (a) CV vs. Ag/AgCl at various scan rates. (b) CV vs. $\text{Fc}^{+/0}$ at various scan rates. (c) Behavior of the peak anodic and cathodic current at different scan rates.

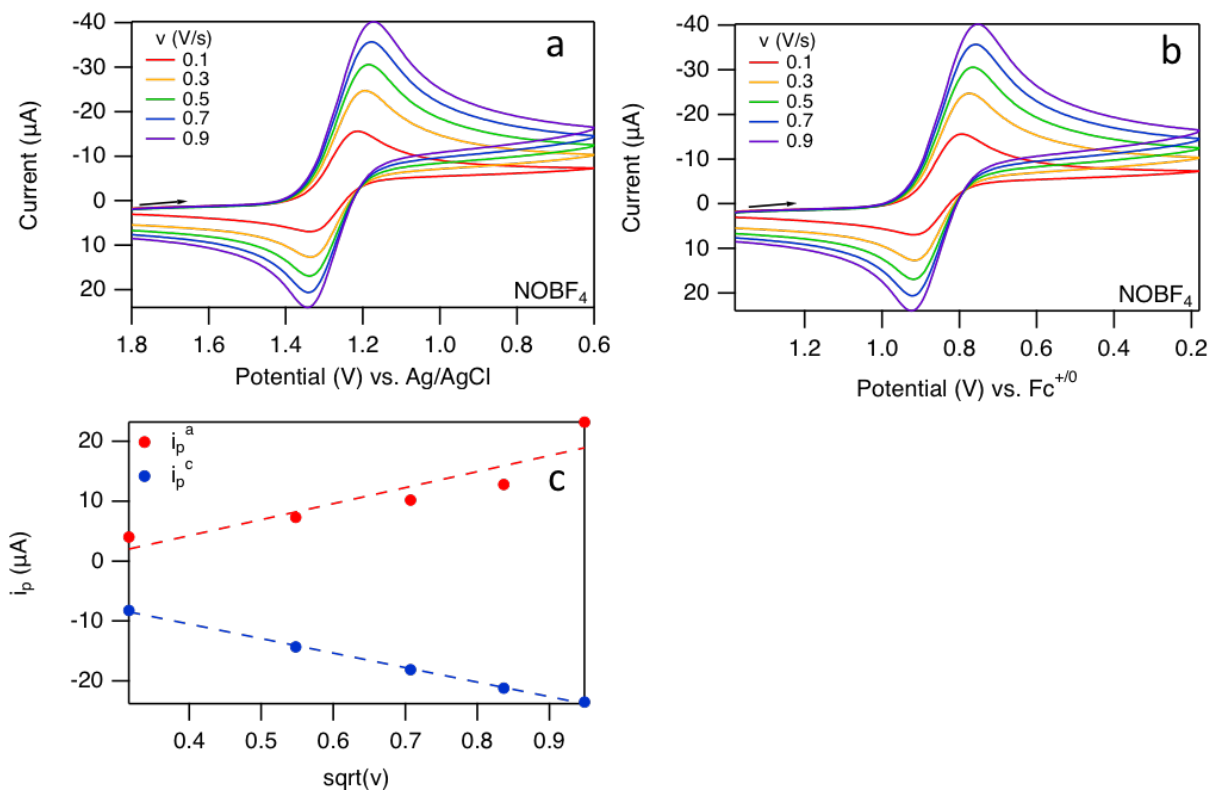


Figure SI 6.13. CVs of NOBF₄ (10 mM in ACN w/ TBAPF₆ as supporting electrolyte). (a) CV vs. Ag/AgCl at various scan rates. (b) CV vs. Fc^{+/0} at various scan rates. (c) Behavior of the peak anodic and cathodic current at different scan rates.

Table SI 6.1. Summary of CV data for all the above oxidants. The values are consistent with previous reports^{46, 47}.

vs. $\text{Fc}^{+/0}$	v (V/s) ¹	E_p^a (V) ²	i_p^a (μA) ³	E_p^c (V) ⁴	i_p^c (μA) ⁵	ΔE_p (V) ⁶	$E_{1/2}$ (V) ⁷	Average $E_{1/2}$ ⁸ (V)
$\text{Me}_{10}\text{FcBF}_4$	0.1	-0.466	0.479	-0.545	-0.513	$0.079 \pm 1.82\%$	-0.506	-0.506
	0.3	-0.466	0.934	-0.546	-1.010	$0.080 \pm 1.80\%$	-0.506	
	0.5	-0.467	1.240	-0.546	-1.380	$0.079 \pm 1.82\%$	-0.506	
	0.7	-0.466	1.510	-0.546	-1.670	$0.080 \pm 1.79\%$	-0.506	
	0.9	-0.466	1.730	-0.547	-1.910	$0.081 \pm 1.77\%$	-0.506	
Me_2FcBF_4	0.1	-0.072	0.552	-0.158	-1.150	$0.086 \pm 0.40\%$	-0.115	-0.114
	0.3	-0.069	0.964	-0.158	-1.750	$0.089 \pm 0.39\%$	-0.114	
	0.5	-0.070	1.301	-0.158	-2.220	$0.088 \pm 0.39\%$	-0.114	
	0.7	-0.070	1.560	-0.160	-2.610	$0.090 \pm 0.39\%$	-0.115	
	0.9	-0.068	1.780	-0.161	-3.000	$0.093 \pm 0.38\%$	-0.115	
FcBF_4	0.1	0.041	0.455	-0.041	-0.408	$0.082 \pm 0.14\%$	0.000	0.001
	0.3	0.041	0.877	-0.039	-0.832	$0.080 \pm 0.14\%$	0.001	
	0.5	0.041	1.160	-0.039	-1.170	$0.080 \pm 0.14\%$	0.001	
	0.7	0.041	1.340	-0.039	-1.410	$0.080 \pm 0.14\%$	0.001	
	0.9	0.041	1.490	-0.039	-2.100	$0.080 \pm 0.14\%$	0.001	
CuTf_2	0.1	0.787	0.073	0.535	-0.083	$0.252 \pm 0.76\%$	0.661	0.675
	0.3	0.860	0.094	0.507	-0.323	$0.353 \pm 0.56\%$	0.684	
	0.5	0.831	0.251	0.518	-0.591	$0.313 \pm 0.63\%$	0.674	
	0.7	0.837	0.294	0.518	-0.761	$0.319 \pm 0.62\%$	0.678	
	0.9	0.844	0.337	0.509	-0.907	$0.335 \pm 0.59\%$	0.677	
NOBF_4	0.1	0.920	4.020	0.790	-8.220	$0.130 \pm 1.87\%$	0.855	0.844
	0.3	0.920	7.310	0.770	-14.300	$0.150 \pm 1.60\%$	0.845	
	0.5	0.920	10.200	0.760	-18.100	$0.160 \pm 1.49\%$	0.840	
	0.7	0.920	12.800	0.760	-21.200	$0.160 \pm 1.49\%$	0.840	
	0.9	0.930	23.200	0.750	-23.500	$0.180 \pm 1.33\%$	0.840	

¹. v = scan rate, ². E_p^a =peak anodic potential (Error $\pm 0.02\%$), ³. i_p^a = peak anodic current (Error $\pm 0.02\%$), ⁴. E_p^c =peak cathodic potential (Error $\pm 0.02\%$), ⁵. i_p^c = peak cathodic current (Error $\pm 0.02\%$), ⁶. ΔE_p = peak separation between anodic and cathodic potentials, ⁷. $E_{1/2}$ = half potential found by averaging E_p^a and E_p^c (Error $\pm 0.30\%$), ⁸. (Error $\pm 0.30\%$)

