A NOVEL APPROACH FOR THE FABRICATION OF ALL-INORGANIC NANOCRYSTAL SOLIDS: SEMICONDUCTOR MATRIX ENCAPSULATED NANOCRYSTAL ARRAYS

Pavel Moroz

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Committee:

Mikhail Zamkov, Advisor
Sri R Kolla
Graduate Faculty Representative
Ksenija Glusac
Marshall Wilson
Mikhail Zamkov, Advisor

The present work introduces a new strategy for low-temperature processing of colloidal nanocrystals into all-inorganic films: semiconductor matrix encapsulated nanocrystal arrays (SMENA). This methodology goes beyond the traditional ligand-interlinking scheme and relies on the encapsulation of morphologically-defined nanocrystal arrays into a matrix of a wide-band gap semiconductor, which preserves optoelectronic properties of individual nanoparticles. Fabricated solids exhibit excellent thermal stability, which is attributed to the heteroepitaxial structure of nanocrystal-matrix interfaces. The main characteristics and properties of these solids were investigated and compared with ones of traditionally fabricated nanocrystal films using standard spectroscopic, optoelectronic and electronic techniques.

We also characterized electron transport phenomena in different types of nanocrystal films using all-optical approach. By measuring excited carrier lifetimes in either ligand-linked or matrix-encapsulated PbS nanocrystal films containing a tunable fraction of insulating ZnS domains, we uniquely distinguish the dynamics of charge scattering on defects from other processes of exciton dissociation. The measured times are subsequently used to estimate the diffusion length and the carrier mobility for each film type within hopping transport regime. It is demonstrated that nanocrystal films encapsulated into semiconductor matrices exhibit a lower probability of charge scattering than nanocrystal solids cross-linked with either 3-mercaptopropionic acid or 1,2-ethanediethiol molecular linkers. The suppression of carrier scattering in matrix-encapsulated nanocrystal films is attributed to a relatively low density of surface defects at nanocrystal/matrix interfaces.
High stability and low density of defects made it possible to fabricate infrared-emitting nanocrystal solids. Presently, an important challenge facing the development of nanocrystal infrared emitters concerns the fact that both the emission quantum yield and the stability of colloidal nanoparticles become compromised when nanoparticle solutions are processed into solids. Here, we address this issue by developing an assembly technique that encapsulates infrared-emitting PbS NCs into crystalline CdS matrices, designed to preserve NC emission characteristics upon film processing. Here, the morphology of these matrices was designed to suppress the nonradiative carrier decay, whereby increasing the exciton lifetime up to 1 μs, and boosting the emission quantum yield to an unprecedented 3.7% for inorganically encapsulated PbS NC solids.
To my parents, Nataliia and Nikolai Moroz

For your constant support and endless love
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CHAPTER I
INTRODUCTION

1.1 COLLOIDAL SEMICONDUCTOR NANOCRYSTALS

Colloidal semiconductor nanocrystals (NCs) represent a unique class of materials. Owing to the effect of quantum confinement these species possess exceptional properties which appear when the size of the nanocrystal is lower than its exciton Bohr radius. As a result, the effect of charge confinement becomes dominant causing changes in the energy bandgap ($E_g$) and density of electronic states. This energy bandgap increases with decreasing size of the nanoparticles, making the optoelectronic properties of semiconductor nanocrystals size- and shape-dependent (Fig. 1.1). Therefore, the degree of quantum confinement in nanocrystals could be controlled during the synthesis by simple optimization of the parameters responsible for the rate of nanocrystal growth. As a result, one could synthesize nanocrystals with a photoluminescence (PL) peak tunable across a wide spectral window using the same set of precursors. Recent modifications of the synthetic protocols resulted in fabrication of the semiconductor NCs with different shapes and dimensionalities including spherical quantum dots, nanorods, nanosheets, nanowires, and tetrapods.

Another great advantage of the semiconductor nanocrystals is high colloidal stability in solution (Fig. 1.1). This property makes it possible to produce nanocrystals using wet inorganic synthesis which is much cheaper and adoptable than most of the other techniques (electron beam epitaxy or lithography). The stability in a solvent is determined by the presence of the passivating agents on the surface of NCs. These surface capping agents (organic ligands or inorganic capping materials) passivate defects and unsatisfied chemical
bonds of domain preserving quantum confinement and stabilizing nanocrystals. The nature of the ligands is responsible for the solubility of the NCs in different solvents. For instance, using various ligand exchange techniques, it is possible to transfer semiconductor NCs from organic to water phase and vice versa\textsuperscript{42,43,45-48}. This transfer is incredibly useful for the utilization of colloidal nanocrystals in biomedical applications which are conducted in aqueous media\textsuperscript{47-49}.

**Figure 1.1** Size-dependent optical properties of CdSe nanocrystals. The reduction of the NC size is accompanied by the blue shift of photoluminescence which corresponds to the stronger quantum confinement (higher $E_g$).
1.2 PASSIVATION OF SEMICONDUCTOR NANOCRYSTALS

The behavior and composition of ligands on the surface of nanocrystals were not determined for a long time. It was assumed that only anionic organic molecules are bonded to the surface making the overall nanocrystal-ligands complex neutral\(^5\). Recent studies determined the ligand-nanocrystal interaction in non-polar solvents using 1D and 2D NMR spectroscopies techniques\(^41,51\).

![Types of the surface ligands which passivate NC surface. Reprinted with permission from ref.41. Copyright 2013 American Chemical Society.](image)

It was shown that the interaction could be described using X-, L- and Z-types ligand exchange models (Fig. 1.2)\(^41\). Each class of these ligands uses different amount of electrons to make a two electron bond with nanocrystals. In theory, if the nanocrystal has 1:1 ratio of elements (M/E=1:1) the overall NC charge will be balanced and the passivation agents will be neutral (L-type ligands: amines or phosphines). Moreover, in this case the ligand exchange can happen only between neutral ligands while any polar species will not participate in ligand
exchange. In case of the “real life” nanocrystals which are metal rich (M/E > 1), the anionic ligands (X-type: carboxilates, phosphonates, halogenides, tholates, etc.) will preferably passivate the surface neutralizing a partial positive charge of the nanocrystal while Z- or L-type ligands will interact with neutral surface atoms. For instance, Owen et al.\textsuperscript{52} determined the precise atomic structures of the nanocrystal-ligands complexes for different sizes CdSe nanocrystals corresponding to Cd\textsubscript{35}Se\textsubscript{20}(O\textsubscript{2}CPh)\textsubscript{30}(H\textsubscript{2}NR)\textsubscript{30}, Cd\textsubscript{56}Se\textsubscript{35}(O\textsubscript{2}CPh)\textsubscript{42}(H\textsubscript{2}NR)\textsubscript{42}, and Cd\textsubscript{84}Se\textsubscript{56}(O\textsubscript{2}CPh)\textsubscript{56}(H\textsubscript{2}NR)\textsubscript{56}, where X= O\textsubscript{2}CPh, L= H\textsubscript{2}NR.

\textbf{A. classes of ligand exchange reactions}

\textbf{X-type}

\[
\begin{align*}
2 \text{H-X}' + \text{MX}_2 & \rightarrow \text{MX}'_2 + 2 \text{H-X} \\
\end{align*}
\]

\textbf{L-type}

\[
\begin{align*}
\text{L}' + \text{L} & \rightarrow \text{L}' + \text{L} \\
\end{align*}
\]

\textbf{Z-type}

\[
\begin{align*}
\text{M'}X_2 + \text{MX}_2 & \rightarrow \text{M'}X_2 + \text{MX}_2 \\
\end{align*}
\]

\textbf{B. Z-type ligand displacement (L-promoted)}

\[
\begin{align*}
2 \text{L} + \text{MX}_2 & \rightarrow \text{L} + \text{L-MX}_2 \\
\end{align*}
\]

\textbf{Figure 1.3} A general scheme representing the (A) types of ligand exchange reactions depending on the nature of the passivating agents and (B) neutral ligand displacement. Reprinted with permission from ref.41. Copyright 2013 American Chemical Society.
The potential ligand exchange follows: certain type of ligands will substitute ligands of the same nature and cannot substitute any other types of ligands (X’ will substitute X; L’ will substitute L etc., Fig. 1.3). This means that if one is using short-chain alcohols during the cleaning of nanocrystals there is a possibility that these alcohols will replace original L- or Z-ligands and destabilize the entire system. Shorter and weaker ligands could be easily detached from the NC creating trap states on the surface and provide an alternative pathway for the photoinduced charges (fig. 1.4). Therefore, such ligand exchange will have a negative effect on nanocrystal properties reducing the PL quantum yield (QY) and stability.

Figure 1.4 Schematic representation of the electron-hole pair generation upon photoexcitation followed by recombination with emission of light or relaxation of the electrons on the surface trap states. CB-conduction band, VB-valence band.

Thus, it is important to select proper and pure precursors along with appropriate cleaning procedure for the fabrication of stable and high quality nanocrystals. Suitable passivation agents can significantly increase key parameters of nanocrystals making them applicable in different kinds of applications.
1.3 SEMICONDUCTOR HETERONANOSTRUCTURES

1.3.1 Types of semiconductor heteronanostructures. Another interesting property of investigated materials is the ability to form heterostructures where two or more semiconductor materials are conjoined in one quantum dot. The combination of semiconductor domains opens up a new degree of freedom in manipulation of quantum confinement in NCs. The localization of each charge can be tuned depending on energetics of semiconductor domains making it possible to either preserve both charges in one semiconductor or spatially separate them through the entire volume of the nanocrystal. There are three kinds of confinement that could be observed in nanocomposites depending on localization regime: Type I, Type $I^{1/2}$, and Type II (Fig. 1.5)$^{8,53,54}$.

![Schematic band diagrams for Type I, Type $I^{1/2}$ and Type II confinement regimes.](image)

**Figure 1.5** Schematic band diagrams for Type I, Type $I^{1/2}$ and Type II confinement regimes.

In a Type I system (CdSe/ZnS, InP/ZnS, PbS/CdS), both, conduction and valence, bands of one material are situated between the band edges of another material$^{7,8}$ preserving electron and
hole in a core (Fig. 1.5 left). Thus, the photoluminescence of Type I core/shells is determined by the core material bandgap. The outer semiconductor shell covers the surface of the core increasing the photoluminescence QY, preventing the interaction of the optically active core with environment, and decreasing the amount of trap states. Moreover, the shell material with a wide bandgap increases the stability against photobleaching. These advantages could be successfully applied in light-emitting diodes (LED) or in vivo imaging where stable and bright emission is required.

The quasi-type two regime (Type I\textsuperscript{1/2}) represents a system where the electron wavefunction is delocalized between both semiconductor materials due to the negligible conduction band offsets while the hole is confined in a core (fig. 1.5, center). In this case, the smaller overlap between electron and hole wavefunctions causes the reduction of the confinement which is accompanied by the significant redshift (0.2-0.4eV) in the optical spectra and increased exciton lifetime in comparison to individual semiconductor NCs. It has been shown that quasi-type two systems with thick (“Giant”) shell can significantly reduce nonradiative losses and increase the efficiency of semiconductor nanocrystals. In many cases, the exciton recombination does not result in the emission of photon but in transfer of the energy to the third carrier, which can be detected using single nanocrystal photoluminescence intensity trajectories measurements. This phenomenon is called Auger recombination and results in “blinking” of single quantum dots. A quasi-type two system with extra thick shell provides a spatial separation of the hole wavefunction from the surface environment suppressing the Auger recombination.

The third type of heteronanostructures (Type II) represents materials where the electron and hole are spatially separated over the entire volume of the NC. Such positions of the
bandedges (Fig. 1.5, right) is typical for a number of composites including ZnSe/CdS; CdSe/CdS; CdTe/CdSe\textsuperscript{8,55,60-64}. Upon the photoexcitation, the electron and hole reach their energetic minima and localize in different domains of the nanocrystal. This phenomenon is characterized by a large red shift (>0.4 eV) in the absorbance and PL spectra. Moreover, the emitted light has much lower energy than the light that could be emitted from each of the domains individually, due to the recombination of charges at the interface of the semiconductors. The decreasing overlap between electron and hole wavefunctions leads to the slower radiative recombination rate. Owing to these properties, Type II nanocrystals are considered as promising candidates for the role of the new generation near-IR emitters\textsuperscript{65,66}, photocatalysts and lasers\textsuperscript{67}.

1.3.2 Synthesis of the core/shell heteronanostructures. The growth of the shell could be easily monitored using optical spectroscopy methods; a slight redshift of the absorption and photoluminescent peaks of the core material could be observed during the evolution of the outer domain. It happens due to the partial expansion of the exciton wavefunction to the shell which results in a reduction of the confinement during the growth of the covering material (Fig. 1.6a). However, the opposite behavior of the absorption and PL peaks could be detected during the growth of the PbS/CdS or PbSe/CdSe core/shells where Pb atoms are substituted by Cd via cation exchange\textsuperscript{68}. Here, the exchange is followed by the reduction of the PbS (or PbSe) size while the size of the entire crystal remains the same. As a result of the size shrinking, absorbance and PL features of the PbS (PbSe) shift to the blue region of spectrum demonstrating a stronger quantum confinement (Fig. 1.6b).
Figure 1.6 Changes in the absorption spectra during the growth of the CdS shell using different synthetic techniques. (a) During the growth of outer shell of CdS on CdSe NCs using hot injection method the confinement getting reduced and red shift could be observed. (b) During the cation exchange of Pb to Cd, the size of PbS core gets smaller, the peak shifts to the blue region representing stronger quantum confinement.

Sometimes the growth of the very thick shell is not beneficial because of the lattice strain\(^6\). Two materials could have a strong tension at interface which may result in the onset of the defects and trap states on the border of the two semiconductors. This phenomenon is accompanied by the drop of the PL quantum yield and exciton lifetime. In that case one should use materials which have a small lattice mismatch or grow a graded shell around a core for the fabrication of thick shell. Consequently, it is possible to smoothly transfer from the materials with smaller lattice mismatch to the materials with greater mismatch and wider band gap using the multicomponent shell material (CdSe/CdS/Cd\(_x\)Zn\(_{1-x}\)S/ZnS)\(^5,7\)
Figure 1.7 Example of different heteronanostructures: (a) ZnSe/CdS nanobarbells, (b) ZnSe/CdS dot-in-a-rod, (c) PbS/CdS core/shell nanocrystal, (d) ZnS/CdS nanoflowers.

The heterostructure architecture is not limited only to a spherical core/shell shape (Fig. 1.7). Owing to recent advances in nanocrystal synthesis it is possible to fabricate a variety of different shapes including dot-in-a-rod, nanobarbells, tetrapods, heterodimers, and nanodambbells. All of these materials can possess different localization regimes which will determine their functionality. The utilization of such systems in applications however is not so common due to the difficulty of synthesis and low uniformity.

1.4 SEMICONDUCTOR NANOCRYSTALS IN DEVICES

The size-tunable optoelectronic properties and high stability in solution have made semiconductor nanocrystals promising light-harvesting resources for different photovoltaic and electronic applications including solar cells, light-emitting devices, field-effect transistors (FET), luminescent solar concentrators (LSC), diode lasers, and memory elements (Fig. 1.8).
Recent advances in nanotechnology pushed forward the utilization and inculcation of the semiconductor nanoparticles even in manufacturing and industry. The tremendous progress in modification of the methods for NC fabrication made it possible to synthesize large amounts of the nanomaterials for different industrial needs. For instance, semiconductor nanocrystals turned to be one of the most promising materials for bio and light-emitting applications, displacing recently popular organic molecules due to the higher stability, brighter fluorescence and resistivity to photo bleaching\textsuperscript{47,49,55,81,85-89}.

**Figure 1.8** Semiconductor nanocrystals in (a) light-emitting films and (b) solar cells.

There are different inexpensive techniques for the fabrication of devices from the nanocrystal solution including spin-coating, dip-coating, inkjet printing, and successive ionic layer adsorption and reaction (SILAR). For the most of applications, it is very important to choose proper passivation strategy to fabricate a stable and efficient device. The ligands of different length and nature could be used depending on the application.

For instance, in solar cells it is important to provide a sufficient charge transfer between neighboring dots. To this end, short-chain molecules could be used to maintain a small interparticle distance and increase the coupling. Besides short interparticle distance, an
appropriate energetics and quality of the interfaces also play a crucial role during the device operation. Recent progress in the development of the PbS and PbSe quantum dots solar cells is corresponded to the introduction of the depleted heterojunction architecture along with new passivation procedure\textsuperscript{90}. Compare to previously popular Schottky architecture\textsuperscript{91-93} where the active layer is placed between two metal contacts, the depleted heterojunction devices have an additional semiconductor oxide layer which increases the depletion region, prevents recombination of charges and eliminates a Fermi-level pinning (fig. 1.9)\textsuperscript{90}. The development of strategy for functionalization of nanocrystals in the film using mercaptpropionic acid along with new architecture allowed Sargent \textit{et al.} to significantly increase the power conversion efficiency of the cell up to 5.1\% in 2010\textsuperscript{90}.

\textbf{Figure 1.9} Architecture of the (a) Schottky solar cell and (b) depleted-heterojunction solar cell.
Better understanding of the interaction between nanocrystals and ligands made it possible to predict more efficient passivation techniques. In particular, it was calculated that PbS and PbSe nanocrystals which size exceeds 3 nm undergo some shape transformations from (111) octahedron to (111)/(100) cub-octahedron\textsuperscript{94}. The new (100) facets cannot be fully passivated by organic molecules due to the high steric hindrance. As a result, bigger semiconductor nanocrystals have higher density of trap states and easily oxidize. Thus, it is important to use additional passivation agents which will cover (100) facets of the nanocrystal\textsuperscript{94-96}. Recent advances in passivation strategies have shown that nanocrystals turn more stable\textsuperscript{95,97} and efficient\textsuperscript{96} after extra treatment with halides.

Bulovic et al. has shown that different ligands on the surface of NC can shift its energy levels\textsuperscript{98}. Significant changes in energetics (shift up to 0.9 eV) are determined by the contributions of the nanocrystal-ligand interface dipole and ligand dipole moment. As a result, the cascade solar cell fabricated by combination of differently passivated PbS nanocrystals with 8.55% efficiency was reported in 2014\textsuperscript{99}.

The influence of the passivation agents on the charge carrier mobility was also studied using field-effect transistors. In these devices semiconductor nanocrystals could successfully compete with other materials due to a number of advantages\textsuperscript{7}. First, the possibility to use nanocrystal inks in a device fabrication can significantly decrease the overall cost of the FETs. Second, the high electronic coupling between nanocrystals makes it possible to overcome the carrier mobility record of many organic FET. Third, unlike most of the organic FETs, quantum dot devices could efficiently operate not only in p-type, but also in n-type and ambipolar regimes. Moreover, the operating regime could vary for the nanocrystals with the same composition but with different passivation agents.
Initial attempts to fabricate FET using nanocrystals with original bulky ligands did not have any success due to a low interparticle interaction\textsuperscript{7}. Binding or interlinking with short-chain organic molecules like dithiols\textsuperscript{100}, ethylenediamine\textsuperscript{101}, hydrazine\textsuperscript{7,102}, pyridine\textsuperscript{103} have all been considered for increasing the charge transport in NC films. Although these materials did not show an impressive stability under ambient conditions, they had promising charge carrier mobility numbers.