SI. 6.7. Kinetics of Addition of Oxidant Solution to InN NC Suspension

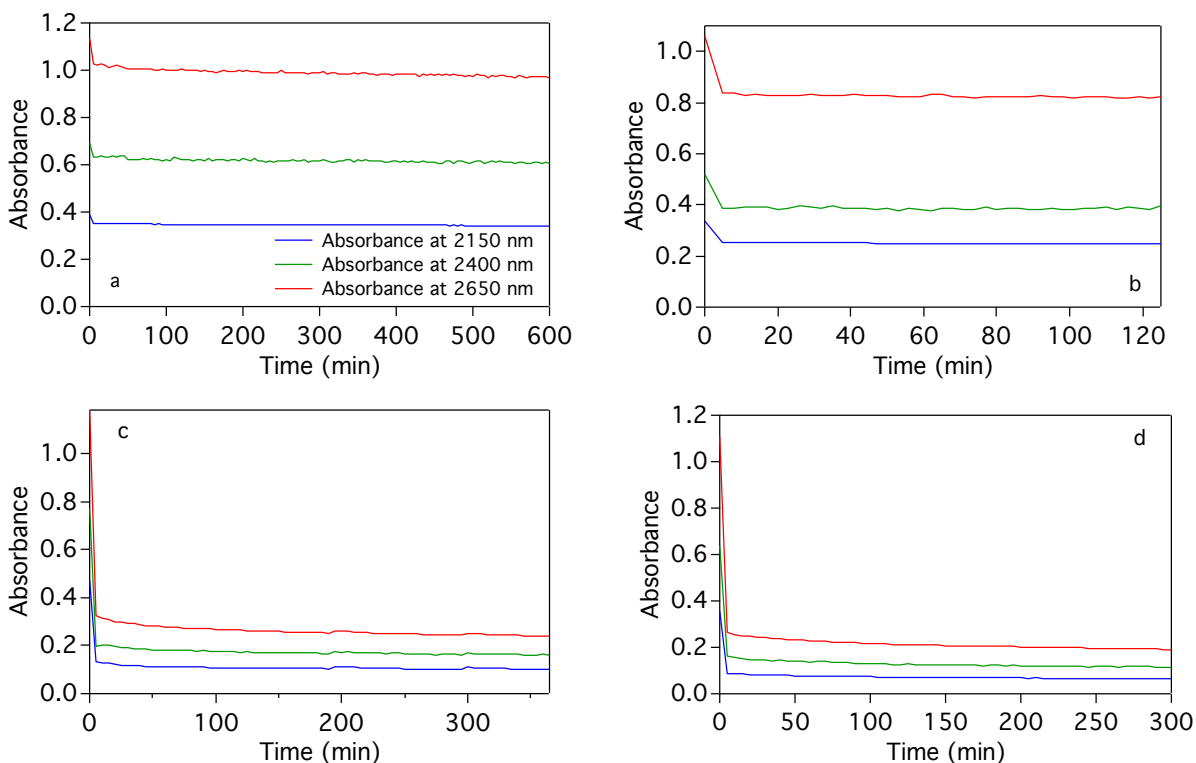


Figure SI 6.14. Absorbance of Et₃OBF₄-treated InN with excess oxidants at 2650 nm, 2400 nm and 2150 nm as a function of time. (a) 6 nm 0.7 μ M InN NCs with 20 μ l 12mM 2Me-FcBF₄. (b) 3.9 nm 3.5 μ M InN NCs with 10 μ l 16 mM FcBF₄. (c) 3.9 nm 2.6 μ M InN NCs with 400 μ l 10 mM CuTf₂ solution. (d) 8.7 nm 0.2 μ M InN NCs with 200 μ l 33.7 mM NOBF₄ solution.

SI 6.8. Titration of InN NCs with different oxidants

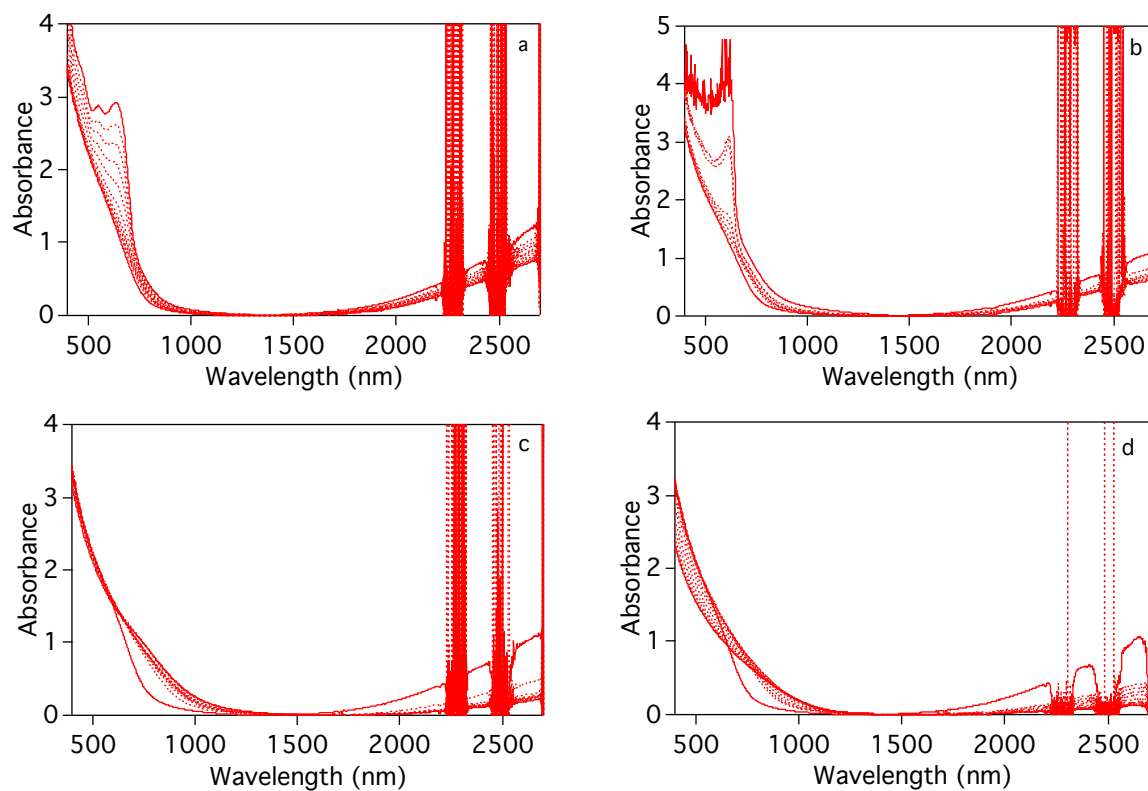


Figure SI 6.15. Absorbance spectra of colloidal InN NCs ([NC] = 0.7 μ M, 6 nm) with 0 - 5000 equivalents of various oxidants. (a) Me_2FcBF_4 , (b) FcBF_4 , (c) CuTf_2 , (d) NOBF_4 .

SI 6.9. Most Oxidized InN NCs of Different Sizes

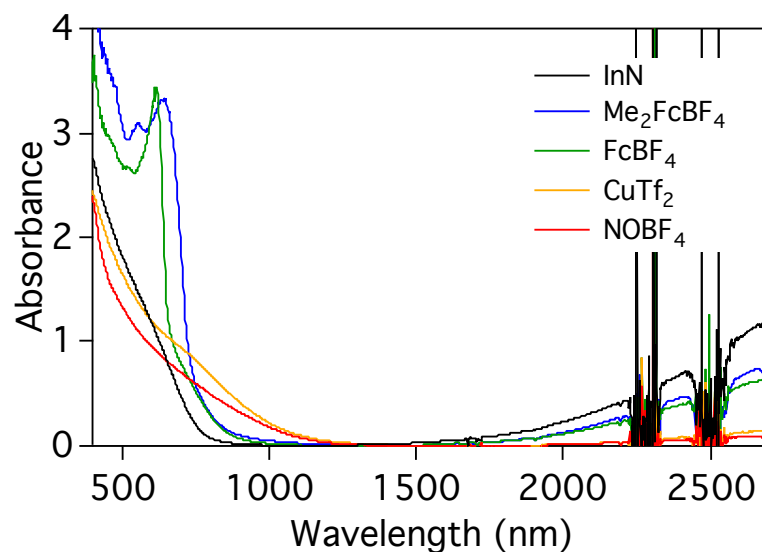


Figure SI 6.16. Absorbance spectrum of InN NCs ($d = 3.9$ nm, $[NC] = 2.3$ μM) with 6 mM oxidants.

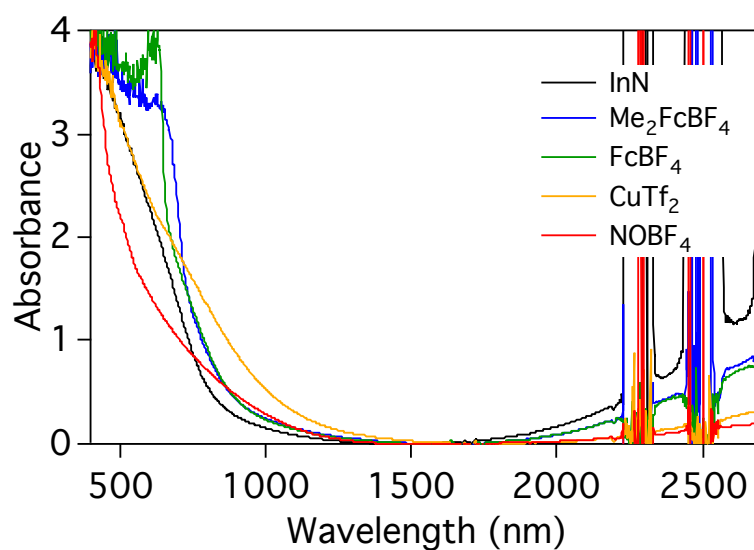


Figure SI 6.17. Absorbance spectrum of InN NCs ($d = 6$ nm, $[NC] = 0.7$ μM) with 6 mM oxidants.

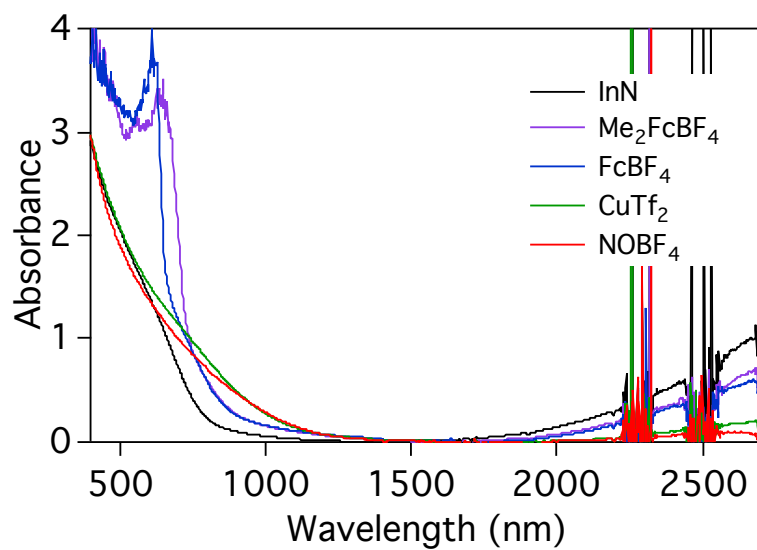


Figure SI 6.18. Absorbance spectrum of InN NCs ($d = 8.7$ nm, $[\text{NC}] = 0.2 \mu\text{M}$) with 6 mM oxidants.

SI 6.10. $\text{Me}_{10}\text{FcBF}_4$ does not oxidize InN NCs

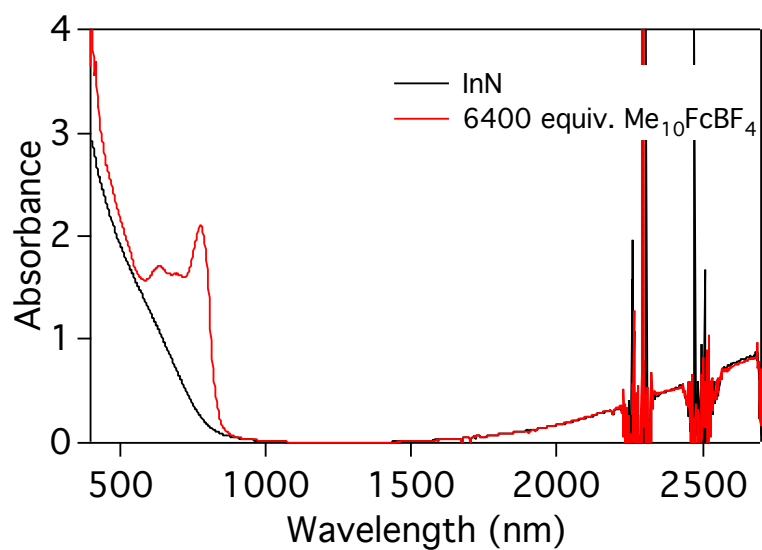


Figure SI 6.19. Absorbance spectrum of as prepared InN NCs ($d = 6.0$ nm, $[\text{NC}] = 0.5$ μM) and with 3.2 mM $\text{Me}_{10}\text{FcBF}_4$.

SI 6.11. Alternative Way to Estimate InN LSPR

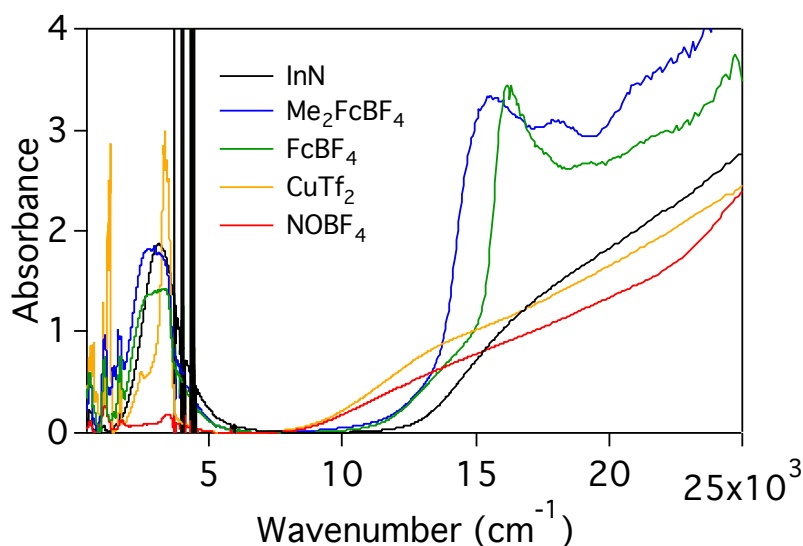


Figure SI 6.20. Absorbance spectra of BF_4^- capped InN NCs (2.3 μM 3.9 nm) with 6mM oxidants. 25000 to 3704 cm^{-1} were measured by UV-vis-NIR. 4000 to 400 cm^{-1} were measured via FTIR. The UV-vis-NIR and FTIR spectra were connected by matching the absorbance in the overlapping region (4000-3704 cm^{-1}).

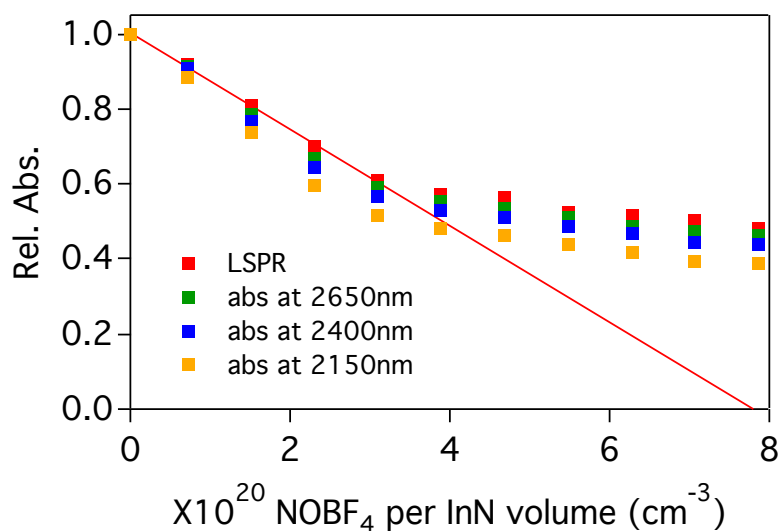


Figure SI 6.21. The relative absorbance of NOBF_4 oxidized InN NCs ($d = 4.2$ nm, $[\text{NC}] = 1.8 \mu\text{M}$) at 2650 nm (green), 2400 nm (blue) and 2150 nm (orange) compared with the relative integrated LSPR absorption.