To increase the coupling and improve the stability of nanocrystal solids, Talapin et al. introduced metal chalcogenide\textsuperscript{44}, halide, pseudohalide and hallometallate ligands\textsuperscript{104}. Short and robust inorganic ligands make the interparticle distance smaller, increasing the electronic coupling between NCs. The best device fabricated using I\textsuperscript{-} - capped CdSe has shown promising electron mobility of \( \sim 12 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\).

Law group proposed a strategy for the stabilization of the air-sensetive S\textsuperscript{2}-capped PbSe nanocrystals using Atomic Layer Deposition (ALD)\textsuperscript{105,106}. It was shown that the infilling of nanocrystals with amorphous Al\(_2\)O\(_3\) significantly increase stability of PbSe and PbS nanocrystals on air, at high temperatures, and under UV irradiation. The fabricated FETs performed with carrier mobilities around 7 cm\(^2\) V\(^{-1}\) s\(^{-1}\).

Unlike solar cells and FETs, nanocrystalline light emitting solids required a presence of long chain ligands which act as insulator. The utilization of the original bulky oleic acid\textsuperscript{107} or other stronger-binding mercaptooctanoic acid\textsuperscript{108} or hexanedithiol\textsuperscript{109} between the nanocrystals helps to suppress the charge transfer and increase the probability of charge recombination which is beneficial in light-emitting devices.

The architecture and passivation modifications made it possible to significantly improve characteristics of nanocrystalline devices in last decade bringing them closer to the market.
Although the stability of these systems still remains a problem, the potential of the semiconductor nanocrystals is very high. The development of new efficient and stable systems with high performance is the issue that needs to be addressed in modern nanoscience.
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CHAPTER II

A NOVEL APPROACH FOR THE LOW-TEMPERATURE FABRICATION OF ALL-INORGANIC NANOCRYSTAL SOLIDS


2.1 ABSTRACT

A general strategy for low-temperature processing of colloidal nanocrystals into all-inorganic films is reported. The present methodology goes beyond the traditional ligand-interlinking scheme and relies on encapsulation of morphologically-defined nanocrystal arrays into a matrix of a wide-band gap semiconductor, which preserves optoelectronic properties of individual nanoparticles while rendering the nanocrystal film photoconductive. Fabricated solids exhibit excellent thermal stability, which is attributed to the heteroepitaxial structure of nanocrystal-matrix interfaces, and show compelling light-harvesting performance in prototype solar cells.

2.2 INTRODUCTION

The development of semiconductor thin films from nanocrystal “inks” is emerging as a powerful alternative to conventional methods of film deposition relying on high-vacuum and high-temperature processing of bulk semiconductors. In addition to the anticipated cost
reduction, the integration of solution-processed nanocrystal (NC) films into device architectures is inspired by the possibility of tuning the energy of electrical charges in NCs via nanoparticle size. This opens up an additional degree of freedom for manipulating material’s optoelectronic properties and controlling charge flow rates at heterostructured interfaces. Owing to these advantages, the deployment of semiconductor NC films in device technologies has been actively explored in the past decade through the demonstration of a wide range of NC-based applications.1-57

Over the years, several strategies for assembling NCs into functional films (also known as NC solids) have been explored. To improve electrical coupling between neighboring nanoparticles, individual NCs in these films are often interlinked with molecular bridges, utilizing either organic molecules, such as short-chain dithiols,58-61 butylamine,62 ethylenediamine,63 3-mercaptopropionic acid (MPA),64 hydrazine,49 pyridine,65,66 or inorganic metal chalcogenide complexes, such as Zintl ions.44,67 Besides enhancing an electrical conductivity of the film, these molecules perform a role of surface-passivating ligands, which presence is critical for preserving carrier localization in NCs and protecting their surfaces from oxidation. For instance, a compelling electrical performance has been reported for PbS or PbSe NC solids cross-linked with hydrazine, MPA, or 1,2-ethanedithiol (EDT)68 molecules. For these films the mobility of charge carriers reached a compelling 0.1-0.7 cm²/(Vs) level,73 which merits the performance of thin-layer devices (l<200 nm), such as solar cells, with reported power conversion efficiency (PCE) of up to 5.1 %64,69 meanwhile, the use of inorganic Zintl ion linkers,67 or recently reported Al₂O₃ in-filling of organically–linked nanocrystals70 have been demonstrated to improve the overall stability of the film. Despite these advances, the development of functional NC solids still faces several important challenges that need to be
properly addressed before electrical characteristics of these films can effectively compete with the rival technologies based on amorphous silicon\textsuperscript{71} or organic polymer films\textsuperscript{72}.

At present, the key factors limiting the competitiveness of NC devices are identified as the poor stability of NC films in heated or oxygenated environments which dramatically impacts the cost-effect characteristics of these materials in heat-intensive applications (solar cells, photodetectors, and LEDs), and the relatively low mobility of electrical charges ($\sim 1$ cm$^2$/Vs)$^{73,74}$ which leads to substantial energy losses in thick-layer devices due to charge trapping and side reactions. Notably, both of these issues are related to the nature of the interlinking mechanism in NC films and not to the properties of isolated nanoparticles. Indeed, the ligands that connect neighboring NCs in the film are attached to NC surfaces through a donor-acceptor interaction and, therefore, can readily desorb when electrically or thermally stimulated. Detachment of even a small fraction of these ligands can lead to significant changes in the film performance due to the formation of trap states,$^{39,75}$ NC oxidation, and the subsequent deterioration of the semiconductor lattice. Furthermore, dissociation of ligands has been claimed to trigger the removal of surface cations from the NC$^{76}$ which leaves behind anion terminated surface associated with deep level surface traps.

Here we address the aforementioned limitations of ligand-bound NC solids through the development of an alternative film processing strategy that goes beyond the traditional cross-linking scheme and employs a thermally and chemically stable, all-inorganic medium to encase morphologically-defined NC arrays. Here, this strategy is demonstrated by encapsulating PbS NC arrays into a matrix of a wide-band gap semiconductor (CdS, ZnS), which preserves some degree of quantum confinement in PbS nanoparticles, yet, enables both an electrical conductivity
of the film, tunable via inter-NC spacing, and an excellent thermal/chemical stability of resulting solids, facilitated by the heteroepitaxial capping of PbS NCs with the matrix material (e.g. CdS).

Figure 2.1 A flow chart showing the key steps involved in the development of semiconductor matrix-encapsulated nanocrystal arrays (SMENA). These stages include colloidal synthesis of PbS NCs (step 1), growth of the CdS shell (step 2), spincoating or dip-coating of NC films, exchange of bulky ligands with thermally degradable molecules (MPA, FA), and crystallographic fusion of NCs – all three performed using a layer-by-layer deposition (steps 3 & 4). In the last step, the pores of the PbS/CdS solid are filled with an additional CdS or ZnS.
material (step 5). In several cases, surfaces of the resulting matrix were further passivated with ZnCl$_2$ or Br (see the Experimental section).

The matrix encapsulation strategy relies on low-temperature ($T < 160\,^\circ C$) processing of semiconductor NCs, performed using spincoating or dip-coating techniques. Specifically, to incorporate an array of $S_1$ semiconductor NCs (e.g. PbS NCs) into a matrix of a wide band gap semiconductor material ($S_2$), colloidal $S_1$ NCs are first overcoated with several monolayers (ML) of $S_2$, yielding type I core/shell hetero-NCs, $S_1/S_2$, (e.g. PbS/CdS, PbS/ZnS), as shown in Fig. 2.1. Subsequently, $S_1/S_2$ nanoparticles are thermally fused into all-inorganic heteroepitaxial arrays, for which charge-confining $S_1$ cores (PbS NCs) are encased within the matrix of the cross-merged shell material, $S_2$, (Fig. 2.1, step 3). To promote a crystallographic fusion of core/shell NCs into a porous solid, at temperatures which preserve $S_1$ domains but allow for the respective shells ($S_2$) to be brought together through quasi-epitaxial bonding, spincoated films of $S_1/S_2$ core/shell NCs are capped with low-boiling-point ligands ($T < 110\,^\circ C$) and subjected to heating at $120-160\,^\circ C$. Following the ligand desorption, the surfaces of $S_2$ semiconductor in the NC solid are treated with an additional $S_2$ material, which is deposited into the pores of the $S_1/S_2$ film via chemical bath deposition (CBD) or successive ionic layer adsorption and reaction (SILAR)$^{77}$ methods (Fig. 2.1, step 5).

The electrical coupling between adjacent NCs in the resulting Semiconductor Matrix Encapsulated Nanocrystal Arrays (SMENA) is controlled either by tuning the inter-NC separation between PbS cores (via $S_2$ shell thickness), or by varying the band gap of the matrix material (CdS, ZnS). An empirical model has been developed to provide a qualitative estimate of PbS-PbS coupling energy as a function of inter-NC separation and the band gap of the matrix
semiconductor. We demonstrate that in the regime of close coupling between 1S(e) states of PbS NCs, the films are rendered photoconductive and can be utilized as an active medium in NC solar cells. Meanwhile, for weakly coupled SMENA solids (Mott insulators), 1S(e) carriers are primarily site localized, which gives rise to the observable fluorescence from PbS cores. This could have important implications for the development of infrared emitting thin-film waveguides.

The architecture of SMENA solids offers several unique advantages that could be of a substantial benefit to the development of NC devices. First, crystallographic fusion of S₁ and S₂ semiconductors into a heterostructured solid can potentially enable the construction of heteroepitaxial monoliths exhibiting a low density of lattice defects, which effectively reduces the trap state formation and minimizes carrier scattering, an important milestone towards increasing the conductivity of NC films. Second, encapsulation of S₁ NCs within a matrix of a lattice-matched semiconductor (S₂), provides an elegant approach for capping NC surfaces with a layer of an inorganic material exhibiting a greater degree of tolerance to heat and oxidation than traditional molecular ligands. Indeed, in contrast to surface molecules, the S₂ matrix (e.g. CdS or ZnS) is not prone to degradation in the ambient environment and thus won’t allow oxygen attacks on S₁ surfaces. The improved stability of matrix-encapsulated NC solids is particularly important for the development of solar-absorber materials in light of the expected thermal loads that photovoltaic panels have to withstand in field conditions. Third, the SMENA morphology allows for a continuous optimization of the inter-nanocrystal coupling, \( \beta \sim \exp\{-\alpha(\Delta x)\} \), tunable via the thickness of the S₂ shell (\( \Delta x/2 \)).
2.3 EXPERIMENTAL SECTION

2.3.1 Materials. 1-octadecene (ODE, 90% Aldrich), oleylamine (OLAM, 70% Aldrich), oleic acid (OA, 90% Aldrich), Hexadecyltrimethyl ammonium bromide (CTAB, Sigma 99%), titanium tetrachloride (TiCl4, 99.9% Aldrich), titanium(IV) isopropoxide (99.999%, Aldrich), lead(II) nitrate (Pb(NO3)2, 99.999% Aldrich), lead(II) oxide powder (PbO, 99.999% Aldrich), sodium sulfide nonanhydrate (Na2S∙9H2O, 98% Alfa Aesar), sulfur (S, 99.999% Acros), titanium dioxide (DSL 90T, DyeSol), selenium powder (Se, 99.5% Acros), tellurium powder (Te, 99.8% Aldrich), ethanol (anhydrous, 95% Aldrich), methanol (anhydrous, 99.8% Aldrich), toluene (anhydrous, 99.8% Aldrich), isopropanol (anhydrous, 99.8% Acros), octane (anhydrous, 99% Aldrich), 3-mercaptopropionic acid (3-MPA, 99% Alfa Aesar), bis(trimethylsilyl) sulfide (TMS2, Aldrich, synthetic grade), zinc chloride (ZnCl2, 99,995% Aldrich), Tri-n-octylphosphine (97%, Strem), and triton X-100 (Alfa Aesar) were used as received without any further purification. Regular acetone was distilled before using and all reactions were performed under argon atmosphere using the standard Schlenk technique. Fluorine-doped tin oxide (FTO) glass (TEC 15, 12-14 Ohm/sq) was obtained from Pilkington Glass.

2.3.2 Synthesis of PbS nanocrystals. PbS NCs were fabricated according to a procedure adapted from Ref. 79. In a typical synthesis, a mixture of 0.49 g PbO in 18 mL of ODE and 1-16 mL of OA (increasing the amount of OA results in larger NCs) was degassed in a three-neck flask at 120°C for 2 hours, switched to Argon, and heated to 135 °C. In another flask, 10 mL of ODE was degassed for two hours at 120°C and allowed to cool down to room temperature, then 0.21 ml of TMS2 was added carefully into the flask and the resulting TMS2/ODE mixture was injected into the Pb precursor solution at 135°C, while stirring. The reaction was stopped after
0-5 minutes (longer reaction time leads to larger NCs) by removing the flask from the heating mantle and placing it into an ice water bath. The nanocrystals were isolated from the mixture by precipitating with distilled acetone, centrifuging, and re-dispersing in toluene. The cleaning procedure was repeated 2-3 times, after which nanocrystals were re-dispersed in a minimal amount of octane or toluene (4-5 ml).

For example, to fabricate PbS NCs with an exciton absorption feature centered at 1140 nm, 14 mL of OA was used and the growth time was limited to 3 min. For NCs with a 1S peak at 1750 nm, 14 mL of OA was used with the growth time of 6 min. For NCs with a 1S peak at 930 nm, 1.5 mL OA was used with the reaction time of 1 min.

**2.3.3 Synthesis of PbS/CdS core/shell nanocrystals through cation exchange.** The growth of the CdS shell on PbS NCs was performed using a cation exchange methodology. To this end, 1 g of CdO was combined with 6 mL of OA and 15 mL of ODE in a one-neck 50 ml flask. This mixture was heated at 280 °C under argon until the solution turned almost clear, upon which the temperature was lowered down to 100 °C. Separately, in a three-neck flask, 20-40 mg of PbS NCs dissolved in toluene were heated under argon to 110 °C for less than 5 min to evaporate most of the excess solvent, and the contents of the Cd precursor flask were added. The mixture was then heated to between 120 and 160 °C depending on the desired shell thickness. The reaction was stopped when the final temperature was reached by placing the flask in an ice bath. PbS/CdS NCs were isolated by adding ethanol and centrifuging at 5000 RPM. The liquid layer was discarded, and the precipitate was re-dissolved in toluene. This procedure was repeated two more times. NCs were finally re-dispersed in 2-3 ml of anhydrous octane.
The following example illustrates how the reaction temperature affects the growth of the CdS shell, which evolution is measured as a blue-shift of the PbS exciton absorbance. To achieve a blue-shift of $\Delta \lambda = 140$ nm (approx. 0.55 nm of the CdS shell), the mixture was allowed to reach $110^\circ$ C in 5 min. For a blue-shift of $\Delta \lambda = 220$ nm, the temperature was allowed to increase to $130^\circ$ C. For a shift of $\Delta \lambda = 45$ nm, the reaction was immediately quenched in an ice water bath after the injection of the Cd precursor into the PbS NC solution.

2.3.4 Preparation of TiO$_2$ on FTO/glass substrates. FTO-coated glass was cut into 2.5 cm x 2.5 cm squares, then washed by hand with detergent (Alconox), and rinsed clean in deionized water. It was then sonicated in methanol, acetone and isopropanol for 5 minutes in each solvent. Once dry, the substrate was placed in a bath of 75 mM TiCl$_4$ solution in deionized water and was heated (in air) for 30 min at 70 °C. The substrate was then rinsed with deionized water, dried under argon, heated to 450 °C for 1 hour and then allowed to cool to room temperature. Meanwhile, the TiO$_2$ DyeSol paste was dissolved in terpinol in a 3:1 ratio by weight. 3 drops of the TiO$_2$ solution was placed in the center of a dry TiCl$_4$-treated FTO/glass slide, and spun for 6 seconds at 700 RPM, and for 1 minute at 2000 RPM. The substrate was then annealed outside the glovebox (ambient oxygen environment) at 450-500 °C to remove organic matter.

2.3.5 Fabrication of PbS/CdS nanocrystal films from solution. To fabricate an all-inorganic film of PbS/CdS NCs layer-by-layer methodology was employed. All steps were performed inside the glovebox. Typically, 4-5 drops of PbS/CdS NCs in octane (in concentration of 10 mg/mL) were placed onto a still TiO$_2$/FTO glass slide, and allowed to spread until it covered the substrate. The NC solution was left to soak until the center dried, then spun at 2500
RPM for 30 seconds. Next, 10 drops of a 1:3 MPA/methanol solution was placed on the film fully covering the surface, then spun at 2500 RPM for 15 seconds. The film was then washed with 10 drops of methanol and subsequently spun at 2500 RPM until dry, then washed once again with 10 drops of octane in the same manner. The film was annealed at 150-160 °C for 15 minutes after every three layers. Overall, 8-10 layers were needed to form a 300-nm SMENA film. The OA \rightarrow formic acid (FA) ligand exchange processed was performed using a dip coating approach. Typically, upon spincoating of 4 drops of PbS/CdS NCs onto an FTO/glass substrate, the sample was placed into a 10 mM solution of FA in acetonitrile for 1 minute and then rinsed with dry acetonitrile for 1 minute.

2.3.6 In-filling of SMENA pores with CdS. To deposit CdS into the pores of an annealed, all-inorganic, PbS/CdS film, a cadmium bath was prepared by dissolving 0.43 g of cadmium acetate in 80 mL of methanol. The sulfur bath was made by combining of 0.38 g of Na2S·9H2O with 80 mL of methanol. The sample was placed in the cadmium bath for 1 minute, then rinsed with methanol for 1 minute, then placed in the sulfur bath for 1 minute, then finally washed in methanol again. This process was repeated 2-16 times, depending on the desired number of CdS monolayers. The film was then annealed at 150 °C for 15 minutes. For in-filling with ZnS, 0.34 g of Zinc acetate in 80 mL of methanol was used in place of Cd.

2.3.7 Passivation of SMENA surfaces. To passivate CdS or ZnS surfaces of SMENA films, two different strategies were used. As one option, ZnCl2 treatment of fabricated films was employed. To initiate this procedure, a combination of 0.1M of ZnCl2 and 0.1M of HCl in water was prepared. The sample was placed in the HCl/ZnCl2 solution for 1 minute, and then rinsed
with deionized water. The cells were subsequently heated under Argon to 150 °C for 15 min. The second surface passivation strategy was based on recently reported CTAB treatment,\textsuperscript{69} which leaves Cd\textsuperscript{2+} cations terminated with Br. Typically, following the SILAR in-filling step, 0.25 mL of CTAB (concentration of 10 mg/mL) was placed on the film and allowed to sit for 1 min, then rinsed with 10 drops of methanol and spun until dry. This was repeated one more time.