SI 6.12. Model and Calculations

The energy of the conduction band under confinement is obtained from a simple particle-in-a-spherical-well model, using the effective mass of the electron. The Hamiltonian is given by:

$$\hat{H} = \frac{-\hbar^2}{2m_e} \hat{\nabla}^2 + V(r) \quad (\text{S1})$$

and the confinement potential is

$$V(r) = \begin{cases} 0 & 0 \leq r \leq a \\ V_0 & r > a \end{cases} \quad (\text{S2})$$

where a is the radius of the spherical box. Focusing only on the zero angular momentum ($l = 0$) lowest state, the Hamiltonian reduces to the well-known radial equation:

$$\frac{-\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + V(r) R(r) = E \cdot R(r) \quad (\text{S3})$$

Which is simplified by taking

$$u(r) \equiv r \cdot R(r) \quad (\text{S4})$$

$$\frac{d^2 U(r)}{dr^2} + k_{in/out}^2 \cdot U(r) = 0 \quad (\text{S5})$$

where the wavenumber k is

$$\begin{aligned}
k_{in} &= \sqrt{\frac{2m_e E}{\hbar^2}} \\
k_{out} &= \sqrt{\frac{2m_e (V_0 - E)}{\hbar^2}}
\end{aligned}
\tag{S6}$$

The wavefunctions inside (in) and outside (out) the spherical well are easily obtained as:

$$\begin{aligned}
R_{in}(r) &= \frac{C_{in}}{r} \sin(k_{in} r) & 0 \leq r \leq a \\
R_{out}(r) &= \frac{C_{out}}{r} e^{-k_{out} r} & r > a
\end{aligned}
\tag{S7}$$

The requirement that both $R(r)$ and $dR(r)/dr$ are continuous imply that:

$$\begin{aligned}
k_{in} \cot(k_{in} a) + k_{out} &= 0 \\
k_{in} \cot(k_{in} a) &= -\sqrt{\frac{2m_e V_0}{\hbar^2} - k_{in}^2}
\end{aligned}
\tag{S8}$$

which can be directly solved graphically to find the allowed value of k_{in} for a given NC radius (a), confinement potential (V_0), and effective mass m_e . The energy of the conduction band level (E) is then obtained directly from eq. (S6) above.

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**Chapter 7: Effects of Free Charge Carriers on the Vibrational Spectra of Doped
InN Nanocrystals**

7.1 Overview

In this chapter, we use InN NCs as a model to investigate the effect of free electrons on nuclear motion of degenerately doped semiconductor NCs. We measured the Raman and absorption spectra of colloidal InN NCs with various electron densities and observed that the vibrational frequency of the LO phonon mode ($\sim 588.5 \text{ cm}^{-1}$) linearly blue shifts by $\sim 7 \text{ cm}^{-1}$ with the reduction of free electron density, while the E_2 (high) phonon mode ($\sim 490 \text{ cm}^{-1}$) is not significantly influenced by the dopant level. This behavior is explained by the screening effect. This analysis allowed to provide the first estimate of the LO phonon mode frequency of pristine (undoped) InN NCs to be 596 cm^{-1} .

7.2 Introduction

In solid-state physics, phonons are the pseudo-particles that describe the collective motion of the lattice. Phonons play important roles in optical, thermal and electrical properties of semiconductor nanomaterials¹⁻⁴ and can greatly affect device performances. Phonons in nanostructures can behave significantly differently from bulk materials, such as reduced thermal conductivity⁵⁻⁸ and slower electronic relaxation due to the confinement of phonons⁹⁻¹⁴, and their response to size,¹⁵⁻¹⁷ surface conditions,^{18, 19} and properties of host lattice.²⁰ Preliminary studies demonstrated that the existence of free carriers can affect the phonon behaviors in doped semiconductor nanomaterials and, that phonon frequencies and spectral shapes were found to be carrier-density-dependent when free

carriers were introduced.^{21, 22} However, early efforts to introduce extra free carriers in semiconductor NCs focused on aliovalent doping or vacancy doping such as Sn^{4+} -doped In_2O_3 , Al^{3+} -doped ZnO , Cu_{2-x}S , in which the introduction of impurity ions or vacancy could change the crystalline lattice and complicates the effect from free carriers.^{23, 24} Photodoped ZnO NCs have been used to study the free carrier effects on phonon behaviors.^{25, 26} The LO phonon mode in ZnO NCs is very weak and requires the participation of resonant Raman scattering technique which can further photoexcite electrons to CB and obscure the quantification of the number of free electrons.

InN NCs are spontaneously degenerately doped. The number of free electrons can be tuned with redox chemistry and quantified via absorption spectroscopy. In this chapter, we use InN NCs as an ideal candidate material to study the effect of free electrons on the vibrational behavior of the lattice. We systematically decrease the free electron density of InN NCs with electron acceptor and monitor the phonon behaviors using Raman spectroscopy.

7.3 Experimental Methods

7.3.1 InN NC Synthesis

The synthesis, purification and ligand exchange of InN NCs were described in Chapter 2, Section 2.3.1.

7.3.2 Physical & Sample Characterization Methods

A. Raman Spectra

Raman spectra were obtained from Renishaw inVia Raman Microscope spectrometer with a 532 nm (2.33 eV) laser line as the excitation source. All spectra were obtained in ACN solution in a 1 mm quartz cuvette.

B. Other Instrumentations

TEM and UV-vis-NIR spectra were described in detail in Chapter 2, Section 2.3.2.

7.4 Results and Discussion

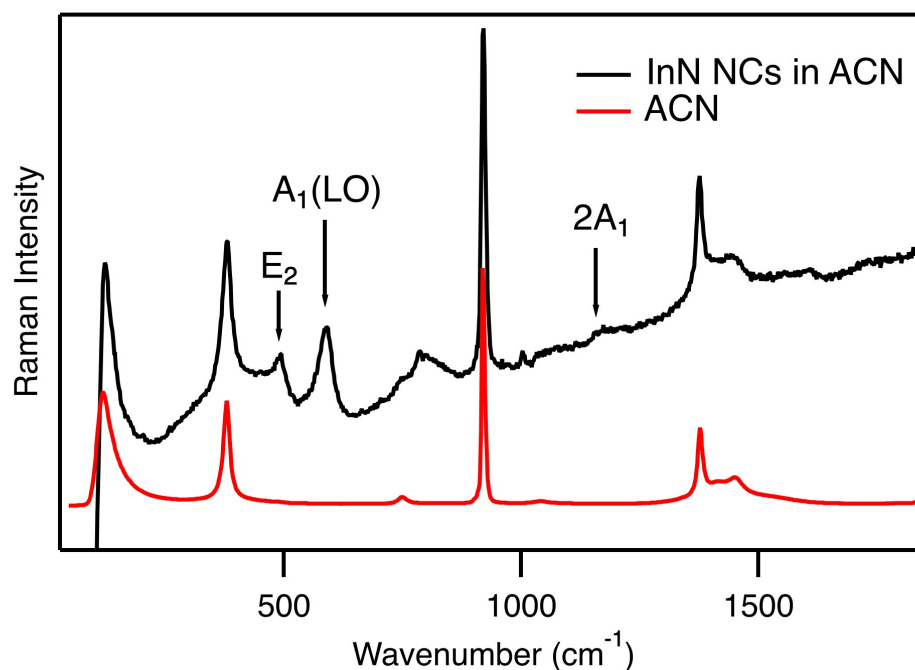


Figure 7.1. Raman spectra of as prepared *i*-InN NCs ($d = 5.1$ nm, $[NC] = 7.6 \mu M$) in ACN and blank ACN excited by a 532nm laser.

Figure 7.1 shows the Raman spectra of colloidal InN NCs suspension in ACN. Under 532 nm excitation, as-synthesized InN NCs exhibit two main peaks, located at 490 cm^{-1} and 588.5 cm^{-1} , which correspond to the E_2 (high) and A_1 (LO) mode, respectively, similar to reported phonon frequencies of bulk InN.^{27, 28} In bulk, the band at 588.5 cm^{-1} is a superposition of $A_1(\text{LO})$ and $E_1(\text{LO})$. The $A_1(\text{LO})$ mode is a In-N stretch along the c-axis, and the $E_1(\text{LO})$ mode is also a In-N stretch, but perpendicular to the c-axis. The energies of both vibrations are similar making the two peaks combined into one peak. However, Raman modes can be different in spherical nanoparticles. In fact, this peak corresponds to a whole-symmetry “breathing” mode of InN NCs. Here, we simply refer this mode as A_1 mode. A weak peak at $\sim 1175 \text{ cm}^{-1}$ likely corresponds to $2A_1$, an overtone of the A_1 fundamental frequency. A broad peak at $\sim 790 \text{ cm}^{-1}$ is also observed, but its origin remains unclear for now.

As determined in Chapter 3, the free carrier density in InN NCs is $\langle N_e \rangle \sim 7.4 \times 10^{20} \text{ cm}^{-3}$ and size-independent, and can be reversibly tuned with redox chemistry. Having determined the phonon modes of InN NCs, we systematically reduced the electron density (or number of electrons per particle) using the nitrosonium ion method described in Chapter 2. The Raman spectra of InN NCs with varying electron densities are reported in Figure 7.2(b). Upon oxidation, the A_1 peak clearly shifts by about 7 cm^{-1} , while the E_2 peak energy remains the same.

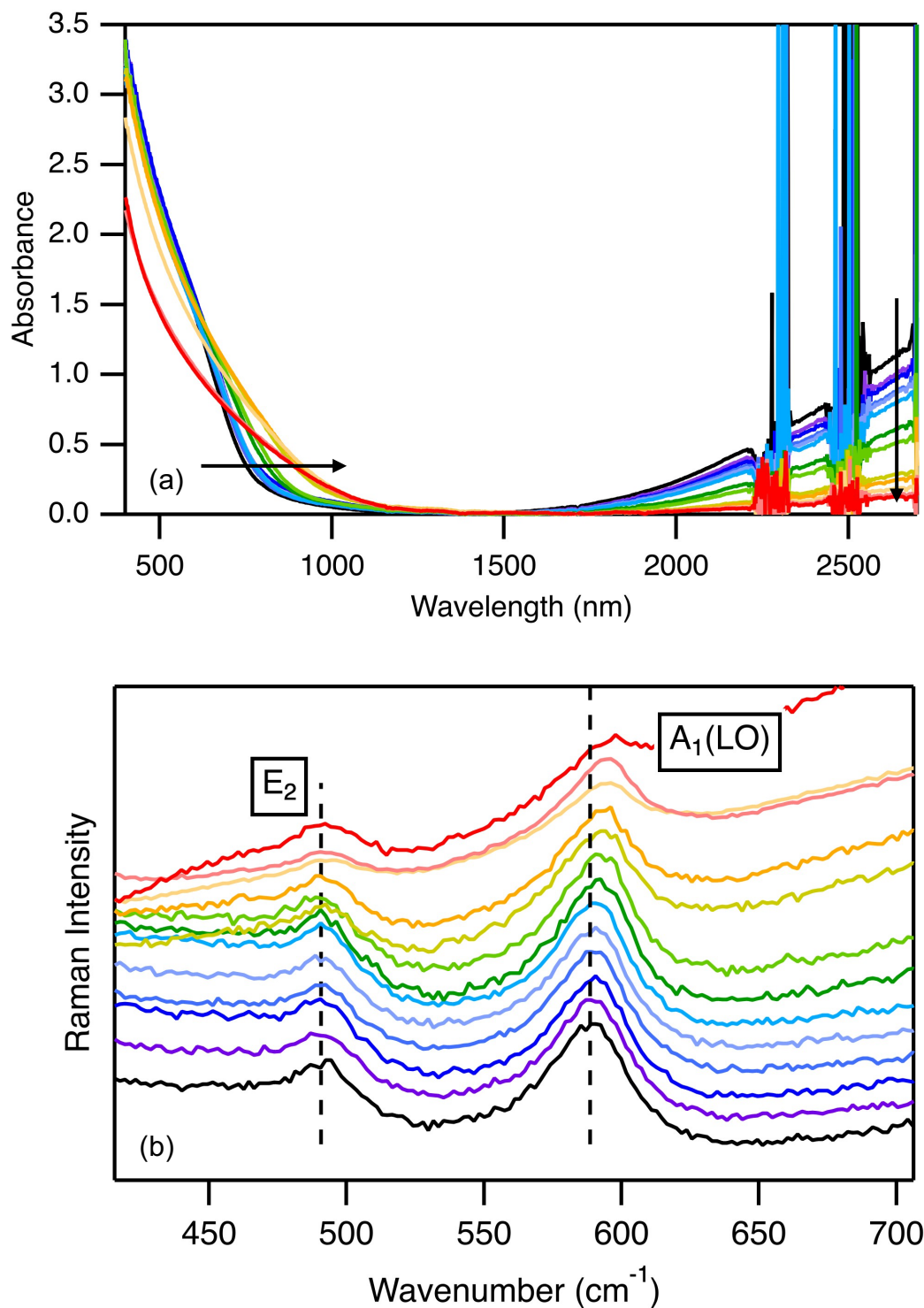


Figure 7.2. (a) UV-vis-NIR spectra of as prepared 5.1 nm InN NCs with the addition of 0, 4, 7, 15, 22, 30, 74, 148, 443, 740, 1480, 4434, 7390 equiv. of NOBF₄ (b) Raman spectra of same InN NCs in (a) excited by a 532nm laser. Dashed lines references of E₂ and A₁(LO) modes energy of as-prepared InN NCs.

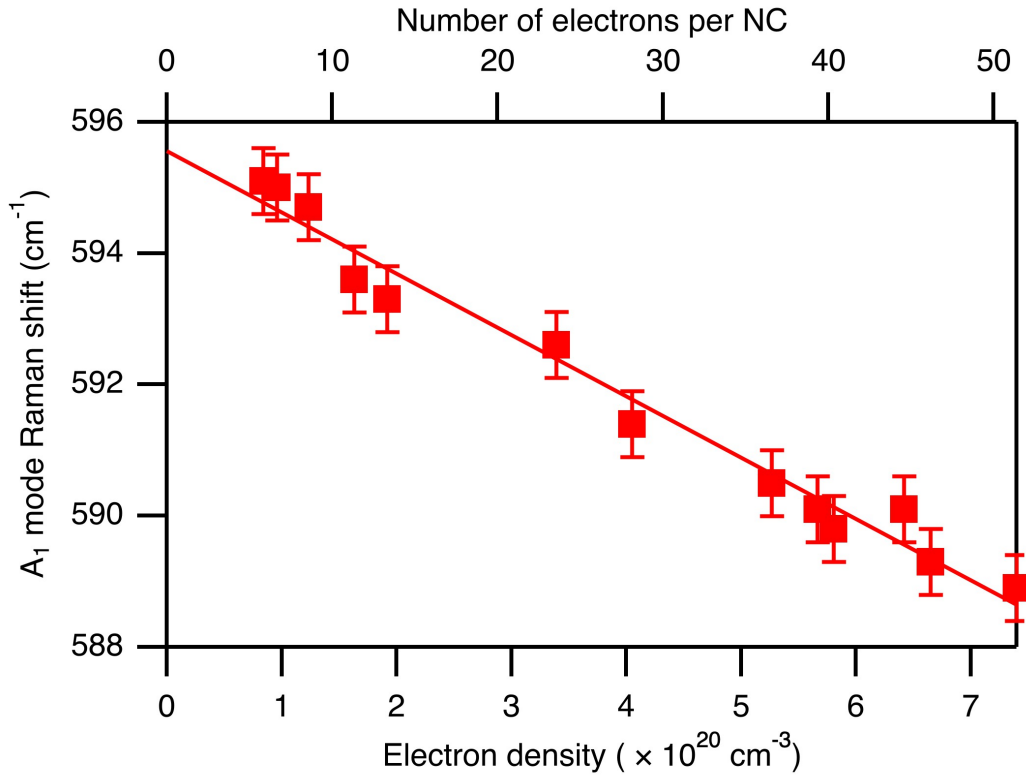


Figure 7.3. A_1 (LO) peak of 5.1nm InN NCs shifts as a function of free electron density and number of free electrons per NC. The solid line a linear fit.

Focusing on the A_1 peak, we observe that the A_1 vibrational energy increases linearly with the reduction of electron density. Figure 7.3 summarizes the quantitative relationship between A_1 energy and electron density. In a 5.1nm InN NC, the A_1 peak shifts by 1 cm^{-1} for every 7 electrons that are extracted. The shift of A_1 phonon mode in InN has been explained with phonon-plasmon coupling.²⁹⁻³¹ However, the shifting direction is the opposite to what we observed here. Ager *et al.*³² have observed similar shifts of the A_1 frequency in InN film, where surface electron accumulation was controlled by an electrolyte gate. As the applied gate potential tuned from positive to negative, the A_1 mode shifted to lower frequencies, yet the direct relationship between free electron density and

A_1 frequency remained unknown. An estimate of pristine InN A_1 energy can be obtained by extrapolating the linear trend to zero electron density, yielding a value of 595.5 ± 0.2 cm^{-1} . This energy is similar as the values reported in InN films, from which photoluminescence was observed indicating low electron density conditions.³³

For harmonic oscillator, the vibrational wavenumber ($\bar{\nu}$) is given by:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{eq. 7.1}$$

where μ is the reduced mass of the two atoms, c is speed of light and k is the force constant of the bond. Here, the reduced mass of InN is assumed to be independent of the doping level, implying that the force constant k must depend on the free electron density. A simple mechanism might explain this fact: at high free carrier densities, free electrons can screen the Coulombic restoring force induced by the phonon displacement, such that the longitudinal oscillation is consequently weakened. Here, as free carriers being removed, the screening effect is reduced so that A_1 mode shifts back to higher energy.