2.3.8 Deposition of Au/Pd counter electrodes. To complete the cell assembly, 20-60 nm of gold-palladium (Au-Pd, 40/60) counter electrodes were coated on top of the film using Polaron E500 sputter, which was equipped with a ≈2-mm diameter shadow mask generating 16 pixels in each device. The area of each pixel was estimated to be 0.03 cm\textsuperscript{2}.

2.3.9 Preparation of the best-performing solar cell. The construction of the cell was initiated with the FTO cleaning procedure and a subsequent deposition of a TiO\textsubscript{2} layer using TiCl\textsubscript{4} bath and TiO\textsubscript{2} DyeSol paste treatment steps, as described above. A sample of PbS/CdS core/shell nanocrystals (PbS/CdS nanoparticles diameter = 3.60 nm, CdS shell thickness ≈ 0.24 nm, 1S absorption feature of the core at λ=1020 nm) was prepared in hexane in the concentration of ≈10 mg/ml. To deposit each layer, 5 drops of NCs in octane were placed on the slide, and allowed to spread until it covers the substrate. The NC solution was left until the center dried, then spun at 2500 RPM for 15 seconds. Next, 10 drops a 1:3 solution of MPA in methanol was placed on the film so that the MPA covers the film, then spun at 2500 RPM for 15 seconds. The film was then washed with 10 drops of methanol then spun at 2500 RPM until dry, then washed once again with 10 drops of octane in the same manner. Every third layer, the film was heated to 150° C for 15 mins. When 9 cycles had been completed, the film had four cycles of pore filling.
with CdS, per the above instructions. After SILAR, 0.25 mL CTAB (concentration of 10 mg/mL) was placed on the film and allowed to sit for 1 min, then rinsed with 10 drops methanol and spun until dry. The films had approximately 60 nm of Au-Pd sputter coated as a back contact. Prior to any measurements being done, a small portion of the film was removed via a cotton swab soaked in acetone, until the FTO surface is exposed enough to make contact.

2.3.10 Characterization. Absorbance spectra were recorded using CARY 50 scan and Simadzu UV-3600 UV-vis-NIR spectrophotometers. High-resolution transmission electron microscopy (HR-TEM) measurements were carried out using JEOL 3011UHR and 2010 transmission electron microscopes, operated at 300 and 200 kV, respectively. To prepare a TEM sample, a small amount of NC film was scraped, dispersed in toluene by sonication, dropped onto a carbon-coated copper grid, and allowed to dry in air. X-ray powder diffraction (XRD) measurements were carried out on a Scintag XDS-2000 X-ray powder diffractometer. Energy dispersive X-ray (EDX) emission spectra were measured using an EDAX X-ray detector located inside the Inspect scanning electron microscope (SEM). The electron beam was accelerated at 10 kV. Current-voltage characteristics were performed under AM 1.5 G (100 mW/cm²) solar simulator using I-V data acquisition system from PV measurements, Inc., while, the incident photon to charge carrier efficiency (IPCE) was measured using a home-build system comprising a xenon lamp, a CM110 1/8 m monochromator, a SR-830 lock-in amplifier.

2.4 RESULTS AND DISCUSSION

A detailed description of the main steps (see Fig. 2.1) involved in the preparation of CdS- and ZnS-encapsulated PbS NC arrays (SMENA) is provided in the Experimental section. Briefly,
hot-injection colloidal syntheses were used to fabricate nearly monodisperse PbS NCs (Δd < 6%, Fig. 2SF1) according to a methodology adapted from Ref. 81. The CdS shell was subsequently grown on PbS NCs through a Pb$^{2+}$→Cd$^{2+}$ cation exchange reaction, which relies on the replacement of an outer layer in PbS NCs with CdS, such that the size of nanoparticles does not change during growth. This allows preserving a low dispersion of nanocrystals diameters during the PbS → PbS/CdS transformation (s.d.: 6% → 7%, Figs. 2SF2, 4a), as was exemplified by the demonstrated ability of PbS/CdS NCs to form ordered patterns upon solvent evaporation (Fig. 2.4a). The thickness of the CdS shell was controlled with a submonolayer precision by tuning the temperature of the growth solution during the cation exchange reaction (see details in the experimental section). According to the high-resolution (HR) TEM analysis of several PbS/CdS core/shell structures (Fig. 2.2b, 2SF2c), CdS shell grew uniformly on the surface of PbS NCs without noticeable lattice defects, which was attributed to a relatively low lattice stress at the interface of PbS and CdS crystal phases (strain≈1.7%). A good lattice match at the core/shell boundary has also enabled the growth of large CdS shells totaling 14-16 monolayers (ML). Notably, even for large-diameter core/shell NCs comprising 14 MLs of CdS, HRTEM examination did not reveal any evidence of stacking faults in the shell phase (Fig. 2.2c), further confirming the existence of low-strain matching between PbS and CdS lattices. The character of charge confinement in PbS/CdS core/shell NCs was substantiated based on steady-state spectroscopy of excitonic transitions in these nanoparticles. According to Fig. 2.2d, the Pb$^{2+}$→Cd$^{2+}$ cation exchange in PbS NCs results in blue-shifting of the absorption and emission features, which is attributed to the decreased length of the carrier confinement in PbS cores. The magnitude of this spectral shift is proportional to the reduction in the PbS diameter (see Eq. 2.SE1 and Fig. 2.SF1) and was used here for estimating the thickness of the PbS layer that was
converted into the CdS shell. In addition to blue-shifting of excitonic transitions, the transformation of PbS NCs into PbS/CdS core/shell structures was accompanied by a 5-10 fold increase in the emission intensity, which reflected a diminishing probability of core-localized charges to be trapped on NC surfaces.

**Figure 2.2** High resolution TEM images showing the formation of the CdS shell over PbS NCs during the cation exchange reaction. (a) – an oleic acid capped PbS NC. (b) – a PbS NC coated with 4-5 monolayers of the CdS shell. (c) A PbS NC coated with 12-14 ML shell of CdS. (d)
Changes in the absorption and emission of PbS NCs resulting from the deposition of approximately 1 ML of the CdS shell. Both features blue-shift by \( \approx 150 \) nm, reflecting a decrease in the core diameter. The PbS fluorescence intensity is enhanced due to the formation of type I heterostructure.

Such enhancement of the emission yield upon shell growth is consistent with the onset of the type I carrier localization in PbS/CdS core/shell heterostructures, for which both electrons and holes reside primarily in the core domain of the composite NC. We note that core-localization of photoinduced charges is important for the development of SMENA solids, as it allows preserving the quantum confinement of matrix-incorporated NCs and enables the tunability of excited state energies via nanoparticle size.

To facilitate a low-temperature fusion of core/shell NCs into an all-inorganic film, the original, oleic acid (OA) ligands on NC surfaces were exchanged with thermally-degradable molecules, such as MPA (\( T=111 \) °C) or formic acid (FA, \( T=101 \) °C). Based on the fact that NCs form better “inks” when dressed with bulky OA ligands, the ligand exchange process was performed after the film deposition, which was achieved by exposing spincoated solids of OA-capped NCs to a solution of a new ligand. Layer-by-layer (LbL) cycling was employed to facilitate a complete replacement of OA with MPA (FA) and to prevent cracking of the film due to the volume reduction. Typically, a 30-nm-thick layer of NCs was deposited on each LbL cycle, followed by the treatment with a solution of an incoming ligand (MPA, FA) and subsequent heating of the film to approximately 140-160 °C. Special settings of the spin-coating process comprising both soaking and spinning stages were necessary for achieving good-quality films. Please see the experimental section for more details.
Figure 2.3 Fourier transform infrared spectroscopy (FTIR) analysis of the organic residue in NC solids. (a-c). Crystallographic fusion of MPA-capped PbS/CdS NCs. (c). A typical FTIR transmission spectrum of OA-capped PbS/CdS NCs in a film, showing characteristic $C_{sp^2}$-H and $C_{sp^3}$-H vibrational transitions of OA molecules. (b). The OA→MPA ligand exchange process is accompanied by the red-shift of both $C_{sp^3}$-H peaks and a simultaneous onset of the COOH feature at $k=2620$ cm$^{-1}$ (a). FTIR spectrum of the NC film heated at 140 °C for 20 min, showing
a significant reduction in the amplitude of MPA vibrational transitions. (d-f). Crystallographic fusion of FA-capped PbS/CdS NCs.

According to FTIR measurements of NC films after the ligand exchange step, most of the original OA ligands were successfully replaced with MPA or FA molecules, as was attested by a 6-7 cm$^{-1}$ redshift of C$_{sp3}$H lines.$^{84}$ The subsequent thermal evaporation of MPA (FA) ligands resulted in quenching of the respective vibrational transitions (Fig. 2.3c), confirming the removal of the organic phase from NC films. Desorption of organic ligands in films annealed at 140-160 °C was consistent with the observation of the crystallographic fusion across adjacent NCs in electron microscope images (Fig. 2.4h).

The effect of ligand desorption on the morphology of NC films was investigated using transmission electron microscopy (TEM). To perform a TEM analysis, fragments of annealed SMENA films were scratched from the FTO substrate using a needle tip, re-dissolved in toluene by sonicating for 15 min and deposited onto a carbon grid from the solution. According to TEM images (Figs. 2.4d and 2.4g), heating of MPA-capped NCs to as low as 100 °C promotes initial clustering, while annealing at 150 °C for 20 min results in the crystallographic fusion of neighboring NC shells, manifested by the formation of continuous fringe pattern across adjacent NCs (Fig. 2.4h,f). For these films the excitonic features of encapsulated PbS NCs were clearly distinguishable in the absorbance spectra (Fig. 2.9d), indicating that the quantum confinement was partly preserved during the fusion process. These measurements agree with previous studies showing that epitaxial fusion of high reactivity facets of NCs can occur at temperatures as low as 60-100 °C, provided that organic ligands are desorbed from NC surfaces.$^{85}$
Figure 2.4 TEM images of PbS/CdS NCs and fragments of the SMENA. (a, b) – PbS NCs capped with a thin shell of CdS (~ 1-2 ML). (c) – A fragment of the SMENA solid fabricated via crystallographic fusion of cubic-shaped PbS/CdS NCs at 150 °C. (d, g) – 4.3-nm PbS/CdS NCs fused at 100 °C. (e, h) - 4.3-nm PbS/CdS NCs fused at 150 °C. (f, g) - Fragments of the SMENA solid fabricated by fusing thick-shelled PbS/CdS NCs (4.3-nm PbS coated with 12-14 ML of CdS) at 150 °C. Epitaxial associations of neighboring CdS shells can be seen in (f).

In order to improve the conductance of SMENA solids, trapping and scattering of carriers should be reduced to a minimum. While the shell growth and the subsequent fusion of core/shell NCs is expected to result in the formation of high quality interfaces at PbS-CdS\textsuperscript{80} and CdS-CdS\textsuperscript{86} boundaries (Fig. 2.2b and 2.4f, respectively), which are associated with little charge scattering,
the surfaces of interfused NCs can still produce carrier traps limiting the carrier diffusion lengths. Ideally, close packing of NCs in a solid with minimal amount of exposed surfaces is desired. This scenario is realized for cubic-shaped core/shell NCs, which form closely packed nanocrystal films upon fusion (Fig. 2.4c). Packing of round NCs on the other hand is less ordered and produces a significant fraction of unpassivated surface areas, at which carriers can trap and subsequently decay without reaching the opposite electrode. To passivate these surfaces, NC solids can be further treated with an additional S₂ material (CdS, ZnS), which is introduced into the pores of fused core/shell NCs via CBD or SILAR methodology. This step results in partial filling of gaps in SMENA, giving rise to monolithic solids, with identifiable CdS lattice structure (see Fig.2.5). The ability of Cd and S ions to penetrate through nanoparticles films has been exemplified in recent experiments on porous TiO₂ films (3-4 µm in thickness), for which CdS material is deposited throughout the entire depth of the film⁸⁷ (judging by the even coloration of both the front and the back sides of the opaque Degussa TiO₂ layer on glass). Notably, filling the pores of inter-fused PbS/CdS core/shell NCs with additional CdS does not increase the inter-NC distance, and thus, does not affect the electrical coupling between nanoparticles in the film.

![Figure 2.5](image-url) **Figure 2.5** Electron microscope images of the SMENA solids following the pore filling step. (a). Scanning electron microscope image of PbS/CdS films. (b). TEM image of a SMENA fragment.
(c). The enlargement of the highlighted area in (b), showing lattices fringes, which correspond to SILAR deposited CdS.

According to Figs. 2.3a and 2.3d, NC solids resulting from fusion and pore-filling steps contain no traces of organic material, and show identifiable excitonic features of incorporated PbS NCs. Based on FTIR and absorbance spectra we thus conclude that the presented strategy yields an all-inorganic encapsulation of PbS NCs exhibiting quantum confinement of electrical charges.

The structure of hetero-interfaces between PbS and CdS domains was further investigated using an x-ray powder diffraction (XRD). Characteristic XRD spectra in Fig. 2.6 compare the diffraction pattern of the three samples comprising OA-capped PbS NCs (a), fused PbS/CdS core/shell NC films annealed at 150 °C (b), and PbS/CdS solids after the CBD pore-filling step (shown in c). According to Fig 2.6a, the Bragg lines corresponding to pure PbS NC powder closely match the PbS rock salt structure, as indicated by the set of blue ticks. Growth of the 0.4-nm CdS shell onto PbS NCs produces the second set of Bragg lines matching the zinc blende phase of the CdS lattice (denoted by green ticks). The absence of an alloying effect (generally manifested by broadening of Bragg peaks) and the low density of irregularities along material boundaries observed in HRTEM images of PbS/CdS NCs were interpreted as evidence of quasi-epitaxial bonding between PbS and CdS lattices. Upon filling the pores of PbS/CdS films with additional CdS semiconductor deposited using 7 SILAR cycles, the diffraction pattern of resulting PbS/CdS solids shifted further towards higher angles (Fig. 2.6c), indicating an increase in the volume fraction of CdS material. An apparent widening of Bragg lines in this case was attributed to unresolved contributions from PbS rock salt and CdS zinc blende crystal phases.
Improving the thermal stability of NC films is of central importance to their deployment in device applications. In organically-interlinked NC arrays, a complete thermal sintering occurs at relatively low temperatures \( (T \approx 150-170 \, ^\circ C) \). In the case of SMENA solids, the presence of the matrix semiconductor on NC surfaces is expected to prevent the early oxidation process, such that the thermal degradation of NCs is expected to occur at higher temperatures \textit{via} phase transition of the lattice. Here, we test this hypothesis by comparing the thermal stability of PbS NCs incorporated into CdS matrices with that of organically-interlinked PbS NC films. To this end, the effect of the substrate temperature on area of the 1S(e)-1S(h) absorption peak in both films was investigated.
Figure 2.7 Comparison of the thermal stability of MPA-linked (a) and CdS-encapsulated (b) PbS NC arrays. (c). Temperature dependence of the 1S peak area. $R_{\text{edge}}$ is defined as the closest edge-to-edge distance between adjacent PbS NCs in the matrix, which is calculated as twice the thickness of the CdS shell.

According to Fig. 2.7, heating of (a) MPA-interlinked and (b) CdS-encapsulated PbS NC films in inert atmosphere results in eventual bleaching of the 1S(e)-1S(h) exciton peak, which was taken as a sintering point of PbS NCs. In the case of PbS films encapsulated with $\approx$ 0.8 nm of CdS shell, the sintering temperature was roughly 50 °C above that of MPA-interlinked PbS NC arrays while for PbS NCs capped with 1.4 nm of CdS the temperature difference,
$T_{c}(\text{PbS/CdS}) - T_{c}(\text{PbS}_{\text{MPA}})$, reached 80 °C. In both cases, SMENA films were not treated with an additional CdS (pore filling step), such that the observed enhancement in the thermal stability of PbS NCs incorporated into SMENA solids was attributed solely to the existence of the CdS shell. Upon filling of the SMENA pores with additional CdS (6 SILAR cycles) in films with CdS shell of 0.55 nm ($R_{\text{edge}}=1.1$ nm), the sintering temperature was increased by additional 18 °C, as evident from the comparison of the black-circle (no SILAR) and black-square (6 cycles of SILAR) curves in Fig. 2.7. The evolution of the absorption spectra for the latter film is shown in Fig. 2SF3. Overall, the above experiments confirm that matrix encapsulation of NC array results in an enhanced heat resistance of incorporated NCs as compared to organically-interlinked NC solids.

In addition to the observed increase in the thermal threshold for sintering, the shape of PbS NCs capped with CdS appeared to evolve differently with increasing temperature than that of MPA-linked solids. As seen in Fig. 2.7a, heating of organically passivated PbS NCs resulted in a progressive red-shifting of the exciton absorption peak, while CdS-capped PbS (Fig. 2.7b) underwent an initial blue-shift followed by an eventual red-shift at $T=170$-$175$ °C. A similar trend was observed for pore-filled SMENA films, which absorbance changes are shown in Fig. 2SF3. The difference in the evolution of absorbance spectra for the two types of films is attributed to the fact that heating of MPA-linked NCs promotes ligand desorption and subsequent clustering of neighboring PbS nanoparticles, as evident by the decrease in the confinement length and associated red-shift of the absorbance peak starting at $T=100$ °C; meanwhile thermal sintering of PbS/CdS SMENA preserves the same length of quantum confinement throughout the 25-170 °C range causing some shrinking of PbS cores due to allowing of the PbS/CdS interface (as manifested by a blue-shift of the exciton peak), before sintering-induced red-shifting.
becomes dominant at higher temperatures \((T > 170 \, ^\circ\text{C})\). This is an important result, indicating that the initial sintering in CdS-capped PbS NC arrays occurs \emph{via} alloying of the PbS/CdS interface and not through clustering of PbS NCs.

One of key parameters that determine the macroscopic properties of NC solids is the degree of coupling between electrical charges in the film.\(^7\) When electronic states of neighboring NCs are strongly coupled, the associated charge carrier wave functions delocalize over the entire NC array. This creates conduction channels for electrons and holes to move freely, much like it happens in an ordinary crystalline solid. These films are thus best suited for applications requiring the transport of charges, which include solar cells, photodetectors, and FETs. Conversely, in films with weakly coupled NCs, the site-localization of excited carriers suppresses the transport of charges across the solid, turning the film insulating. The existence of large potential barriers between NCs in this case enables the radiative decay of excitons, which can find potential use in such applications as lasers, waveguides, and LEDs.