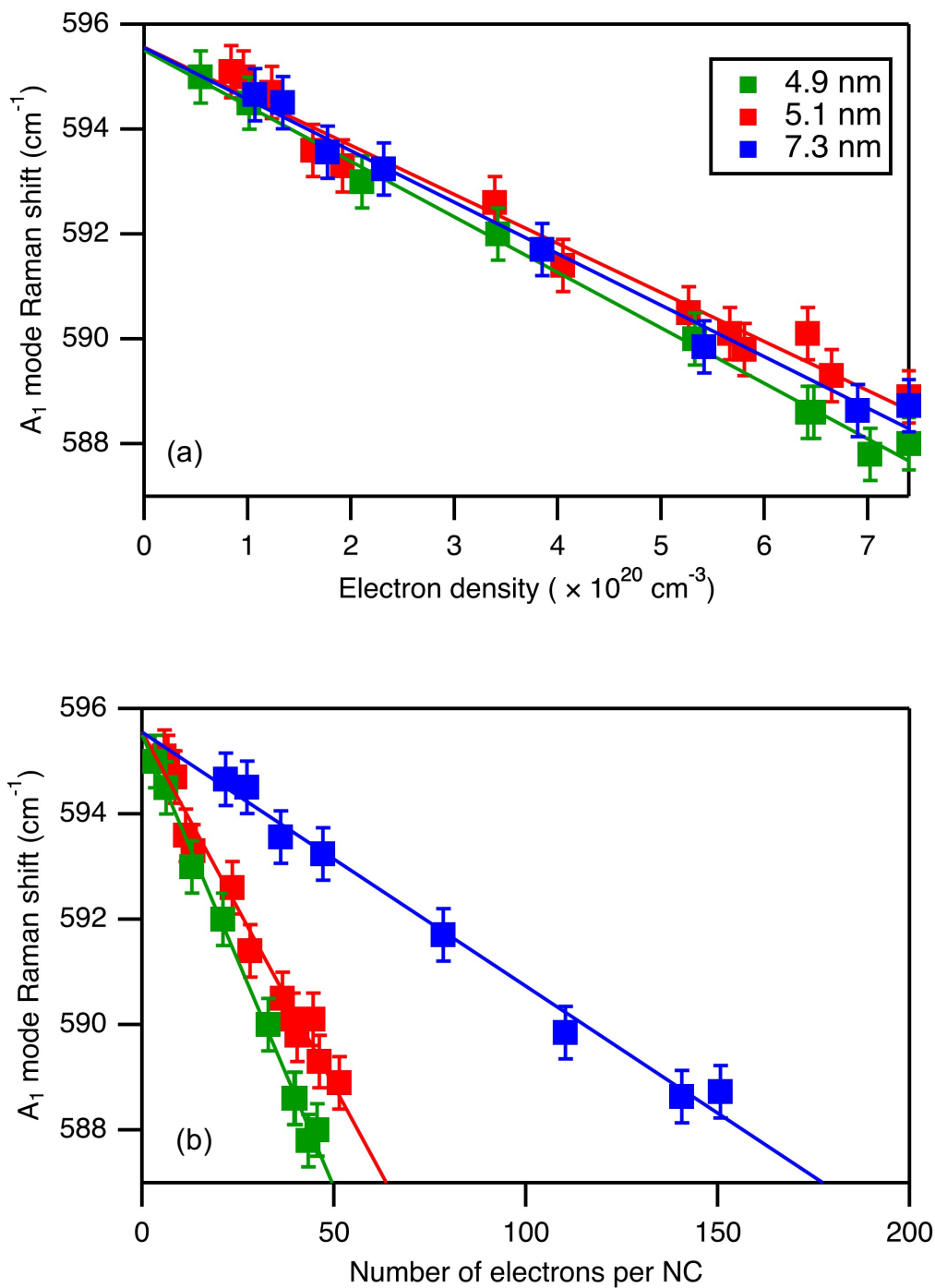


Figure 7.4. (a) A₁ (LO) Raman shift as a function of free electron density of 4.9 nm (green squares), 5.1 nm (red squares) and 7.3 nm (blue squares) InN NCs. The oxidation of InN NCs exhibits a size-independent linear variation of the Raman shift vs free electron density. (b) Same data as above, but expresses in the number of free electrons per NC, yielding a volumetrically-scaled weakening effect.

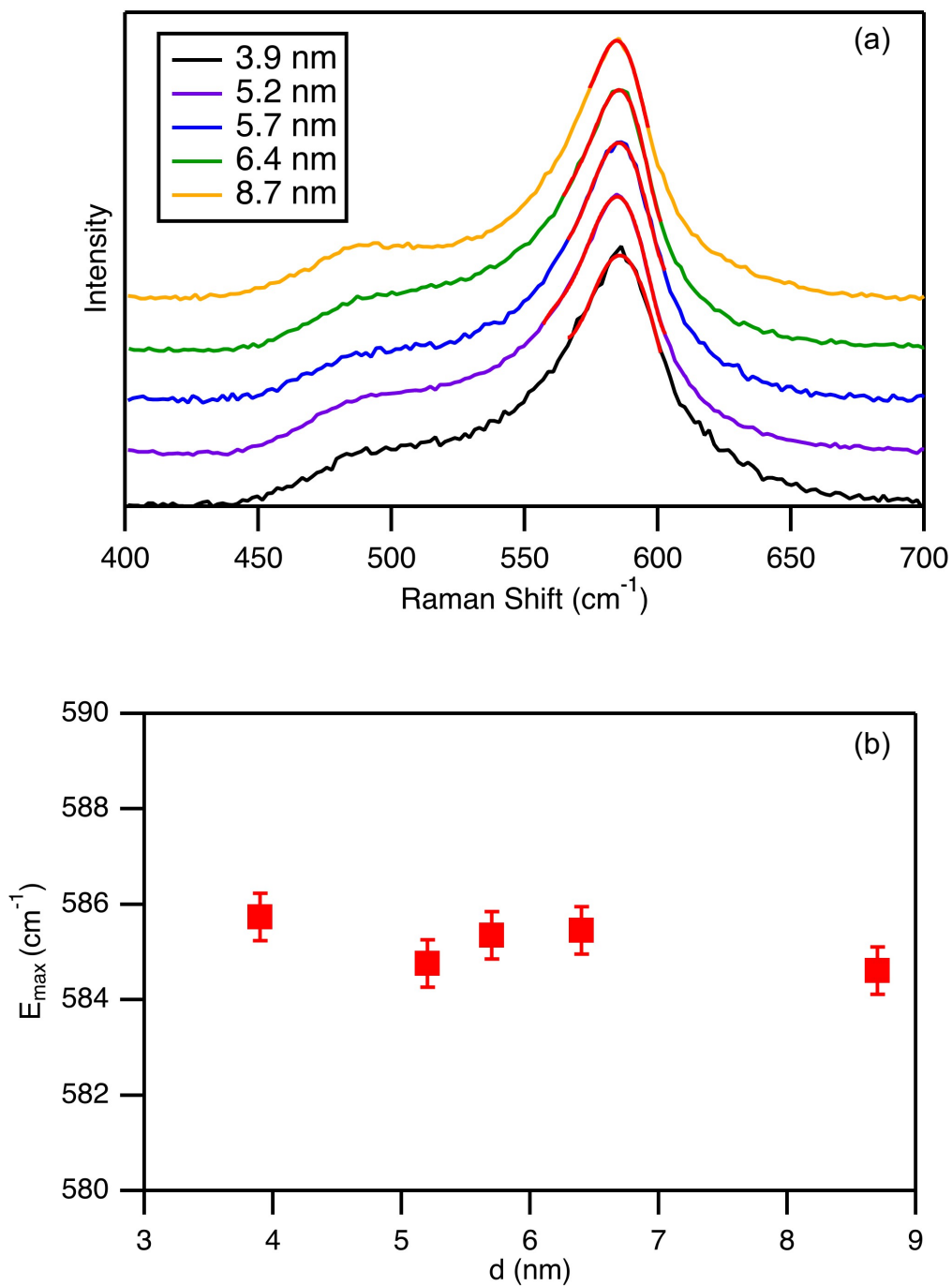


Figure 7.5. (a) Raman shift of as prepared InN NCs of different sizes. Red line is a polynomial fitting to determine the A₁ (LO) energy. (b) The A₁ (LO) mode energy (E_{max}) were plotted as a function of InN NCs sizes.