Theoretically, the energy of inter-nanocrystal coupling in a film can be expressed within the Wentzel-Kramers-Brillouin (WKB) approximation as,\(^9\)

\[
\beta \approx h \nu \exp \left( -2 \frac{m^* \Delta E / h^2}{R_{\text{edge}}} \right) \tag{2.1}
\]

where \(\nu\) is a constant with the units of frequency, \(m^*\) is the carrier effective mass, and \(R_{\text{edge}}\) is the shortest edge-to-edge distance between the adjacent NCs in the film. This fairly simple approach takes into account only the resonant tunneling mechanism of charge coupling between adjacent nanocrystals, and does not include the effects of disorder or level-broadening in the system. The magnitude of the energy term in Eq. 2.1 determines the type of charge coupling in NC films, which is inferred from the ratio of the coupling energy \((\beta)\) to the charging energy \((E_c)\), defined as
the energy required for adding an extra charge to a NC,\(^91\) as well as the ratio of \(\beta\) to the room-temperature \(k_BT\). Since for most NC films, \(E_c\) is greater than \(k_BT\) (at \(T = 30^\circ C\)), one can define three distinct regimes of charge localization in NC solids. First, when \(\beta < k_BT\) carriers are strongly localized, such that the resulting NC film is essentially insulating. In this case, the charge transport can occur only through tunneling. In the regime when \(k_BT < \beta < E_c\), carrier wave functions overlap across domains of several NCs but the states are still separated by the Coulomb gap.\(^92\) In the third regime, when \(\beta > E_c\), also known as the Mott metal–insulator transition (MIT),\(^91,93\) wave functions become delocalized throughout the entire solid, such that the film properties start to resemble those of crystalline bulk materials.

Here we estimate the nature of electric coupling in fabricated SMENA solids by modeling the electron coupling energy as a function of inter-NC separation (\(R_{\text{edge}}\)) for the three SMENA systems: 4-nm PbS NCs in a CdS matrix, 6-nm PbS in a CdS matrix, and 4-nm PbS in a ZnS matrix. Figure 8a shows a relative alignment of band edges for these hetero-nanomaterials, which was partly confirmed in this work through the observation of the characteristic optical properties (e.g. Fig. 2.2d). According to the energy diagram, the strongest localization of electrons is expected to occur in a PbS/ZnS system, while 4-nm PbS NC arrays encased within a CdS matrix should exhibit the highest degree of state delocalization. Notably, when the diameter of PbS is less than 4 nm, the PbS/CdS NCs could transition into a quasi type II heterostructure.\(^94-96\) In such nanoparticles, electrons are delocalized over the entire volume of the solid, causing the loss of the quantum confinement in the system. While this type of NC coupling constitutes an interesting case of bulk-like NC solids, the present experiments are mainly focused on systems for which a non-vanishing inter-NC potential barrier still exists, such that the energies of excites states could be tuned \(\text{via}\) the nanoparticle size.
Figure 2.8 (a). Energy diagram showing a relative alignment of conduction and valence band edges at hetero-interfaces of three NC/matrix combinations: 4.0-nm PbS/CdS, 6.0-nm PbS/CdS, 4.0-nm PbS/ZnS, representing the cases of delocalized, domain localized, and site localized 1S(e) wave functions, respectively. (b). The plot illustrates the dependence of coupling energy ($\beta$) on inter-NC distance ($R_{\text{edge}}$) for the three material systems shown in (a). The colored areas (red, blue, and green) indicate the regime of delocalized electrons, while grey-shaded areas highlight the regime of strongly localized charges.

The results of model calculations are summarized in Fig. 2.8b. For each of the investigated material systems, we identify three coupling regimes, denoted as: 1- delocalized electrons (colored area, $\beta > E_c$), 2 - domain localized electrons or tunneling coupling regime ($k_B T < \beta < E_c$), and 3 - site localized electrons or Mott insulator regime (grey shading, $\beta < k_B T$). The
$R_{\text{edge}}$ parameter is calculated in relative units of length, which preserve the correct length ratio of MIT to Mott transitions between the three investigated SMENA systems. For instance, according to Fig. 2.8b, the same inter-NC separation, $R_{\text{edge}}$, turns 4-nm-PbS/CdS solids conductive, while rendering 4-nm-PbS/ZnS films insulating. These calculations also indicate that the value of $R_{\text{edge}}$ associated with the MIT transition in 4-nm-PbS/CdS solids is 1.5 times greater than that of 6-nm-PbS/CdS, and 3.1 times greater than that of 4-nm-PbS/ZnS solids.

The predicted regimes of NC coupling are in line with the experimental results obtained using the two types of NC solids representing the case of highly delocalized and strongly insulating films. The former was fabricated by incorporating $\approx$ 3.8-nm PbS NCs into a CdS matrix, such that the inter-NC spacing, $R_{\text{edge}}$, was 0.7 nm (1S exciton feature at $\lambda$=1070 nm). For these solids, the OA→MPA ligand exchange step quenched most of the original PbS band-edge fluorescence, indicating the onset of the strong coupling even in the presence of short-chain ligands on PbS surfaces. The subsequent crystallographic fusion of the respective shells resulted in the complete suppression of fluorescence and simultaneous widening of the exciton absorption peak, which was interpreted as evidence of further delocalization of 1S electrons. The presence of characteristic quantum confinement features in the absorbance spectra of annealed NC films (Fig. 2.9d), however, indicated that the regime of strong delocalization (regime 1) was not reached for $R_{\text{edge}}= 0.7$ nm. Only by decreasing $R_{\text{edge}}$ in PbS/CdS solids to less than 0.5 nm, we were able to reach the regime of strong coupling, characterized by a significant widening of the 1S exciton absorbance. The conductance of 3.8-nm PbS/CdS films with an expected, domain-localization of NC charges, was found to be comparable to that of MPA-linked solids, as was attested by similar performances of CdS-encapsulated (Fig. 2.9b) and MPA-linked (Fig. 2.SF4) PbS films in prototype solar cells.
To fabricate NC solids showing strong localization of charges (regime 3), 3.0 nm PbS NCs were coated with 2.4 nm of CdS shell followed by 0.4 nm of ZnS shell. In this case, the direct deposition of more than 1 ML of ZnS onto PbS NCs did not result in the formation of a uniform shell, possibly due to a significant mismatch of lattice constants for these semiconductors (strain ≈ 8.2%). The employment of a CdS intermediate layer facilitated a gradual relieve of the lattice stress and allowed depositing 0.4 nm of ZnS (R_{edge} = 2 \times (0.4+2.4) \text{ nm} = 5.6 \text{ nm}). The resulting PbS/CdS/ZnS NCs solids, were developed on top of FTO glass (sufficient surface roughness was required for the films to adhere to the substrate) by fusing MPA-capped NCs at 150 °C, followed by the ZnS pore in-filling step. According to Fig. 2SF4, the band edge emission of all-inorganic PbS/CdS/ZnS solids was still distinguishable after the annealing step, indicating a strong localization of both carriers at PbS sites. The insulating character of these films was confirmed in photocurrent measurements, for which the resulting current density did not exceed 0.01 mA/cm² at AM1.5 illumination.

The photovoltaic characteristics of SMENA films were investigated using a depleted heterojunction (DH) solar cell architecture, schematically illustrated in Fig. 2.9a. In comparison with a commonly used Schottky barrier NC cell, where the p-n junction is formed at the metal-electrode interface, the DH architecture relies on a heterojunction of the two semiconductors to separate charges between FTO and Au electrodes. This design feature allows increasing an open circuit voltage of the device (V_{os}), which is explained by the fact that the Fermi level of the metal electrode is no longer pinned by the defect states at the semiconductor-metal interface. In addition, the DH cell design relies on the incorporated TiO₂ layer to block photoinduced holes from the working electrode. This increases the shunt resistance of the cell resulting in a greater fill factor (FF) of the device.
Figure 2.9 (a). Schematics of the depleted heterojunction solar cell comprising an FTO/glass working electrode, TiO₂ layer, PbS/CdS SMENA layers (~ 250-400 nm) and a Au/Pd counter electrode. (b) Best J-V outputs of the five types of PbS/CdS solar cell: [1] - 3.1-nm PbS/CdS (Redge=0.46 nm, 2 SILAR cycles), [2] - 3.1-nm PbS/CdS (Redge=0.51 nm, 4 SILAR cycles), [3] - 3.1-nm PbS/CdS (Redge=0.51 nm, 0 SILAR cycles), [4] - 3.2-nm PbS/CdS (Redge=1.20 nm, 8
To fabricate a prototype DH cell, SMENA solids were developed on top of a TiO₂ film and then capped with 20-60 nm Au/Pd electrodes. A TiO₂ film was spincoated from DyeSol nanoparticle precursor on FTO-coated glass (resistance = 12 Ω/sq) and subsequently annealed at 450-480 °C to remove organic traces (see the Experimental section). The thickness of the resulting layer of TiO₂ ranged from 200 to 400 nm, as was estimated from SEM measurements. To develop the light-absorbing layer, PbS/CdS core/shell NCs capped with original OA ligands were spincoated onto TiO₂ layer using 8-10 LbL cycles, totaling 350-400 nm. The film was heated to 150-160 °C for ~ 15 min after every three cycles. Upon deposition of the NC layer, the pores of the resulting solid were further filled with additional CdS (2-10 SILAR cycles), and the film was capped with Au/Pd electrodes through a shadow mask. The area of each metal pixel was roughly 0.03 cm². To improve the quality of deposited NC films, a modified spincoating methodology comprising both soaking and spinning cycles was developed (see Exp. Section). Without the use of such prolonged soaking (1 min) prior to spincoating, the quality of the resulting films was generally poor, as was identified by the low surface reflectivity and a large density of pinholes.

Figure 2.9b shows the set of best J-V measurements of the five types of PbS/CdS solar cells (FTO/TiO₂/SMENA/ Au/Pd), representing different combinations of the inter-NC
separation (R_{edge}) and the number of in-filling SILAR cycles (denoted as M in the figure). The highest PCE value under AM1.5 illumination (\(\eta = 4.0\%\); FF = 0.38) was realized for the cells fabricated with 2 CdS in-filling cycles (M=2) and R_{edge} of 0.48 nm, meanwhile, the use of 8 in-filling cycles and R_{edge} of 1.2 nm produced lower PCE (< 0.8%) but consistently yielded large values of the open circuit voltage (\(V_{OC} > 0.72 \text{ V}\)). The relatively low value of the cell fill factor was attributed to a high in-series resistance of the device, which could be related to charge trapping on remaining dangling bonds in the system. This hypothesis was supported by the fact that for SMENA cells which pores were not filled with CdS (but were terminated with either ZnCl_2 or CTAB) the best efficiency was limited to \(\eta = 1.38\%\) (Fig. 2.9b, pink curve). The increase in the R_{edge} from 0.5 to 4.4 nm (Fig. 2.9b, orange curve) was accompanied by a significant drop in the cell efficiency to less than 0.1%, and was attributed to the onset of carrier localization (see Fig. 2.8, red curve). For best-performing cells (R_{edge} \approx 0.4-0.6 nm, M \geq 2 cycles), the typical range of cell efficiencies was \(\eta = 1.5-4.0\%\), where \(\eta\) is the PCE of the best-performing pixel (out of 16) in a cell. For high quality films (as characterized by their smooth, reflective appearance and even coloration of the NC layer) about half of all pixels showed efficiencies within 60% of the best-performing pixel. Based on the absorbance profile of a typical SMENA solar cell (Fig. 2.9d) showing a distinguishable exciton feature, we infer that carriers in the film show some degree of domain localization. Overall, the observed range of PCE values for SMENA devices was somewhat lower than those of best reported NC solar cells,\(^{64,97,98}\) for which \(\eta\) can reach 6%. The SMENA cells stored in ambient conditions (open to air and moisture) for up to three months showed 20-30% reduction in the performance, which is on the par with the stability of EDT-interlinked PbS solar cells reported in Ref.99. The primary causes of the SMENA cell degradation were not clear and could be related to a physical damage
of the 30-nm Au/Pd contact resulting from multiple applications of the spring-loaded probe tip. We also note that only a minimal optimization of the cell performance was undertaken in the course of this study and future work will be needed to address the effect of the film morphology (R_{edge}, NC diameter, matrix material) on the cell efficiency.

The light harvesting characteristics of SMENA cells are summarized in Fig. 2.9e, showing Incident-Photon-to-electron Conversion Efficiency (IPCE) profiles and optical absorbance of the two types of SMENA cells corresponding to the two best J-V outputs in Fig. 2.9b (marked as 1 and 2). The IPCE of the 2.3%-cell (R_{edge}= 0.5 nm, M=4 cycles) reveals a distinguishable contribution from PbS NCs into the observed photocurrent, as manifested by the identifiable 1S exciton feature in the IPCE spectrum. The IPCE profile of the second cell prepared with zero CdS in-filling cycles (M=0) shows a similar profile, which amplitude is proportionally decreased compared to that of CdS-treated film. The lower value of the photocurrent in this case is attributed to higher rate of charge trapping on surfaces of interfused PbS/CdS NCs, resulting from the diminished potential barrier between 1S carriers in PbS and the surfaces of CdS. The contribution of the CdS matrix into the photocurrent could not be evaluated in these measurements due to spectral limitations of the IPCE collection system. Nevertheless, as an indirect evidence of non-vanishing effect of the CdS material on photocurrent, the J-V output of the cell 4 in Fig. 2.9b (for which the CdS-to-PbS volume ratio was substantial) yielded high values of V_{OC} (> 0.7 V), consistent with the CdS band gap value.

2.5 CONCLUSION

In conclusion, a novel strategy for assembling semiconductor nanocrystals into all-inorganic solids is presented. The reported methodology is designed to overcome the key
limitations of the “cross-linking” approach to assembly of NC films, associated with poor thermal and chemical stability of the ligand-nanocrystal system, by encasing nanocrystal arrays into a matrix of a wide-band gap semiconductor. Here, we employ CdS and ZnS matrices to encapsulate PbS NC arrays, such that the quantum confinement of incorporated nanocrystals is partly preserved and can be controlled by tuning the inter-NC separation in the film. Fabricated films exhibit good thermal stability, which is attributed to the heteroepitaxial structure of nanocrystal-matrix interfaces, and show compelling light-harvesting performance in prototype solar cells. Model calculations have been performed to evaluate the effect of inter-NCs separation in the film on the degree of electrical coupling between adjacent NCs in the solid. The results of these calculations were supported by experiments performed on ZnS- and CdS-encapsulated NC arrays. It is expected that the matrix-encapsulation approach could be extended to other type I semiconductor/matrix combinations to aid the “bottom-up” development of all-inorganic NC films showing high carrier mobility, quantum confinement of incorporated charges, and compelling air-stability.

2.6 SUPPORTING INFORMATION

The wavelength of the 1S exciton transition versus the PbS NC diameter.

\[
\lambda (1S_c \rightarrow 1S_h) = 1240/\left(0.41 + \frac{1}{0.0252d^2 + 0.283d}\right) \quad (2.SE1)
\]

where \(d\) is the PbS NC diameter (nm) and \(\lambda\) is the 1S\(_c\)-1S\(_h\) absorption peak position (nm).
Figure 2SF1 TEM images of 3.1- and 4.5-nm PbS NCs along with the corresponding absorbance spectra. The lower plot shows the relation between the diameter of PbS NCs and the spectral position of the first exciton absorption peak.
Figure 2.SF2 TEM images of 3.1-nm PbS NCs coated with ≈ 2.1 nm of CdS

Figure 2.SF3 The blue curve shows the emission spectra of PbS/CdS/ZnS NC solids fabricated from 3.0-nm PbS NCs capped sequentially with 2.4-nm CdS and 0.4-nm ZnS shell. After fusion at T=150 °C, the pores of the resulting film were filled with additional ZnS
**Figure 2.SF4** The J-V curve of the MPA-interlinked PbS solids on TiO$_2$ (depleted heterojunction architecture) reported previously.$^{24}$
2.7 REFERENCES


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CHAPTER III
SUPPRESSED CARRIER SCATTERING IN CDS-ENCAPSULATED PbS NANOCRYSTAL FILMS


3.1 ABSTRACT

One of the key challenges facing the realization of functional nanocrystal devices concerns the development of techniques for depositing colloidal nanocrystals into electrically-coupled nanoparticle solids. This work compares several alternative strategies for the assembly of such films using an all-optical approach to the characterization of electron transport phenomena. By measuring excited carrier lifetimes in either ligand-linked or matrix-encapsulated PbS nanocrystal films containing a tunable fraction of insulating ZnS domains, we uniquely distinguish the dynamics of charge scattering on defects from other processes of exciton dissociation. The measured times are subsequently used to estimate the diffusion length and the carrier mobility for each film type within hopping transport regime. It is demonstrated that nanocrystal films encapsulated into semiconductor matrices exhibit a lower probability of charge scattering than nanocrystal solids cross-linked with either 3-mercaptopropionic acid or 1,2-ethanedithiol molecular linkers. The suppression of carrier scattering in matrix-encapsulated
nanocrystal films is attributed to a relatively low density of surface defects at nanocrystal/matrix interfaces.

3.2 INTRODUCTION

Colloidal semiconductor nanocrystals are emerging as promising nanomaterials for solution-processing of thin film devices. Due to quantum confinement of electrical charges in these nanostructures, their optoelectronic properties can be continuously tuned via the nanoparticle size.\(^1\) This enables the optimization of the film’s key characteristics, either by adjusting the band gap of the semiconductor nanocrystal,\(^2\) enhancing the nanoparticle fluorescence quantum yield through shell growth,\(^3\) or by balancing the driving force at heteromaterial interfaces.\(^4\) Furthermore, processing of thin-film devices from solutions of colloidal nanoparticles is less expensive than traditional methods of film deposition, which rely on high vacuum and high temperature treatments. Owing to these benefits, a great deal of experimental work in the past decade has been focused on the development of strategies for assembly of colloidal nanocrystals into films and superlattices, as well as on improving nanocrystal films’ properties towards practical applications, including lasers,\(^5-7\) solar cells,\(^8-27\) light-emitting diodes (LEDs),\(^28-36\) thermoelectric elements,\(^37,38\) and field-effect transistors.\(^39-45\)

At present, the key issue limiting the performance of nanocrystal devices is related to the poor conductivity of nanocrystal films caused by the energy disorder\(^46\) and charge scattering on imperfectly passivated surface atoms.\(^47,48\) It was previously shown that cationic dangling bonds create trap states below the conduction band minimum, while unpassivated anionic sites result in the formation of traps above the valence band maximum.\(^49\) Because of the high surface-to-volume ratio in semiconductor nanocrystals, the density of such trap states can be significant. As
a result, the charge transport in nanoparticle films is hampered by the premature recombination of electrical charges on surface states, which is detrimental to device operation.\textsuperscript{27}

Traditionally, nanocrystal solids are fabricated by bridging neighboring nanoparticles with organic or inorganic ligands that render NC films electrically conductive. A potential drawback of this strategy concerns the fact that even a slight imbalance between the number of ligand molecules and surface atoms results in a considerable population of states within the nanocrystal band gap, causing scattering of electrical charges. As was demonstrated by a recent study from the Sargent group, the density of trap states just below the conduction band edge for either organically or inorganically cross-linked nanocrystal films is on the order of $10^{17}$ cm$^{-3}$eV$^{-1}$.\textsuperscript{50} This figure is at least three orders of magnitude greater than the trap state density of most single crystalline semiconductors. While a hybrid passivation strategy\textsuperscript{27} involving a combination of organic and small inorganic ligands was recently shown to reduce the density of traps in nanocrystal films down to $2\times10^{16}$ cm$^{-3}$eV$^{-1}$, a more radical treatment of surface states is still necessary for the development of competitive thin-film NC devices, which electrical conductivity is on the par with rival technologies operating in band transport regime.

A promising alternative to a traditional, ligand-based assembly of nanoparticle solids is provided by ligand-free film deposition routes,\textsuperscript{51-55} which rely on the use of a stable inorganic medium for passivating nanocrystal surfaces in a solid. Of particular interest is a recently reported matrix-encapsulation strategy, which employs a wide band gap CdS or ZnS semiconductor matrix to encapsulate arrays of evenly-spaced CdSe or PbS nanocrystals.\textsuperscript{53,54} The matrix medium efficiently preserves the quantum confinement of embedded nanocrystals while protecting their surfaces from interactions with external environment. The key advantage of such an encapsulation scheme is the passivation strategy itself, which forces every cation and anion on
the surface of semiconductor nanocrystals to be heteroepitaxially bonded to their respective counter-ions of the CdS matrix. As a result, trap states cannot form directly on the surface of nanocrystals. While charge trapping can still occur on the boundaries of the matrix itself, the probability of this process is relatively low since charges are confined by the potential barrier of the matrix. Consequently, one can expect that the formation of trap states in matrix-encapsulated nanocrystal films will be suppressed relative to ligand-linked NC solids.

Here, we compare electrical transport characteristics of matrix-encapsulated and ligand-linked nanocrystal solids by measuring the corresponding rates of charge trapping and exciton dissociation processes. To distinguish the dynamics of defect trapping from other mechanisms of exciton decay, we introduce a controlled amount of “insulating” ZnS nanoparticles into a film of PbS NCs, which serves to suppress the transfer of excitation energy between PbS dots (see Fig.3.1). In this geometry, the photoinduced charges in PbS domains of ZnS/PbS NC films are forced to dissipate primarily through trapping on surface states, whose dynamics can then be monitored via fluorescence (FL) intensity decay.

By varying the fraction of ZnS nanoparticles in PbS NC films, we demonstrate that the rate of carrier trapping on surface defects is slower for matrix-encapsulated solids than in the case of films where nanocrystals are connected by ligands. In addition to charge scattering rates, the observed dynamics of carrier decay was used to determine the rates of exciton dissociation processes, which were then converted into carrier mobilities and diffusion lengths for different film architectures. It was found that CdS-encapsulated PbS NC films yielded the highest carrier diffusion length, followed by 3-mercaptopropionic acid (MPA)-linked PbS films featuring Cl-surface passivation. Meanwhile, 1,2-ethanedithiol (EDT)-linked PbS NC films gave rise to the shortest length of carrier diffusion. Overall, a comparative analysis of carrier dynamics in films
comprising different matrix morphologies as well as several types of interlinking ligands have shown that the matrix encapsulation strategy may ultimately provide a conceptually better scheme for the surface passivation of embedded nanoparticles, which helps suppressing carrier scattering.

![Suppression of PbS-to-PbS charge/energy transfer in a NC solid](image)

**Figure 3.1** Illustration of the strategy for determining carrier trapping rates in NC films. The decay of the photoinduced charges in PbS NC films (either ligand-linked or matrix-encapsulated) occurs through several pathways, including radiative recombination, interparticle charge/energy transfer, variable range hopping, and charge trapping on surface dangling bonds. The rates of other processes of exciton dissociation were found to be negligibly slow. When wide band gap ZnS NCs are introduced into the PbS NC film, the interparticle charge and energy transfer...
becomes strongly suppressed, such that the resulting fluorescence lifetime becomes dominated by trapping of photoinduced charges on surfaces (see text). Consequently, the measured fluorescence lifetime in PbS NC films saturated with ZnS nanoparticles approaches that of carrier surface trapping time.

3.3 EXPERIMENTAL SECTION

3.3.1 Chemicals. 1-octadecene (ODE, 90% Aldrich), oleic acid (OA, 90% Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), lead(II) oxide powder (PbO, 99.999% Aldrich), sodium sulfide nonanhydrate (Na2S•9H2O, 98% Alfa Aesar), sulfur (S, 99.999% Acros), ethanol (anhydrous, 95% Aldrich), hexane (anhydrous, 95% Aldrich), methanol (anhydrous, 99.8% Aldrich), toluene (anhydrous, 99.8% Aldrich), isopropanol (anhydrous, 99.8% Acros), octane (anhydrous, 99% Aldrich), 3-mercaptopropionic acid (MPA, 99% Alfa Aesar), 11-Mercaptoundecanoic acid (MUA, 95% Aldrich), Diethylzinc (Et2Zn, 15% wt., 1.1 M solution in toluene, Aldrich), bis(trimethylsilyl) sulfide ((TMS)2S, Aldrich, synthetic grade), Tri-n-octylphosphine (TOP, 97% Strem), cadmium chloride (CdCl2, 99.99% Aldrich), acetone (anhydrous, Amresco, ACS grade), zinc acetate (98+% Acros), Tetradecylphosphonic Acid (TDPA, 97% Aldrich), 1,2-ethanedithiol (EDT, 98+% Fluka), and triton X-100 (Alfa Aesar) were used as received without any further purification. All reactions were performed under argon atmosphere using the standard Schlenk technique. Fluorine-doped tin oxide (FTO) glass (TEC 15, 12-14 Ohm/sq) was obtained from Pilkington Glass.

3.3.2 Synthesis of PbS nanocrystals. The synthesis of PbS NCs was based on the procedure reported by Hines, et al.\textsuperscript{56} For the growth of PbS NCs with the diameter of 3.8 nm
(exciton absorption feature at 1050 nm), a mixture of 0.49 g (2mmol) PbO, 18 mL of ODE and 2 mL of OA in a three-neck flask was pumped at 120°C for 2 hours. After degassing the mixture, the flask was connected to argon and heated to 135 °C. Meanwhile, 10 mL of ODE was degassed for 2 hours at 120°C, switched to argon and cooled down to room temperature. The solution of sulfur precursor in ODE was prepared by injecting 0.21 ml of (TMS)$_2$S into the second flask with stirring for 2 mins. Subsequently, the full amount of (TMS)$_2$S/ODE solution was injected into the first flask and kept at that temperature for 1 minute, after which the reaction was quenched by placing the flask into a cold water bath. PbS NCs were isolated from the solution by precipitating with 50 ml of acetone and centrifugation. After centrifugation the decantate was removed and nanocrystals were redispersed in ~15 ml of toluene. To remove all residues, the cleaning cycle was repeated 2 times and final sample was redispersed in a minimal amount of hexane (4-5 ml).

3.3.3 Preparation of CdCl$_2$ precursor for the synthesis of hybrid passivated PbS nanocrystals. For the preparation of the metal-halide precursor for additional passivation of PbS NCs, 0.30 g (1.64 mmol) of CdCl$_2$ and 0.033 g (0.12 mmol) of TDPA in 5 ml of oleylamine were degassed for 18 hours at 100°C, switched to argon and kept at 80°C to prevent solidifying.

3.3.4 Synthesis of the hybrid passivated PbS nanocrystals. The hybrid passivated PbS nanocrystals were prepared using the procedure developed by Ip et al.$^{27}$ The synthesis of OA-capped PbS nanocrystals was performed according to the usual protocols, as described above, followed by the additional treatment of the reaction mixture during the final cooling process. Namely, after removing the flask from the heating mantle, 1ml of the CdCl$_2$ solution prepared in
the previous step was added to the reaction mixture. When the temperature reached 30°C, ~50ml of acetone was added to precipitate NCs. The reaction mixture was then centrifuged, the decantate was removed, and nanocrystals were redispersed in ~15 ml of toluene. To remove all residues, the cleaning cycle was repeated two times and final sample was redispersed in a minimal amount of hexane (4-5 ml).

3.3.5 Synthesis of PbS/CdS core/shell nanocrystals. PbS/CdS core/shell nanoparticles were synthesized according to the procedure from Ref. 57 using a cation exchange methodology. To this end, 0.5 g (3.8 mmol) of CdO was dissolved in 3 ml of OA and 9 ml of ODE under Ar at 235 °C until the solution became clear. Then, the temperature of this solution was set at 80°C. Meanwhile, 4 ml of PbS seed nanocrystals (d = 4.2 nm) solution in hexane (concentration 10 mg/ml) was kept under argon gas flow at 75 °C for 2 minutes to remove excess of solvent and then was injected into the cadmium solution under vigorous stirring. The reaction mixture was kept at 75 °C for 1 minute and then stopped by removing the flask from the heating mantle. The purification process included the separation of nanoparticles from the solution with ~30 ml of ethanol, centrifugation and dissolution of the precipitated nanocrystals in a minimal amount of hexane. The cleaning cycle was repeated two times. Under these conditions the absorbance peak was found to blue-shift by 80 nm (approx. 0.35 nm of the CdS shell). The growth of the CdS shell depended on the size PbS NCs and the reaction time. Longer reaction times, higher temperatures and higher ratios of OA/ODE were used to obtain a thicker shell of CdS.

To determine the shell thickness in thin-shell nanocrystals (where TEM images do not provide the sufficient accuracy) the following approach was used. First, the size of original PbS dots was determined from the position of the exciton absorption edge. The reduction in the
average size of the PbS domain upon Pb\textsuperscript{2+} to Cd\textsuperscript{2+} cation exchange was determined from the new position of the PbS exciton peak. The thickness of the shell was then calculated under the assumption that the diameter of the PbS/CdS core/shell structure remained the same as the diameter of the original PbS dot.

3.3.6 Synthesis of ZnS nanoparticles. In a typical procedure, 2 ml of TOP solution was degassed for 2 hours at 120°C and switched to argon. Then, 1 ml of diethyl zinc and 0.2 ml of (TMS\textsubscript{2})S were injected separately into the reaction mixture while stirring. The solution was then cooled down and stirred for 30 minutes at 90°C. To avoid the solidifying of unreacted TOPO, 5 ml of butanol were added into the flask right after the injection of precursors. ZnS nanocrystals were separated from the solution by precipitation in 25 ml of acetone. After centrifugation, the decantate was removed and nanocrystals were redispersed in ~6 ml of hexane.

3.3.7 Preparation of the FTO/glass substrate. FTO-coated glass was cut into 2.5 cm x 2.5 cm squares, then washed by hand with detergent (Alconox), and rinsed clean in deionized water. It was then sonicated in methanol, acetone and isopropanol for 5 minutes in each solvent.

3.3.8 Fabrication of nanocrystal films. The deposition of ligand-linked NC films was performed under argon atmosphere inside the glovebox using standard layer-by-layer techniques.\textsuperscript{58} All-inorganic NC films (SMENA) were fabricated according to developed procedure.\textsuperscript{53}

To deposit a layer of all-inorganic CdS-encapsulated NC film onto the FTO/glass substrate, 5-6 drops of the PbS/CdS core/shell NC solution in hexane (concentration 10mg/ml)
were placed onto the glass until the surface was covered and then the film was spun until dry at 3000 rpm for 10 seconds. To replace original OA ligands with thermally-degradable MPA molecules, 7-10 drops of MPA/Methanol solution (ratio1:4) were deposited on the center of the glass slide, soaked for 10 seconds and spun at 3000 rpm for 10 seconds. After the MPA treatment, the film was washed by covering with 10 drops of methanol and spinning the slide for 10 seconds, followed by rinsing with octane in the same manner. Upon the deposition of 2 layers the films were annealed at 120-140°C for 15 mins. The total of 6-7 layers were deposited. To fabricate all-inorganic films with additional ZnS NCs, the initial solution of PbS/CdS NCs was mixed with the ZnS solution in ratios, which were calculated by dividing the optical density of ZnS colloidal precursor (at $\lambda = 270$ nm) by that of PbS/CdS NCs (at $\lambda$ ex $= 850$-900 nm).

MPA-linked PbS NC films were deposited using a layer-by-layer spincoating process under an argon atmosphere. For each layer, the solution of PbS NCs in hexane (concentration 20 mg/ml) was deposited on the glass substrate and span at 3000 rpm for 10 seconds. Subsequently, 7-10 drops of MPA/Methanol solution (ratio1:4) were deposited on the center of the glass slide, soaked for 10 seconds and spun at 3000 rpm for 10 seconds. The total amount of layers was varied from 6 to 10. Ratios of PbS with ZnS were calculated by dividing the optical density of ZnS colloidal precursor at the center of the exciton absorption future (at $\lambda = 270$ nm) by that of PbS/CdS NCs.

The fabrication of ethanedithiol(EDT)-linked NC films was performed using a dip-coating technique. After the deposition of 5-7 drops of PbS NCs onto FTO/glass substrate, followed by spinning at 3000 rpm for 10 seconds, the film was immersed into 0.1M EDT solution in acetonitrile for 1 minute, dried and washed with 10 drops of acetonitrile. Overall, 7-10 cycles were required to fabricate a film with EDT-cross-linked PbS NCs and PbS with ZnS.
NCs. Ratios of PbS with ZnS for the mixed films were calculated the same way as in the case of MPA-linked films.

3.3.9 In-filling of SMENA pores with ZnS. For the pore-filling process, the SILAR method was applied. Briefly, the deposition of the additional layer of the wide band gap ZnS was conducted by the sequential soaking of the annealed, all-inorganic NCs film in the methanol solutions containing Zn and S precursors. For this purpose, the zinc bath was prepared by dissolution of 0.10 g of zinc acetate in 20 mL of methanol and the sulfur bath by placing 0.098 g of Na2S•9H2O in 20 mL of methanol. One SILAR cycle included a soaking of the film in the zinc bath for 1 minute, then rinsing the film with methanol for 1 minute, then soaking it in the sulfur bath for 1 minute with sequential washing in methanol. 2-10 cycles of pores filling process was applied for all-inorganic films with longest lifetime. The films were then annealed at 150 °C for 15 minutes.

3.3.10 Characterization. Absorbance spectra were recorded using CARY 50 scan and Simadzu UV-3600 UV-vis-NIR spectrophotometers. Photoluminescence spectra were recorded using a Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High-resolution transmission electron microscopy (HR-TEM) measurements were carried out using JEOL 3011UHR and 2010 transmission electron microscopes, operated at 300 and 200 kV, respectively. To prepare a TEM sample, a small amount of NC film was scraped, dispersed in toluene by sonication, dropped onto a carbon-coated copper grid, and allowed to dry in air. X-ray powder diffraction (XRD) measurements were carried out on a Scintag XDS-2000 X-ray powder diffractometer. FL lifetime measurements were performed using a time-correlated single photon
counting setup utilizing SPC-630 single-photon counting PCI card (Becker & Hickie GmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), an id50 avalanche photodiode (Quantique), and long pass filters on 400nm, 532nm and 750nm.

3.4 RESULTS AND DISCUSSION

To determine the rate of charge trapping in nanocrystal films, the dynamics of this process should be uniquely distinguished from other mechanisms of exciton decay, which include charge tunneling between adjacent nanoparticles, variable range hopping (VRH), and the resonant energy transfer to a dark state. All of these processes result in the dissociation of nanocrystal excitons causing a corresponding drop in the FL lifetime. Notably, the exciton binding energy is relatively small compared to the thermal energy of photoinduced charges, such that the carrier ionization time is approximately the same as the time of carrier tunneling or hopping. Consequently, the FL lifetime of PbS nanocrystals can be used to determine the cumulative rate of carrier removal from the excited state. Namely, the rate of fluorescence intensity decay of nanocrystals in a solid can be expressed as:

\[
\Gamma_{\text{FL decay}} = \Gamma_{\text{rad}} + \Gamma_{\text{non-rad}} = \Gamma_{\text{rad}} + \Gamma_{\text{trapping}} + \Gamma_{\text{tunneling}} + \Gamma_{\text{VRH}} + \Gamma_{\text{energy transfer}}
\]

When the electrical coupling between neighboring nanocrystals is strong, the radiative decay rate becomes negligibly small compared to the rate of carrier removal via transfer processes, \( \Gamma_{\text{rad}} \ll \Gamma_{\text{non-rad}} \). As a result, the band edge emission from individual NCs in the film is suppressed, and the FL lifetime, \( \tau_{\text{FL}} = 1/\Gamma_{\text{FL decay}} \), becomes roughly equal to the exciton decay time via non-radiative processes, \( \tau_{\text{FL}} \approx \tau_{\text{non-rad}} = 1/(\Gamma_{\text{trapping}} + \Gamma_{\text{tunneling}} + \Gamma_{\text{VRH}} + \Gamma_{\text{energy transfer}}) \). On the contrary, for weakly coupled nanocrystal films (Mott insulator regime), the energy and charge transfer processes between PbS NCs in the film have a relatively low probability. This
causes the contribution of the radiative decay into the total exciton decay rate to become more significant, which is manifested by the enhancement of the fluorescence lifetime and the corresponding increase in the emission quantum yield of nanocrystal films featuring large interparticle distances.\textsuperscript{54}

According to Eq. 3.1, one can determine the averaged charge trapping time for the case of nanocrystal films with strong electrical coupling between neighboring nanoparticles ($\Gamma_{\text{rad}} \ll \Gamma_{\text{non-rad}}$), provided that the remaining processes of exciton dissociation are suppressed, $\Gamma_{\text{tunneling}} + \Gamma_{\text{VRH}} + \Gamma_{\text{energy transfer}} \rightarrow 0$. This scenario can be artificially created if wide-band-gap ZnS semiconductor nanocrystals are introduced into the film of PbS nanoparticles, as shown in Fig. 3.1. The addition of ZnS dots increases the interparticle separation between PbS NCs, which causes the reduction of tunneling, short-range hopping, and energy transfer rates. Indeed, the amplitude of the energy transfer process is inversely proportional to the fourth power of the interparticle distance and will be significantly diminished when PbS NCs become surrounded by ZnS NCs. At the same, wide band gap ZnS will provide a substantial potential barrier to conduction and valence band charges in the film, such that PbS-to-PbS tunneling is expected to be negligible as well. Finally, the VRH process, which couples the resonant states of closely lying PbS nanocrystals will also be reduced by the presence of ZnS “insulating” dots. In particular, the rate of short-range hopping between the neighboring nanoparticles will clearly diminish with increasing fraction of ZnS nanocrystals in the film. The long-range hopping between the resonant states of non-neighboring dots, on the other hand, will only be partly suppressed as hopping of excited charges in resonance will still be possible across longer distances. It should be noted that the term suppression does not necessarily imply a complete eradication of a certain decay pathway but rather a significant reduction of its rate.
Figure 3.2 (a). Illustration of the general strategy for encapsulation of colloidal nanocrystals into semiconductor matrices. (b-c) Characteristic TEM images of PbS/CdS core/shell and ZnS NCs used as nanoparticle precursors during film assembly.