Systematic oxidation of InN NCs have been carried for other sizes, allowing for the evaluation of the size dependence of the screening effect. An interesting observation is that the Raman shift of the A_1 mode is independent of size (Figure 7.4). Potentially, this free-electron density-dependent Raman shift relationship can be used as an easy way to estimate free electron density ($N_e \times 10^{20} \text{ cm}^{-3}$) in InN NCs system:

$$N_e = (582.54 \pm 17.6) - (0.97794 \pm 0.2298) E_{\text{max}} \quad \text{eq. 7.2}$$

In Figure 7.4(a), the A_1 frequency of as prepared InN NCs seems varies with certain trend. We compared Raman spectra of InN NCs of different sizes. As shown in Figure 7.5(a), Raman spectra were measured on InN NCs with sizes vary from 4 to 9 nm and the A_1 phonon mode energy were plotted in Figure 7.5(b). The A_1 energy varies with samples, however, we did not observe any trend with InN NCs sizes.

7.5 Conclusions

In summary, we investigated the phonon behavior of InN NCs. A blue shift of the A_1 (LO) phonon frequency was observed by systematically oxidizing InN NCs, while the E_2 (high) phonon energy was not significantly modified. This was explained by screening effect that free electrons can weaken the Coulombic restoring force induced by the phonon displacement. A direct relationship between free electron density and A_1 (LO) phonon frequency helps to quantify the effect of free electrons on phonon behaviors. Furthermore, this relationship potentially provides a way to estimate free electron density of InN NCs by measuring Raman spectroscopy.

APPENDIX

SI 7.1 Absorbance spectra

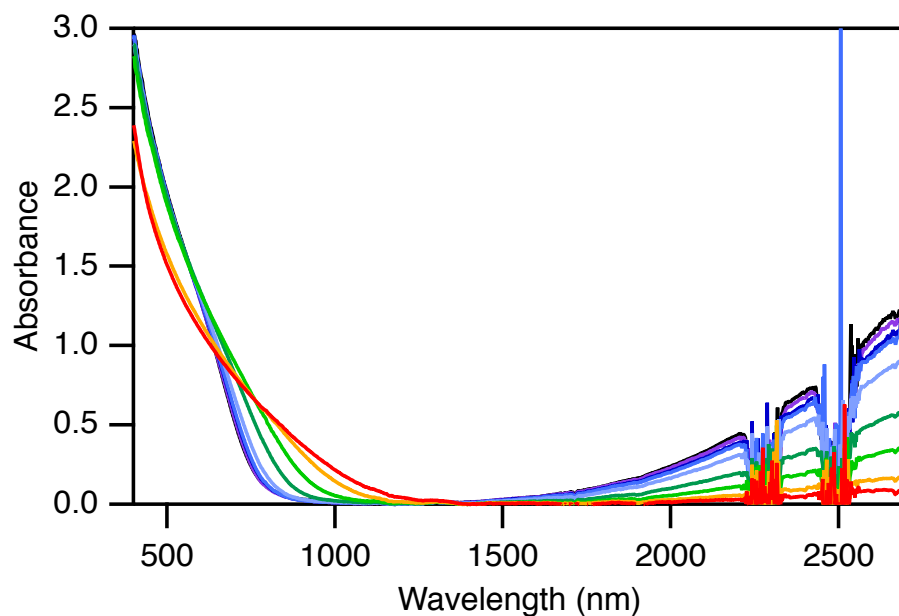


Figure SI 7.1. Absorbance spectra of 4.9 nm *i*-InN NCs with the addition of 0, 4, 17, 34, 85, 255, 510, 1700, 8500 equiv. of NOBF₄ various free electron density.

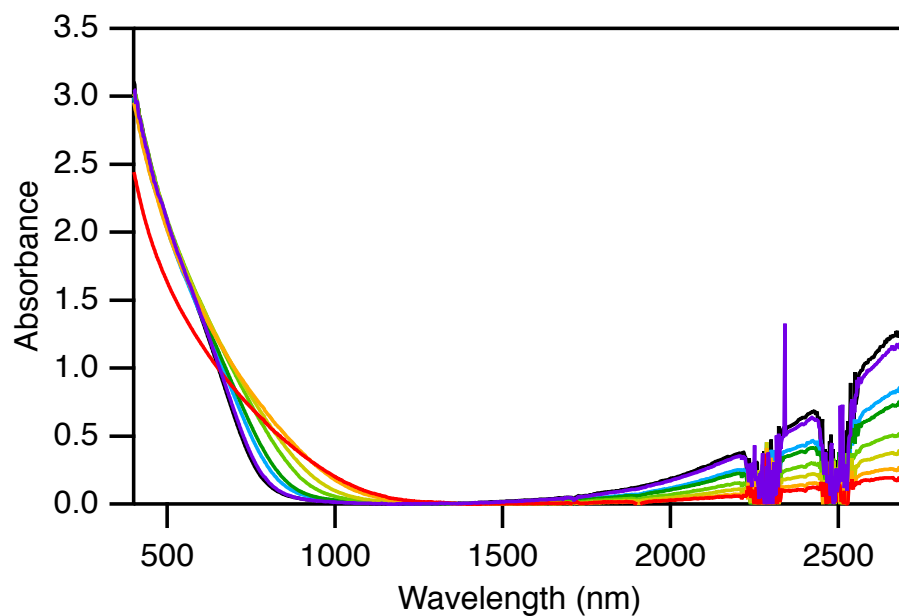


Figure SI 7.2. Absorbance spectra of 7.3 nm *i*-InN NCs with the addition of 0, 6, 87, 125, 374, 750, 2500, 12500 equiv. of NOBF₄ various free electron density.

SI 7.2 Raman spectra

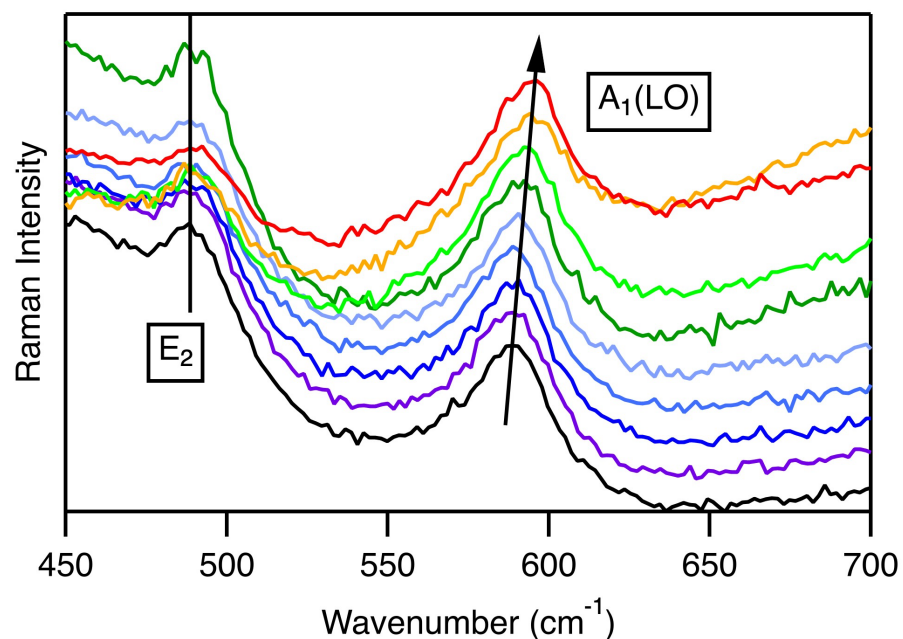


Figure SI 7.3 Raman spectra of 4.9 nm *i*-InN NCs with the addition of 0, 4, 17, 34, 85, 255, 510, 1700, 8500 equiv. of NOBF₄ various free electron density.