To understand whether the addition of ZnS NCs to PbS NC solids can facilitate the suppression of charge and energy transfer between adjacent PbS nanoparticles, we have fabricated several mixed films featuring different ratios of ZnS to PbS NCs and measured the corresponding lifetimes of the fluorescence intensity decay. A previously developed, semiconductor matrix-encapsulated nanocrystal arrays (SMENA) approach was used to incorporate both ZnS to PbS NCs into ZnS matrices (see Fig. 3.2a). To this end, PbS NCs capped with a shell of CdS semiconductor (see Fig. 3.SF1 for absorbance data) were mixed with ZnS NCs, spincoated onto a glass substrate, subjected to a ligand exchange with MPA molecules, and
baked at approximately 120 °C. The heating step resulted in a removal of the organic phase, as was confirmed by FTIR measurements, and simultaneous fusion of the neighboring shells. The pores of the resulting matrix were then in-filled with additional ZnS using the successive ionic layer adsorption and reaction (SILAR)\textsuperscript{59} approach. The XRD spectrum in Fig. 3.3 shows the diffraction patterns of the PbS NCs (Fig. 3.3a), PbS NCs placed within a CdS matrix (Fig. 3.3b), and a mixture of PbS and ZnS nanoparticles placed within a CdS matrix (Fig. 3.3c). Films featuring both PbS and ZnS nanocrystals showed a distinguishable band edge emission of PbS NCs while exhibiting a characteristic ZnS diffraction pattern, indicating that both types of nanoparticles were successfully encapsulated into CdS matrices. A TEM image of CdS-imbedded PbS nanocrystals is shown in Fig. 3.3e.

**Figure 3.3** XRD spectra of NC films corresponding to several stages of film development. (a). An XRD spectrum of 4.0-nm PbS NCs, showing characteristic Bragg peaks of rock salt PbS crystal phase. (b). An XRD spectrum of fused PbS/CdS core/shell NCs. (c). XRD spectrum of

Figure 3.4b illustrates the effect of the increasing fraction of ZnS nanoparticles in CdS-encapsulated PbS/ZnS NC films (fabricated without a pore in-filling step) on the ensuing PbS exciton lifetime. Prior to the addition of ZnS, the FL lifetime of band edge excitons in PbS NCs exhibited a biexponential decay (Fig. 3.4b, black curve) with fast and slow components being approximately equal to 1.6 ns and 50 ns, respectively. A relatively short lifetime of the fast exponent in this case is attributed to a high rate of interparticle charge and energy transfer, which causes a rapid dissociation of bound electron-hole pairs resulting in the suppression of the band gap emission. With the increasing fraction of “insulating” ZnS NCs in the matrix, such dissociation process becomes inhibited causing the fast component of the PbS exciton decay to increase sharply from 1.6 to 8.9 ns (Figs. 3.4b and 3.5a). The slow decay component also grows with the increasing fraction of ZnS NCs but at a much slower pace changing from 50 ns for no-ZnS films to 87 ns for ZnS-rich solids. Both the fast and the slow exponents eventually saturate, exhibiting no significant changes upon further addition of ZnS.

The origin of the fast and slow components in the FL decay of PbS excitons is revealed by their characteristic dependence on the fraction of insulating ZnS nanocrystals in the film. To explain a substantial growth of the fast decay component in ZnS-saturated films, we recall that prior to the addition of ZnS, the edge-to-edge distance between neighboring PbS NCs, $R_{edge} = 2 \times 0.32 \text{ nm} = 0.64 \text{ nm}$, is sufficiently short to promote tunneling of charges. In fact, this value is typical of photoconducting NC devices, such as solar cells, while larger $R_{edge}$, especially in the
excess of 2 nm, tend to render the solids insulating. When the fraction of ZnS NCs in the film is high, PbS NCs become fully surrounded by wide-band-gap ZnS nanoparticles, such that the minimum $R_{\text{edge}}$ distance between PbS NCs reaches $R_{\text{edge}} = 2\Delta H + d_{\text{ZnS}}$, where $\Delta H$ is the CdS shell thickness, and $d_{\text{ZnS}}$ is an average diameter of ZnS NCs ($d = 4.6$ nm). Consequently, upon saturation of the PbS/CdS matrix with ZnS, $R_{\text{edge}}$ increases from 0.64 nm to at least 5.2 nm, causing a dramatic suppression of the PbS-to-PbS transport. Considering that PbS NCs are well spaced by the ZnS insulating barrier, we propose that when the saturation fraction of ZnS NCs is reached, all interparticle transfer processes including, tunneling, short-range hopping, and resonant energy transfer are suppressed. This behavior is consistent with the results of photocurrent measurements performed on the same nanoparticle films, which confirm that increasing concentration of ZnS “insulators” in the film causes the suppression of the photoinduced current (see Fig. 3.5c). Based on these observations, the fast component of the FL decay was assigned to exciton dissociation processes (as illustrated in Fig. 3.4c), which result in the energy and charge transfer between neighboring PbS nanocrystals.

Figure 3.4 (a). Steady-state emission and fluorescence intensity decay (insert) of PbS/CdS core/shell NCs in solution ($\Delta H_{\text{CdS}} = 0.32$ nm). (b). Fluorescence intensity decay of PbS NCs embedded into CdS matrices ($R_{\text{edge}} = 0.64$ nm) as a function of the increasing fraction of ZnS.
nanoparticles in the film. Steady-state emission of mixed PbS/ZnS nanoparticle films in ZnS matrices is shown in the insert. (c). Biexponential fit of the FL intensity decay curves showing the fast and slow components, which were attributed to exciton dissociation and charge trapping processes, respectively.

As stated above, the suppression of exciton dissociation pathways in ZnS-saturated PbS NC solids ($R_{\text{edge}} \approx 0.64$ nm) results in the inhibition of the fast decay component and the corresponding reduction of the film photoconductivity. Nevertheless, the slow component of the FL decay undergoes only small changes, growing from 50 to 87 ns (Fig. 3.5b). In the meantime, the lifetime of the slow decay component in ZnS-saturated PbS NC films is still considerably shorter than the radiative lifetime of 3.3-nm PbS/CdS core/shell NCs in solution ($\tau \geq 1120$ ns), which lower bound was estimated from the emission lifetime of these nanoparticles in chloroform (Fig. 3.4a insert). A 20-fold difference between $\tau_{\text{rad}}$ and $\tau_{\text{FL,slow}}$ values points toward the existence of yet another non-radiative decay channel, which is largely independent of the interparticle distance. According to Eq. 3.1, this process is trapping of electrical charges on nanocrystal surfaces. Since all transfer processes are suppressed, the characteristic timescale for such carrier trapping becomes approximately equal to the measured FL lifetime of the slow component in ZnS-saturated PbS NC films, $\tau_{\text{trapping}} \approx \tau_{\text{FL,slow}} = 87$ ns.

The character of trapping processes in PbS solids is further elucidated through the unique dependence of the slow component of the FL decay on the fraction of ZnS nanocrystals in the film. According to Fig. 3.5b, $\tau_{\text{FL,slow}}$ is growing from 50 to 87 ns, indicating that some of the trapping events become inhibited by ZnS domains, while others are independent of the ZnS “insulation”. To explain these phenomena, we would like to introduce the concept of local and
global traps, as illustrated in the scheme of Fig. 3.5. Namely, when the photoinduced charges become trapped within the same PbS dot (local traps) the rate of trapping will not be affected by the increasing fraction of ZnS NCs, meanwhile when trapping occurs on the surface of a neighboring dot and therefore requires carrier transport (global trap), the rate of this process will be dramatically reduced when ZnS is added. Consequently, the slow component of the FL decay in pure PbS films (no-ZnS) reflects a combinations of local and global traps (see Fig. 3.5b), while carrier decay in ZnS-saturated films is determined primarily by the local traps.

**Figure 3.5** Summary of the FL decay dynamics for CdS-embedded PbS NC solids. (a). Evolution of the fast FL decay component with increasing fraction of ZnS NCs in the film. The exciton dissociation time is given by the FL lifetime of no-ZnS PbS films. (b). Evolution of the

\[ \tau_{\text{diss}}, \tau_{\text{trap(local)}}, \tau_{\text{trap(global+local)}} \]

\[ \text{Photocurrent (} \mu\text{A)} \]

\[ (\text{ZnS/PbS}) \text{ approx. volume fraction} \]
slow FL decay component with increasing fraction of ZnS NCs in the film. The ZnS-saturated FL lifetime is approximately equal to the characteristic time of charge trapping on “local” defects, while the FL lifetime no-ZnS solids indicates the time of carrier trapping on both “global” and “local” defect states. (c). Photoconductivity measurements performed on the same films as in parts (a) and (b). Au/Pd electrodes were sputtered through a shadow mask.

To confirm that global traps do exist in PbS films, we have looked into the FL decay of OA-capped PbS NC solids. It is reasonable to expect that upon transferring of OA-capped PbS NCs from solution into a solid form new traps won’t be created. Consequently, if the slow component of the FL decay was determined only by the local traps it would remain constant for both the solution and the solid forms. However, our measurements (see Fig. 3SF2) show that there is at least a 30% drop in the FL lifetime of PbS excitons when nanocrystals are deposited into films. In contrast to PbS NC solutions where FL lifetime appears to be single–exponential, the FL decay curve of a PbS solid picks up a fast (dissociation) component with the slow component decreasing from 380 to 290 ns. Consequently, some global trapping between neighboring dots must be taking place. This process is clearly inhibited for dots in solution but becomes feasible for solid-bound nanocrystals even if new traps are not created.

While the evolution of the fast and the slow components in the FL decay of PbS/ZnS solids appears to be consistent with proposed assignments of dissociation and trapping mechanisms, the lack of the FL lifetime saturation in ZnS-rich films needs further explanation. Namely, when the volume fraction of ZnS nanoparticles in the ZnS/PbS film reaches the 10-15 range, one can expect that all charge and energy transfer processes should be inhibited. Nevertheless, the fast component is still present in the decay trace of ZnS-dominated PbS/ZnS
films (see Fig. 3.4b and 3.4c). Furthermore, the photoconductivity of nanoparticle solids does not
go to zero completely, even when all PbS nanocrystals are presumably surrounded by insulating
ZnS nanoparticles (see Fig. 3.5c). To explain this phenomenon, we propose the existence of the
long-range hopping mechanism, which couples non-neighboring PbS dots in resonance. Indeed,
if the photoinduced charge transfer can occur across long-range distances, even high volume
fractions of ZnS NCs may not be sufficient to suppress the exciton dissociation, as evident by the
lingering fast component in Fig. 3.4b. Similarly, the existence of long-range hopping can explain
the non-vanishing carrier conductivity in the film, evidenced as the residual photocurrent in ZnS-
saturated solids. Temperature-dependent photoluminescence studies can be performed in the
future to confirm the VRH contribution to the charge transport in films comprising large
ZnS/PbS volume fractions.

To find further evidence supporting the proposed assignments of fast and slow FL decay
components to the processes of dissociation and trapping, we have looked into the dynamics of
FL decay in weakly coupled PbS solids. To this end, the $R_{\text{edge}}$ distance in the PbS/CdS matrix
was increased from 0.64 to 2.7 nm, by augmenting the thickness of the CdS layer in PbS/CdS
film-precursor nanoparticles to 1.3 nm. Since the CdS layer provides a small potential barrier to
both types of charge carriers (see Fig. 3.5F3), the processes of exciton dissociation (e.g. via PbS-
to-PbS charge transfer) and charge trapping on surface states of core/shell nanoparticles are
expected to be inversely proportional to the thickness of the shell. For instance, if we assume that
tunneling of photoinduced carriers from PbS cores to the surface of the shell is the main
mechanism of carrier trapping, then the probability of this process can be estimated using
Wentzel-Kramers-Brillouin (WKB) approximation\textsuperscript{62} as a single-exponential dependence on the
shell thickness, $\Gamma_{\text{thick}}/\Gamma_{\text{thin}} = \exp(-\Delta H_{\text{thick}})/\exp(-\Delta H_{\text{thin}})$, where $\Gamma$ is the charge trapping rate. In
principle, lattice defects forming along core/shell interfaces can also contribute into the exciton
dissociation, but the characteristic time associated with such deexcitation process is much greater
than that of other trapping mechanisms. Indeed, the lower limit of the interfacial trapping time is
given by the FL lifetime of core/shell NCs in solutions ($\tau = 1120 \mu$s, Fig. 3.4a), which exceeds
the exciton lifetime of film-bound PbS NCs by two orders of magnitude. Such a low probability
of charge trapping along PbS/CdS interfaces is expected due to nearly matched lattice parameters
of rock-salt PbS and zinc-blende CdS crystal phases (strain $\approx 1.7\%$, see Fig. 3.3d).

![Figure 3.6](image)

**Figure 3.6** (a). Fluorescence intensity decay of weakly-coupled PbS NCs embedded into CdS
matrices ($R_{\text{edge}} = 2.7$ nm) as a function of the increasing fraction of ZnS nanoparticles in the film.
(b). Evolution of the fast fluorescence decay component with increasing fraction of ZnS NCs in
the film. The exciton dissociation time is given by the FL lifetime of no-ZnS PbS films. (c).
Evolution of the slow fluorescence decay component with increasing fraction of ZnS NCs in the film. The ZnS-saturated FL lifetime is approximately equal to the characteristic time of charge trapping on “local” defects, while the FL lifetime no-ZnS solids indicates the time of carrier trapping on both “global” and “local” defect states.

Figure 3.6 illustrates the changes in the FL lifetime of CdS-encapsulated PbS NC solids (R_{edge} \approx 2.7 \text{ nm}) with increasing fraction of ZnS nanoparticles in the film. Prior to the addition of ZnS NCs, the fast component of the FL decay, limited primarily by PbS-to-PbS excitation transfer processes (see Eq. 3.1), was found to be 11.6 ns. Notably, this value is substantially greater than the corresponding FL lifetime of strongly-coupled PbS NC films featuring R_{edge}= 0.64 \text{ nm}. The positive correlation between the FL lifetime of PbS excitons and R_{edge} distance in the matrix (prior to the addition of ZnS) is attributed to the suppressed tunneling, short-range hopping, and energy transfer across an increased layer of the CdS potential barrier (R_{edge} = 0.64 \text{ nm} \to 2.7 \text{ nm}). According to WKB approximation, the expected reduction in the exciton dissociation rate (fast component) is exponential with R_{edge}, \exp(-0.64)/\exp(-2.7) = 7.8, which is close to the observed lifetime ratio, \tau_{2.7 \text{ nm}}/\tau_{0.64 \text{ nm}} = 11.6/1.6 = 7.25. When ZnS is introduced into the film, charge transfer processes become further suppressed causing the fast lifetime component to continue climbing in value while diminishing in amplitude (see Fig. 3.6b).

Similarly to the case of R_{edge}=0.64 \text{ nm}, the fast exponent of the FL decay in PbS films with R_{edge} = 2.7 \text{ nm} eventually becomes overwhelmed by the slow component, which represents charge trapping processes. The slow exponent eventually saturates with the continuous increase of the ZnS volume fraction in the film, ultimately reaching \tau_{FL, \text{slow}} = 370 \text{ ns}. Since charge and energy transfer processes are strongly suppressed for this film morphology, trapping of charges on local
surface traps becomes the main mechanism of exciton dissociation, $\tau_{\text{trapping (local)}} \approx \tau_{\text{FL, slow}} = 370 \text{ ns}$. The observed trapping time for weakly coupled PbS NC films is approximately $370/87 = 4.25$ times greater than the corresponding value of strongly-coupled PbS NC solids ($R_{\text{edge}}=0.64 \text{ nm}$). The observed reduction of the trapping rate falls somewhat short of the WKB estimates, $\exp(-0.64)/\exp(-2.7) = 7.8$, which indicates that additional relaxation pathways may begin to play a role when the FL lifetime extends into hundreds of nanoseconds.

![Figure 3.7](image)

**Figure 3.7** (a). Illustration of the in-filling strategy based on SILAR deposition of ZnS. (b). The effect of SILAR treatment on the fluorescence intensity decay of CdS-encapsulated PbS/ZnS nanoparticle film, with suppressed charge/energy transfer processes. The enhanced FL lifetime of pore in-filled films is attributed to the reduction in the charge trapping rate.

In-filling of interparticle “pores” in matrix–encapsulated nanocrystal films can result in the further suppression of charge trapping on surface states. Since interfaces of PbS/CdS core/shell NCs are generally defect free ($\Gamma_{\text{trap (interfacial defects)}} < 1/450 \text{ ns}$), we expect that the primary contribution into carrier trapping must come from scattering of photoinduced charges on unpassivated surfaces of the CdS matrix. To reduce the probability of such surface trapping, the width of the potential barrier separating PbS-localized carriers from surface states could be enhanced, for instance, by depositing additional layers of the CdS or ZnS semiconductor on surfaces of interfused nanocrystals. Here, to understand the effect of such surface treatment on
the carrier dynamics, several monolayers of ZnS have been deposited onto both no-ZnS and ZnS-saturated PbS NC matrix (R_{edge} = 0.64 nm) via SILAR methodology. In the case of no-ZnS films where carrier trapping occurs both locally and globally, the addition of 6 ZnS monolayers lead to a 35% increase in the FL lifetime of the slow component (Fig. 3.SF4). Such a moderate enhancement of the trapping time can be attributed to the existence of global traps which originate from below the surface layer and thus cannot be filled. In the case of ZnS-saturated solids featuring only local traps (situated on the same dot), the SILAR treatment results in a more substantial, three-fold increase in the slow decay component, \( \tau_{\text{FL, slow}} = 87 \to 257 \text{ ns} \) (see Fig. 3.7b), indicating that atomic layer deposition effectively passivates surface traps. Notably, the fast decay component in ZnS-saturated PbS films was not fully inhibited by the in-filling step. The continuing presence of this decay component is corroborated by the proposed long-range hopping mechanism, which rate is primarily determined by the interparticle distance rather than surface passivation.