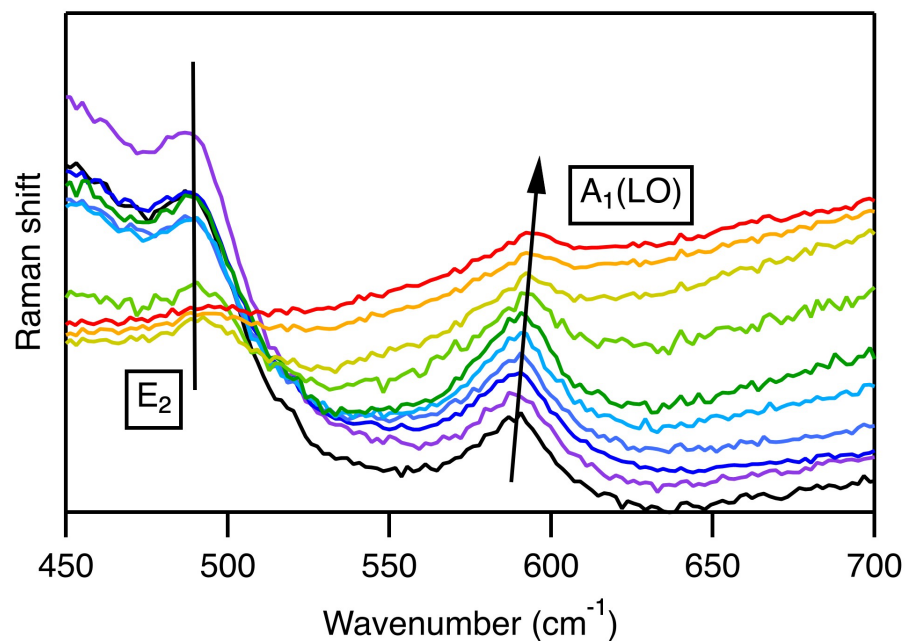


Figure SI 7.4 Raman spectra of 7.3 nm *i*-InN NCs with the addition of 0, 6, 87, 125, 374, 750, 2500, 12500 equiv. of NOBF₄ various free electron density.

SI 7.3. TEM Images and Size Distribution Analyses

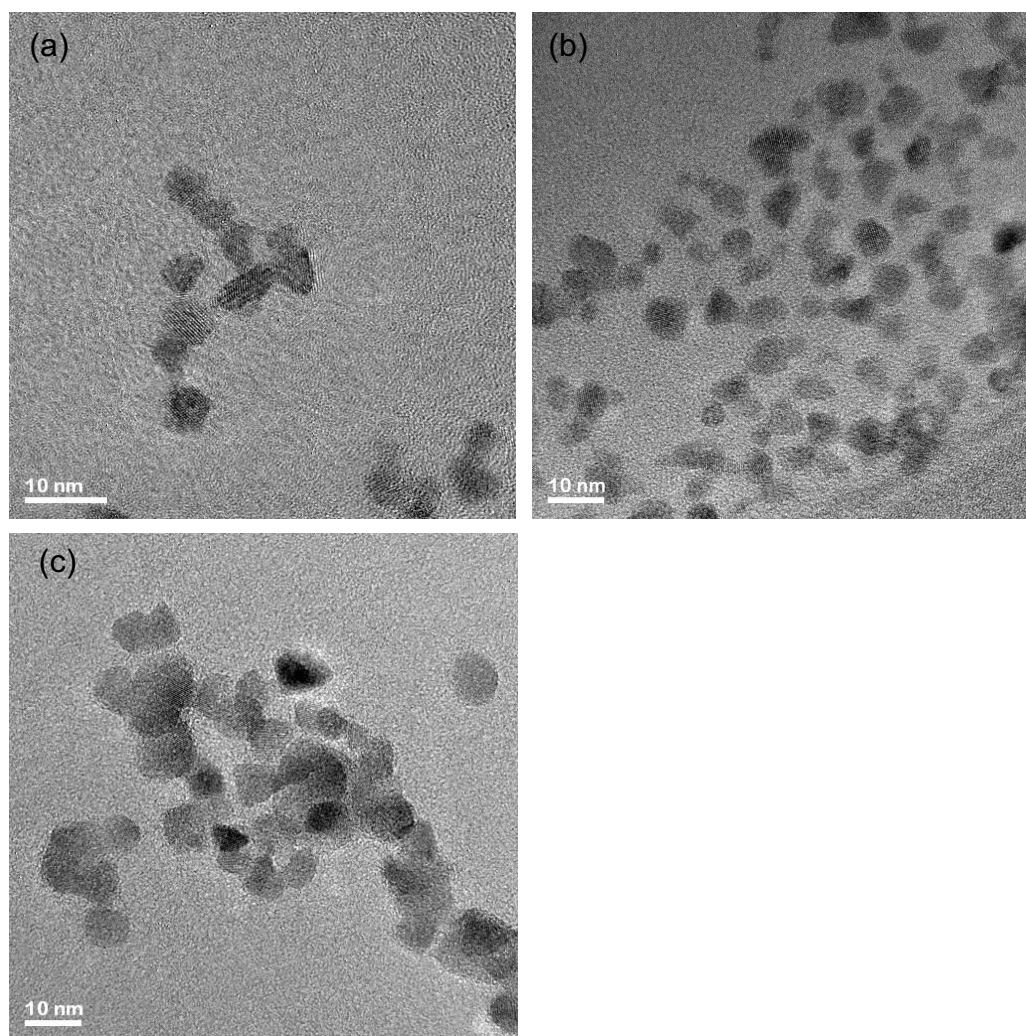


Figure SI 7.5. TEM images of different sizes InN NCs. (a) 4.9 nm, (b) 5.1 nm, (c) 7.3 nm.

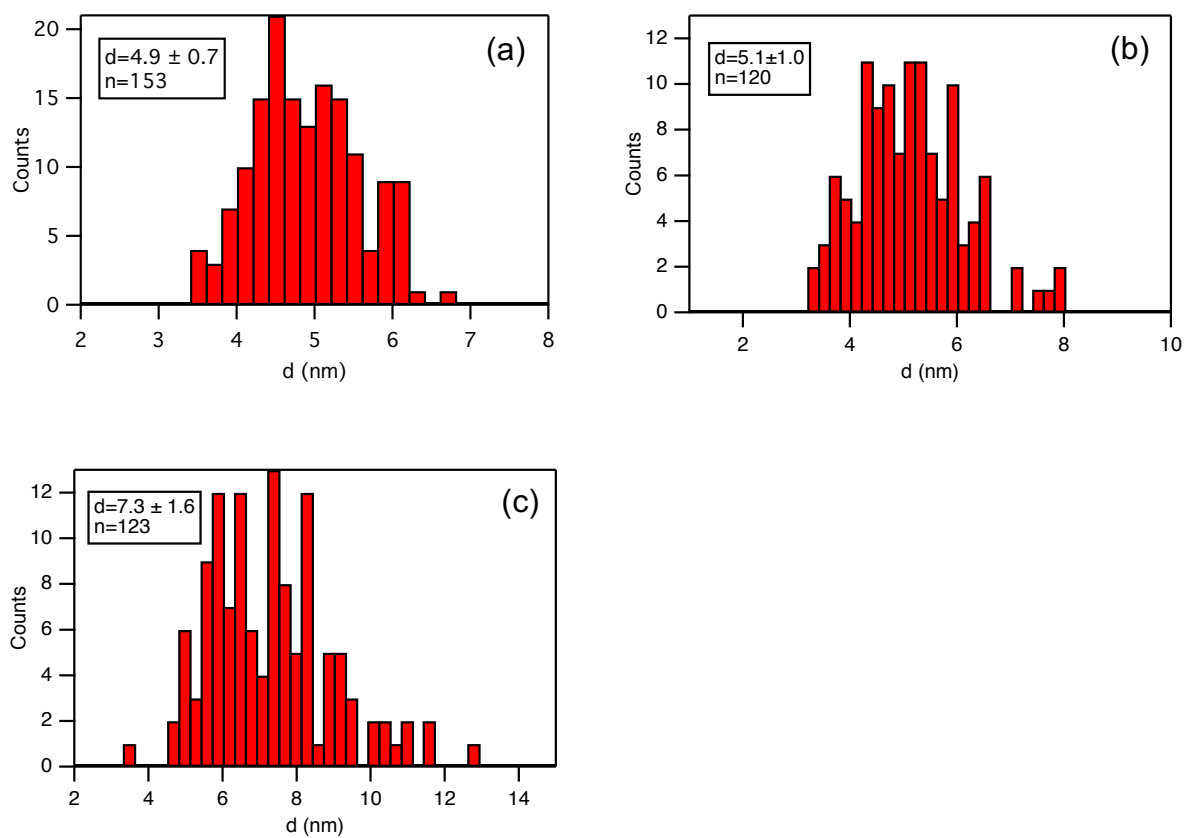


Figure SI 7.6. Histograms of different sizes InN NCs. (a) 4.9 nm, (b) 5.1 nm, (c) 7.3 nm.

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