We now turn our attention to ligand-linked PbS NC solids, for which nanoparticle surfaces are passivated by short-chain molecules. Here, by varying the fraction of ZnS nanocrystals in a film, we seek to determine whether ligand-linked and CdS-encapsulated NC solids exhibit different rates of exciton dissociation and charge trapping, a question, which is directly related to the material’s electrical performance. For this study, we have narrowed our choice of ligands down to three representative molecules, which include MPA, 1,2-Ethanedithiol (EDT), and a hybrid combination of MPA/Cl ligands. All of these materials have been previously employed as charge-conducting surfactants in best-performing nanocrystal devices.27,
Figure 3.8 (a-c). Steady-state emission of PbS NCs passivated with EDT (a), MPA (b), and MPA/Cl (c) in different environments, as indicated in the figure. The inserts in (b) and (c) show the corresponding FL intensity decay for nanocrystals in solution. (d-f). Fluorescence intensity decay of PbS NC films, cross-linked with EDT (d), MPA (e), and MPA/Cl (f) molecules as a function of increasing fractions of ZnS nanoparticles in the film. (g-j). The dependence of the PbS exciton lifetimes (fast and slow components) on the concentration of ZnS nanoparticles for the three types of molecular linkers.

We start our analysis with MPA-linked PbS nanoparticle films, fabricated via spincoating process according to standard protocols.58 The addition of ZnS NCs into MPA-linked PbS NC film (d = 3.2 nm) results in the suppression of the charge transfer processes much like it was
observed for matrix-encapsulated NC solids. According to Figures 3.8e, and 3.8h, the FL lifetime of the fast decay component in all-PbS films prior to the addition of ZnS was 1.04 ns, while the lifetime of oleic acid-passivated PbS NCs in nonpolar solvents is 480 ns. The reduction in the emission lifetime of PbS excitons accompanying the transfer of PbS nanoparticles from solution into a solid film is again attributed to the combination of competing exciton dissociation processes, which include resonant charge transfer, resonant energy transfer to a dark state, hopping, and charge trapping. In theory, the transfer of photoinduced holes to MPA ligands can also contribute into carrier ionization. The rate of the latter process, however, is too slow to compete with other energy and charge transfer mechanisms, since the FL lifetime of 11-Mercaptoundecanoic acid (MUA)-capped PbS dots in water/methanol solution is 220 ns (see Fig. 3.SF5).

Increasing the fraction of ZnS nanocrystals in MPA-linked PbS NC films results in the enhancement of the fast FL decay component, which reflects the suppression of charge transfer processes between neighboring PbS dots. The slow decay component, associated with charge trapping on NC surfaces, grows from $\tau = 35$ ns for no-ZnS films (global + local traps) to a saturation level of $\tau_{MPA}^{\text{trap}} = 60.5$ ns (averaged over 3 different films), which corresponds to carrier decay on local traps only. Notably, this later value is approximately four times as short as $\tau_{\text{trap, local}}$ of matrix-encapsulated PbS films in-filled with ZnS, $\tau_{\text{CdS}}^{\text{trap}} = 257$ ns. Similar results were obtained for EDT-linked films (see Table 3.1), where the charge trapping time has grown from 25 to 45 ns.

One of the best performing solar cell devices utilizing ligand-linked NC films was recently made by employing a combination of MPA and halide anion ligands. Halide atoms, such as chlorine, are compact enough to infiltrate difficult-to-access sites of nanocrystals providing
better surface passivation, leading to the reduced density of midgap trap states.\textsuperscript{27} Here, to understand the role of halide passivation, we have measured the exciton dissociation dynamics in PbS NC solids comprising hybrid MPA/Cl ligands (Figs. 3.8f, 3.8j). The addition of chlorine ligands to the surface of PbS NCs during the solution growth step has resulted in a 10\% enhancement of the FL lifetime (Fig. 3.8c, insert) and the associated 20-25\% increase in the FL quantum yield. In a solid form, MPA/Cl-passivated PbS NCs showed an expected biexponential character of the FL decay with fast and slow components being equal to 3.1 ns and 30 ns, respectively for no-ZnS films. With the addition of ZnS nanoparticles, the latter lifetime increased to 193 ns (Fig. 3.8f), reflecting an approximate time of carrier decay on local traps. Expectedly, the use of chlorine capping resulted in the reduced rate of charge trapping on NC surfaces ($\tau_{\text{trap}} = 193$ ns) compared to MPA-linked PbS films, which agrees well with the predictions of a recently developed diffusion model.\textsuperscript{63} The use of hybrid ligands, however, has yielded a longer exciton dissociation time (Fig. 3.8f, 3.8j), which was attributed to the existence of the surface potential barrier associated with a chlorine layer on PbS NCs. A somewhat surprising outcome of these measurements was the observation of similar (no-ZnS) decay times for MPA-only and MPA/Cl-passivated PbS films. This could be ascribed to a relatively high density of rare deep traps\textsuperscript{63} in MPA/Cl films, which promote global trapping of photoinduced charges.

The comparison of the FL lifetimes between matrix-encapsulated and ligand-linked PbS NC solids featuring similar interparticle distances reveals an important trend: trapping of photoinduced charges in CdS-encapsulated PbS NC matrices is reduced in comparison with ligand-linked PbS films. To get a quantitative interpretation of the observed charge transport characteristics, we recall that for a typical p-n junction, carrier transport relies on drift in the
depletion region, and diffusion elsewhere. If the minority carrier lifetime, $\tau$, is known, the characteristic lengths of drift and diffusion can be estimated using the following equations:

\[
l_{\text{drift}} = \mu E \tau, \quad l_{\text{diffusion}} = \sqrt{D \tau}
\]

where $\mu$ is the charge carrier mobility, $D$ is the diffusion coefficient, and $E$ is the electric field in the drift region. Since charge trapping is the primary process of carrier scattering in both types of NC films, we assume that minority carrier lifetime is approximately the same as the trapping time $\tau \approx \tau_{\text{trap}}$. In order to estimate $l_{\text{drift}}$ and $l_{\text{diff}}$ values for investigated films, charge carrier mobility, $\mu$, and the diffusion coefficient, $D$, have to be determined first. Fortunately, an estimate of $\mu$ and $D$ for a nanocrystal solid in the hopping transport regime can be obtained from the Einstein’s relation between mobility and diffusion:

\[
\mu = \frac{e d^2}{6 k T \tau} \quad ; \quad D = \frac{\mu k T}{e}
\]

where $d$ is the center-to-center distance between PbS NCs in a film, and $(1/\tau)$ represents the cumulative rate of carrier diffusion processes, including charge transfer, energy transfer to a dark state, and hopping. The approximation is based on the assumption that carrier diffusion is accompanied by the transfer of the excitation energy to a neighboring nanocrystal. Therefore, the band transport regime cannot be described using this approach, and the resulting $\mu_{\text{diff}}$ represents diffusion-limited charge carrier mobility in a nearest-neighbor hopping approximation. We note that $\mu_{\text{diff}}$ is different from the field effect transistor (FET) mobility, $\mu_{\text{FET}}$, which characterizes solids with an altered position of the Fermi level, as controlled by the gate voltage. In order to estimate $\mu_{\text{diff}}$ for investigated film architectures, the carrier diffusion rate $(1/\tau_{\text{diff}})$ has to be determined first. Here, this was achieved by measuring the fast component of the FL decay in PbS-only films. Namely, since all charge transfer processes are allowed in the absence of ZnS
NCs, the rate of the FL decay becomes:

$$\Gamma_{\text{FL decay}} = \Gamma_{\text{trapping}} + \Gamma_{\text{rad}} + \Gamma_{\text{diff}} (\Gamma_{\text{tunneling}} ; \Gamma_{\text{VRH}} ; \Gamma_{\text{energy transfer}})$$

where the latter term represents exciton diffusion processes characterized by the fast component in the FL decay, $\tau_{\text{diff}} \approx \tau_{\text{ex, dissociation}}$ (no ZnS). Consequently, equation 3.3 can be expressed as:

$$\mu_{\text{diff}} = \frac{ed^2}{6kT}\frac{1}{\tau_{\text{no ZnS}}^{\text{no ZnS}}} \quad ; \quad D = \frac{\mu kT}{e} = \frac{d^2}{6\tau_{\text{no ZnS}}^{\text{no ZnS}}}$$ \hspace{1cm} (3.4)

Finally, the charge carrier diffusion length becomes:

$$l_{\text{diffusion}} = \sqrt{D\tau_{\text{trap}}} = d \times \sqrt{\frac{\tau_{\text{trap}}}{6\tau_{\text{FL, fast}}}} = d \times \sqrt{\frac{\tau_{\text{FL,slow}}}{6\tau_{\text{FL, fast}}}}$$ \hspace{1cm} (3.5)

where $\tau_{\text{FL,slow}}$ corresponds to the slow component of either no-ZnS (local and global traps) or ZnS-saturated (local traps only) FL lifetime in NC solids.

Table 3.1 summarizes the FL lifetime data for matrix-encapsulated and ligand-linked PbS NC solids. Arguably, the most significant outcome of the above comparison is the suppressed carrier trapping observed for matrix-encapsulated nanocrystal films. In particular, charge trapping rates for strongly-coupled PbS/CdS films appear to be 1.5 – 4 times lower than for the three investigated types of ligand-linked nanoparticle solids. Cl-passivated PbS NC solids were likewise fairly efficient in inhibiting carrier trapping on “local” defects with the characteristic scattering time ($\tau_{\text{trap}} = 193$ ns) exceeding that of MPA-only films by a factor of 3. As discussed above, this serves as indirect evidence that matrix-encapsulated and Cl-passivated NC solids exhibit comparatively low densities of surface trap states. On the other hand, the diffusion carrier mobility for all-inorganic PbS/CdS films, $\mu_{\text{diff}} = 0.57 \times 10^{-3}$ cm$^2$/V/s, was found to be somewhat lower than the corresponding mobility value for MPA-linked PbS solids ($\mu_{\text{diff}} = 0.9 \times 10^{-3}$ cm$^2$/V/s). It should be noted, however, that electrical coupling of CdS-encapsulated films, determined by
the PbS-to-PbS interparticle distance, was below its previously reported maximum, which corresponds to $R_{\text{edge}} = 0.5$ nm. Based on the comparison of $R_{\text{edge}} = 0.64$ nm and $R_{\text{edge}} = 2.7$ nm PbS/CdS solids (lines 1 and 2 in Table 3.1), we conclude that $R_{\text{edge}}$ plays a critical role in the ensuing value of $\mu_{\text{diff}}$. Therefore, the mobility of CdS-encapsulated films can potentially be increased by using a sufficiently low $R_{\text{edge}}$, which promotes fast exciton dissociation yet partly preserves quantum confinement of charges. Further studies will be needed to confirm this hypothesis.

**Table 3.1** FL lifetime data and derived transport characteristics of matrix-encapsulated and ligand-linked PbS nanocrystal solids.

<table>
<thead>
<tr>
<th>Type of NC film</th>
<th>$\tau_{\text{diss}}$ (ns)</th>
<th>$\tau_{\text{trap}}$ (ns)</th>
<th>$\tau_{\text{trap}}$ (ns)</th>
<th>$\mu$ (cm$^2$/V/s)</th>
<th>$l_{\text{diffusion}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_{\text{fast}}$, no ZnS</td>
<td>$\tau_{\text{slow}}$, no ZnS</td>
<td>$\tau_{\text{slow}}$, ZnS-sat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS/CdS SMENA (Redge = 0.64 nm)</td>
<td>1.6</td>
<td>65</td>
<td>257.0</td>
<td>$0.57 \times 10^{-3}$</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>(with SILAR)</td>
<td>(with SILAR)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS/CdS SMENA (Redge = 2.7 nm)</td>
<td>11.6</td>
<td>171</td>
<td>370</td>
<td>$1.8 \times 10^{-4}$</td>
<td>9.0</td>
</tr>
<tr>
<td>MPA-linked PbS NCs</td>
<td>1.04</td>
<td>35</td>
<td>60.5</td>
<td>$0.9 \times 10^{-3}$</td>
<td>9.0</td>
</tr>
<tr>
<td>EDT-linked PbS NCs</td>
<td>3.4</td>
<td>25</td>
<td>45</td>
<td>$0.2 \times 10^{-3}$</td>
<td>4.2</td>
</tr>
<tr>
<td>Hybrid (MPA/Cl)-linked PbS NCs</td>
<td>3.1</td>
<td>33</td>
<td>193</td>
<td>$0.3 \times 10^{-3}$</td>
<td>5.1</td>
</tr>
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</table>
Another point that merits explanation is the nature of the calculated diffusion mobility, which was found to be at least one order of magnitude lower than a typical value of $\mu_{\text{FET}}$ for MPA-linked films. In this regard, we recall that within the approximation of hopping transport regime, charge carriers are presumed to be localized within individual dots, such that the mobility is determined by tunneling to the nearest unoccupied state. Meanwhile, in the case of FET measurements, the raised (or lowered) position of the Fermi level leads to the population of over-barrier states, which enhances the delocalization of carriers and increases the mobility.

In case of photovoltaic applications of semiconductor nanocrystals, increasing carrier mobility beyond $10^{-2}$ cm$^2$/V/s does not proportionally avail the device performance since exciton dissociation is already quite efficient\textsuperscript{46}. The true advance can be achieved through the eradication of the carrier recombination centers, typically midgap surface traps, which would result in the enhancement of an average $l_{\text{diff}}$ and $l_{\text{drift}}$ in the film. This study demonstrates that trapping of charges in nanocrystal solids can be reduced if matrix-encapsulation is used in lieu of the cross-linking approach. Indeed, the comparison of $l_{\text{diff}}$ (Table 3.1) and $l_{\text{drift}}$ (Table 3.ST1) values, reveals that CdS-encapsulated nanocrystal solids provide somewhat longer scatter-free travel of carriers than other types of films. The longer diffusion length for these materials indicates that a long minority carrier lifetime outweighs a relatively lower mobility of carriers in matrix-encapsulated films.

3.5 CONCLUSIONS

In conclusion, the dynamics of exciton dissociation and charge scattering processes in several types of PbS nanocrystal solids have been studied using fluorescence lifetime spectroscopy. To determine the characteristic timescale of charge scattering for each film type, a controlled amount of “insulating” ZnS nanoparticles was introduced into the solids of PbS NCs.
The presence of ZnS nanoparticles in the film causes the suppression of both energy and charge transfer processes between PbS dots, allowing carriers to decay primarily by trapping on nanocrystal surfaces. FL lifetime technique can then be employed to measure the dynamics of photoinduced charge scattering separately from other processes of charge and energy transfer. Based on the observed relaxation times, we have determined the rates of exciton dissociation and charge trapping for several types of NC films, featuring either matrix-encapsulation or cross-linking assembly strategies. The observed decay rates were also used to determine the diffusion carrier mobility and scattering lengths for all film types within the hopping regime of carrier transport. Overall, matrix-encapsulated PbS NC films showed lower rate of charge trapping on surfaces and longer diffusion lengths than any type of ligand-linked PbS nanocrystal films.

3.6 SUPPORTING INFORMATION

Figure 3.SF1 Absorbance of the 3.2-nm PbS NCs (black) and 3.2-nm PbS/CdS core/shell NCs (brown curve) featuring 3.0 nm core diameter. The insert shows the absorbance of ZnS nanoparticles in octane.
Figure 3.SF2 Fluorescence intensity decay of oleic acid-capped PbS nanocrystals in solution (black) and in a solid (red) forms.

Figure 3.SF3 Relative positions of the excited energy levels for PbS NCs and bulk CdS.
Figure 3.SF4 FL intensity decay of CdS-encapsulated PbS NC films ($R_{\text{edge}} = 0.64$ nm) before (black) and after (red) the additional in-filling step. The solids did not contain any “insulating” ZnS nanocrystals.

Figure 3.SF5 Fluorescence intensity decay of MUA-capped PbS NCs in methanol.
Table 3.ST1 Estimated drift scattering lengths for the different types of nanocrystal solids.

<table>
<thead>
<tr>
<th>Type of NC film</th>
<th>$l_{\text{drift}}$ (local + global traps)</th>
<th>$l_{\text{drift}}$ (local traps only)</th>
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<tr>
<td>CdS-encapsulated PbS NCs</td>
<td>19.0</td>
<td>75.04</td>
</tr>
<tr>
<td>(R$_{\text{edge}}$ = 0.5 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdS-encapsulated PbS NCs</td>
<td>9.4</td>
<td>20.3</td>
</tr>
<tr>
<td>(R$_{\text{edge}}$ = 1.5 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPA-linked</td>
<td>15.0</td>
<td>25.9</td>
</tr>
<tr>
<td>PbS NCs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDT-linked</td>
<td>1.9</td>
<td>3.5</td>
</tr>
<tr>
<td>PbS NCs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid (MPA/Cl)-linked PbS NCs</td>
<td>6.6</td>
<td>38.7</td>
</tr>
</tbody>
</table>
3.7 REFERENCES


(22) Luther, J. M.; Law, M.; Song, Q.; Reese, M. O.; Beard, M. C.; Ellingson, R. J.; Nozik, A. J. *Nano Lett.* **2008**, *8*, 3488–3492.


CHAPTER IV

UTILIZATION OF PBS NANOCRYSTALS ENCAPSULATED IN CDS MATRIX FOR THE FABRICATION OF IR EMITTING NANOCRYSTAL SOLIDS


4.1 ABSTRACT

Colloidal semiconductor nanocrystals (NCs) are emerging as promising infrared-emitting materials, which exhibit spectrally-tunable fluorescence, and offer the ease of thin film solution processing. Presently, an important challenge facing the development of nanocrystal infrared emitters concerns the fact that both the emission quantum yield and the stability of colloidal nanoparticles become compromised when nanoparticle solutions are processed into solids. Here, we address this issue by developing an assembly technique that encapsulates infrared-emitting PbS NCs into crystalline CdS matrices, designed to preserve NC emission characteristics upon film processing. An important feature of the reported approach is the heteroepitaxial passivation of nanocrystal surfaces with a CdS semiconductor, which shields nanoparticles from the external environment leading to a superior thermal and chemical stability. Here, the morphology of these matrices was designed to suppress the non-radiative carrier decay, whereby increasing the exciton lifetime up to 1 μs, and boosting the emission quantum yield to an unprecedented 3.7% for inorganically encapsulated PbS NC solids.
4.2 INTRODUCTION

Near-infrared light emitting materials operating in the 700-2000 nm spectral range are commonly employed by a wide scope of applications ranging from biomedical imaging to telecommunication technologies. This spectral window is notoriously difficult to access since the emission quantum yield of most organic or inorganic infrared materials is substantially lower than that of visible-range counterparts. In light of this constraint, semiconductor nanocrystals exhibiting bright and tunable infrared fluorescence represents a promising material class for the development of near-IR technologies.¹ Of a particular interest are lead chalcogenide nanoparticles, where the quantum confinement of photoinduced charges enables an emission quantum yield (QY) of up to 50% in solution,²-⁴ far above the typical QY range of indirect gap Ge or Si semiconductors.

A significant challenge for optical applications of colloidal NCs concerns their integration into transparent host matrices, which preserve their size-dependent optical properties. Besides enabling bright band gap emission, these matrices should be designed to maintain the monodispersity of embedded nanocrystals, exhibit a good thermal and chemical stability, and possess a high refractive index in order to be pertinent for utilization in waveguide-based applications. The existing matrix encapsulation strategies relying on organic polymer mixes⁵-¹⁰ are reasonably successful in converting nanoparticle solutions into device-compatible films, but suffer from poor thermal stability as well as polymer/semiconductor phase separation. Both of these issues can be traced back to the existence of molecular ligands preserved on surfaces of matrix-encapsulated nanocrystals. These molecules tend to desorb when thermally or electrically stimulated and are known to cause poor nanoparticle miscibility with the polymer environment. The employment of sol-gel titania matrices¹¹-¹³ has helped resolving some of these difficulties
through the use of titania functional groups tethered directly to alcohol–terminated amine ligands, however, this and other emerging strategies\textsuperscript{14-16} still suffered from poor stability of ligand-terminated NC surfaces. One viable solution to the stability problem was recently offered by the work of Kovalenko \textit{et al.}\textsuperscript{2} who have employed an encapsulation strategy utilizing metal chalcogenide complexes (MCC).\textsuperscript{17,18} This methodology relied on sintering of hybrid ligands comprising MCCs into As\textsubscript{2}S\textsubscript{3} amorphous matrices, which gave rise to an all-inorganic film architecture exhibiting compelling stability and a large refractive index.

Despite recent advances in enhancing the stability of nanocrystal solids,\textsuperscript{2,19-21} the emission characteristics of these metamaterials require further improvement. In the visible range, the fluorescence quantum yield (QY) of titania-encapsulated CdSe NCs was reported to undergo a seven-fold drop upon transferring of nanoparticles into a solid form.\textsuperscript{12} Similar trend was observed in the case of infrared emitting nanocrystals. A spincoated film of PbSe NCs typically exhibits an emission QY of 1-2\%,\textsuperscript{22} which constitutes a significant reduction from a 50\% value observed for these nanoparticles in solution.\textsuperscript{23} The quantum yield of PbS NC solids can be increased to 4-12\% through the use of polymer matrices,\textsuperscript{9} however, a brief exposure of these films to $T = 100$ C\textdegree or above results in a rapid loss of emission. Inorganic films of infrared nanocrystals are more stable but less emissive. The fluorescence QY of As\textsubscript{2}S\textsubscript{3}-encapsulated PbS NC solids, is around 0.1\%.\textsuperscript{24} The addition of a CdS shell prior to capping with MCC ligands results in an improved quantum yield value, however, sintering of colloidal nanocrystals into a glassy matrix\textsuperscript{1} is still accompanied by the 4.5-time drop in the exciton lifetime.

Amongst the primary non-radiative processes that compete with the radiative decay of matrix-encapsulated NCs, two mechanisms of exciton dissociation that have been previously identified to contribute the most into quenching of the nanoparticle fluorescence.\textsuperscript{25,26} First, dot-
to-dot charge transfer can lead to the formation of a “dark” excited state, whereby reducing the probability of the radiative recombinination. Likewise, an interparticle energy transfer increases the probability of defect filling due to multiple dot-to-dot transitions, thus contributing to a non-radiative decay. Second, charge trapping on dangling bonds and nanocrystal/matrix interfaces can cause exciton dissociation followed by a non-radiative relaxation of carriers. With respect to the interparticle charge transfer process, the rate of dot-to-dot carrier tunneling was previously shown to have a nearly exponential dependence on the width and the height ($\sqrt{\Delta E}$) of the potential barrier separating adjacent nanocrystals. Therefore, the charge transfer pathway of exciton dissociation can be readily suppressed by choosing a wide gap matrix material or by employing a sufficient interparticle separation.

Trapping of excited carriers on surfaces and interfaces of encapsulated nanoparticles, however, represents a more serious problem. In the case of polymer or titania matrices, the surfaces of encapsulated nanocrystals retain original, long-chain organic ligands to help lower the density of surface traps. This strategy, however, suffers from the propensity of ligand molecules to detach from NCs as a result of a thermal or electrical stimulation. The desorption of ligands inevitably compromises the stability of the NC emission in a film, regardless of the stability of the matrix medium. In the case of glassy matrices, hybrid or fully inorganic ligands serve as a surface passivation layer, which warrants a compelling thermal stability. The glass sintering step, however, may result in an imperfect surface passivation, which could be partly responsible for a low emission yield observed in the case of As$_2$S$_3$-encapsulated PbS NC solids. Ideally, well defined stoichiometric relationships should exist between encapsulated nanoparticles and a matrix medium, which itself should exhibit a high thermal and chemical stability.
Here, we demonstrate a solution-phase assembly of PbS nanocrystals into inorganic solids exhibiting bright infrared emission and superior thermal stability. The reported methodology takes the advantage of crystalline semiconductor matrices, heteroepitaxially bonded to surfaces of encapsulated PbS nanocrystals. Such passivation strategy promotes a reduced density of surface traps, which is manifested in this work through the observation of a compelling emission quantum yield. The suppressed defect trapping is also apparent through the detection of long exciton lifetimes approaching 1 microsecond for best-performing films. This constitutes a noticeable improvement over NC solids assembled via conventional ligand-linking or amorphous-matrix strategies.

4.3 EXPERIMENTAL SECTION

4.3.1 Materials. 1-octadecene (ODE, 90% Aldrich), oleic acid (OA, 90% Aldrich), lead(II) oxide powder (PbO, 99.999% Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), sodium sulfide nonanhydrate (Na₂S·9H₂O, 98% Alfa Aesar), sulfur (S, 99.999% Acros), ethanol (C₂H₅OH, anhydrous, 95% Aldrich), methanol (CH₃OH, anhydrous, 99.8% Aldrich), toluene (C₇H₈, anhydrous, 99.8% Aldrich), isopropanol (C₃H₇OH, anhydrous, 99.8% Acros), octane (C₈H₁₈, anhydrous, 99% Aldrich), hexane (C₆H₁₄, anhydrous, 95% Aldrich), 3-mercaptopropionic acid (3-MPA, 99% Alfa Aesar), bis(trimethylsilyl) sulfide ((TMS)₂S, Aldrich, synthetic grade), chloroform (CHCl₃, anhydrous, 99%, Aldrich), cadmium acetate dihydrate ((CH₃COO)₂Cd·2H₂O, 98%, Acros), zinc acetate ((CH₃COO)₂Zn, 98+% Acros), acetone (C₃H₆O, anhydrous, Amresco, ACS grade) were used as received without any further purification. All reactions were performed under argon atmosphere using the standard Schlenk
technique. Glass substrates (Corning Microscope Slides, 0.96-1.06 mm, 0215 Glass) were obtained from Corning Inc.

4.3.2 Fabrication of PbS nanocrystals. PbS nanocrystals were fabricated according to a procedure adapted from Hines et al.\textsuperscript{35} In a typical synthesis, a mixture of 0.49 g (2mmol) PbO in 18 mL of 1-octadecene (ODE) and 1-16 mL of oleic acid (OA) (increasing the amount of OA results in larger NCs) was degassed in a three-neck flask at 120°C for 2 hours, switched to Argon, and heated to 135 °C. Meanwhile, 10 mL of ODE was degassed for two hours at 120°C and allowed to cool down to room temperature. Then, 0.21 ml of (TMS)$_2$S was added carefully into the flask and the resulting (TMS)$_2$S/ODE mixture was injected into the Pb precursor solution at 135°C, while stirring. The reaction was stopped after 0-5 minutes (longer reaction time leads to larger nanocrystals) by removing the flask from the heating mantle and placing it into an ice water bath. The nanocrystals were isolated from the mixture by precipitating with acetone, centrifuging, and re-dispersing in toluene. The cleaning procedure was repeated 2-3 times, after which nanocrystals were re-dispersed in a minimal amount of hexane (4-5 ml).

For example, to fabricate PbS nanocrystals with an exciton absorption feature centered at 1050 nm ($d_{\text{PbS}} = 3.5$ nm), 2 mL of oleic acid was used and the growth time was limited to 1 min. For nanocrystals with a 1S peak at 1300 nm ($d_{\text{PbS}} = 4.6$ nm), 14 mL of oleic acid was used with the growth time of 4 min. For nanocrystals with a 1S peak at 930 nm ($d_{\text{PbS}} = 3.0$ nm), 1.5 mL oleic acid was used with the reaction time of 1 min.

4.3.3 Synthesis of PbS/CdS core/shell nanocrystals. The growth of the CdS shell on PbS nanocrystals was performed using a cation exchange methodology.\textsuperscript{3} To this end, 0.95 g (7.6
(0.3 mmol) of CdO was dissolved in 10 ml of oleic acid and 18 ml of 1-octadecene under argon at 235 °C until the solution became clear. Then, the temperature of this solution was set at 130°C. Meanwhile, 4 ml of PbS seed nanocrystals (d = 4.2 nm) solution in hexane (concentration 10 mg/ml) was kept under argon gas flow at 80°C for 2 minutes to remove excess of solvent and then was injected into the cadmium solution under vigorous stirring. The reaction mixture was kept at 135 °C for 7 minute and then stopped by immersing the flask in the ice water bath. The purification process included the separation of nanoparticles from the solution with ~30 ml of ethanol, centrifugation and dissolution of the precipitated nanocrystals in a minimal amount of hexane. The cleaning cycle was repeated two times. Under these conditions the absorbance peak was found to blue-shift by 330 nm (approx. 0.8 nm of the CdS shell). The growth of the CdS shell depended on the size PbS nanocrystals and the reaction time. Longer reaction times, higher temperatures and higher ratios of OA/ODE were used to obtain a thicker shell of CdS.

To determine the shell thickness in thin-shell nanocrystals (where TEM images do not provide the sufficient accuracy) the following approach was used. First, the size of original PbS dots was determined from the position of the exciton absorption edge. The reduction in the average size of the PbS domain upon Pb²⁺ to Cd²⁺ cation exchange was determined from the new position of the PbS exciton peak. The thickness of the shell was then calculated under the assumption that the diameter of the PbS/CdS core/shell structure remained the same as the diameter of the original PbS dot.

4.3.4 Synthesis of CdS nanoparticles. For the fabrication of CdS seeds an approach proposed by Yu et al. was used.36 The mixture of 0.0384 g (0.3 mmol) CdO, 1 ml OA and 11 ml ODE in a 50 ml 3-neck flask was heated to 300°C until solution turned optically clear and
colorless. Then, the temperature of the reaction mixture was set up at 250ºC and a sulfur precursor solution made by dissolving sulfur powder 0.0048 g (0.15 mmol) at 200ºC in 1-octadecene (4.5 mL) was quickly injected. The reaction was stopped by removing the flask from the heating mantle after 5-9 minutes. CdS nanocrystals were separated from the solution by precipitation with methanol followed by repeated hexane/methanol extractions. The final nanocrystals had diameter 3.5-4.5 nm (depending on the reaction time) and were stored in hexane.

4.3.5 Preparation of the glass substrate. Before the deposition of nanocrystals the glass substrates were cleaned and dry for better performance. To this end, glass squares 2.5 cm x 2.5 cm were washed with detergent (Alconox) and rinsed in deionized water. Subsequently, substrates were sonicated in methanol, acetone and isopropanol for 5 minutes in each solvent and dry under argon flow.

4.3.6 Fabrication of nanocrystal solids. The fabrication of all-inorganic NC films was performed using previously reported Semiconductor Matrix Encapsulated Nanocrystal Array (SMENA) methodology. To deposit a layer of all-inorganic CdS-encapsulated NC film onto the FTO/glass substrate, 3-5 drops of the PbS/CdS core/shell NC solution in hexane (concentration 10mg/ml) were placed onto the spinning at 3000 rpm glass until the surface was covered and then dry. To replace original oleic acid ligands with thermally-degradable MPA molecules, 7-10 drops of MPA/Methanol solution (ratio 1:4) were deposited on the center of the glass slide, soaked for 10 seconds and spun at 3000 rpm for 10 seconds. After the MPA treatment, the film was washed by
covering with 10 drops of methanol and spinning the slide for 10 seconds, followed by rinsing with octane in the same manner. Upon the deposition of 2 layers the films were annealed at 120-140°C for 15 mins. The total of 4-6 layers were deposited. To fabricate modified SMENA with additional CdS nanocrystals, the initial solution of PbS/CdS nanocrystals was mixed with the CdS solution in ratios, which were calculated by dividing the optical densities at the 1st excitonic peak for CdS ($\lambda = 430$ nm) and PbS/CdS NCs ($\lambda \approx 850-900$ nm) colloidal precursors. The final volume ratios of nanocrystals were calculated using TEM data from utilized solutions, as discussed in the text.

4.3.7 In-filling of SMENA pores with CdS. For the pore-filling process, the successive ionic layer adsorption and reaction (SILAR) method was applied.\textsuperscript{38} Briefly, the deposition of additional layers of CdS was conducted by sequential soaking of the annealed NC films in methanol solutions of Cd and S precursors. For this purpose, the cadmium bath was prepared by dissolution of 0.113 g of cadmium acetate in 20 mL of methanol and the sulfur bath by placing 0.098 g of Na$_2$S•9H$_2$O in 20 mL of methanol. One SILAR cycle included soaking of the film in the cadmium bath for 1 minute, then rinsing the film with methanol for 1 minute, then soaking it in the sulfur bath for 1 minute with sequential washing in methanol. 2-10 cycles of pores filling process was applied for all-inorganic films followed by annealing at 150 °C for 15 minutes.

4.3.8 Characterization. Absorbance spectra were recorded using CARY 5000 and Shimadzu UV-3600 UV-vis-NIR spectrophotometers. Photoluminescence spectra were recorded using a Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer and using a home-built photoluminescence spectroscopy apparatus including an Argon ion laser Reliant 150M (Laser
Physics), an Acton SP-2357 Monochromator (Princeton Instrument) and an IR detector PDA30G (Thorlabs). High-resolution transmission electron microscopy (HR-TEM) measurements were carried out using JEOL 3011UHR and 2010 transmission electron microscopes, operated at 300 and 200 kV, respectively. To prepare a TEM sample, a small amount of NC film was scraped, dispersed in toluene by sonication, dropped onto a carbon-coated copper grid, and allowed to dry in air. Photoluminescence lifetime measurements in 900nm region were performed using a time-correlated single photon counting setup utilizing SPC-630 single-photon counting PCI card (Becker & Hickle GmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), an id50 avalanche photodiode (Quantique), and long-pass optical filters with edges at 400nm, 532nm, 750nm and 900nm. Time – resolved PL traces in 1300 nm region were obtained by Time-Correlated Single Photon Counting (TCSPC) system based on InGaAs TE cooled single photon avalanche photodiode (ID Quantique) of 200 ps time resolution, adjusted for 10% quantum efficiency, SPC-130-EM Counting Module and BDL-488-SMN laser (Becker & Hickle) with pulse duration of 50 ps and wavelength of 488 nm, CW power equivalent of about 0.5 mW, externally triggered at 1MHz repetition rate. PL emission from the samples passed through long-pass optical filters with edges at 500nm 1300 nm in order to reject excitation laser line and possible emission from CdS matrix.

4.3.9 Fluorescence quantum yield measurements. The absolute value of quantum yield was measured by method, similar to the one described in Ref.39. In our case the advantage was the elimination of a reference and a possibility of simultaneous measurement of absorbance at excitation wavelength, with correction to reflectance and scattering losses using integrating sphere. As excitation source CW Laser Diode Module with wavelength of 808nm with power of
1 W modulated by optical chopper at 30Hz, was used. For spatial averaging the integrating sphere IS200-4, (Thorlabs) was applied. This light was measured by broadband (0.1-20 µm) UM9B-BL-DA pyroelectric photodetector(Gentec-EO). The modulated signal from the detector was recovered by lock-in amplifier SR 830 (Stanford Research). The signal coming out from the integrating sphere was attenuated with neutral density filter in order to set the light intensity to the optimum of dynamic range for detector and lock-in amplifier. The ratio between emitted and absorbed light gives an energy yield. This value than is transformed to the quantum yield taking into the account difference in photon energies for laser and PL band (for PL band was used average energy). The quantum yield value was corrected by transmission of applied edge-pass filters.

4.4 RESULTS AND DISCUSSION

The matrix encapsulation technique developed in this work builds upon a recently reported semiconductor matrix embedded nanocrystal array (SMENA) approach,\textsuperscript{37,40} which allows for a gap-free inclusion of colloidal NCs into host matrices of wide band gap semiconductors. Typically, nanocrystals are encapsulated using a three-step procedure (see Fig. 4.1a). First, hot-injection chemistry is used to grow monodisperse PbS nanocrystals, onto which a shell of a lattice-matched semiconductor (CdS) is deposited. The matrix semiconductor is chosen to form a type I band edge alignment with PbS, thus promoting core-localization of both carrier types (Fig. 4.2a). In the second step, core/shell nanocrystals (PbS/CdS) are spincoated onto a suitable substrate, capped with thermally degradable ligands, and subsequently heated to 140-160 °C to promote the ligand removal (as monitored by FTIR) and to induce merging of respective shells (CdS-CdS) \textit{via} the crystallographic fusion process. In the final step, the pores of
the CdS matrix are filled with an additional CdS material through the successive ionic layer adsorption and reaction (SILAR) method.\textsuperscript{41} This step helps passivating exposed surfaces of the CdS matrix (thus neutralizing carrier traps) and increases an average refractive index (n) of the film. The pore filling step also promotes an enhanced stability of the PbS NC array.

**Figure 4.1** (a). Illustration of the key steps involved in the development of conventional Semiconductor Matrix-Encapsulated Nanocrystal Arrays (SMENA). These stages include colloidal synthesis of PbS/CdS core/shell NCs (step 1), spincoating or dip-coating of NC films (step 2), exchange of bulky ligands with thermally degradable MPA molecules, crystallographic
fusion of core/shell NCs performed using a layer-by-layer deposition (steps 3), and in-filling the pores of the resulting matrix with additional CdS (step 4). (b). In a modified SMENA approach, PbS/CdS core/shell NCs are mixed with CdS-only NCs (of a similar diameter) in the first step.

To enhance the radiative portion of the excited state decay in matrix-encapsulated nanocrystals, the localization of photoinduced charges should be increased. In a conventional SMENA approach, this goal is achieved by augmenting the thickness of the shell, $\Delta H$, in core/shell precursor NCs, which determines the ultimate value of the minimal edge-to-edge distance between PbS domains in the film ($R_{\text{edge}} = 2 \times \Delta H$). Indeed, larger $R_{\text{edge}}$ results in the suppression of the interparticle charge and energy transfer processes, leading to enhanced probability of the radiative recombination. This situation is illustrated in Fig. 4.2b, showing the relationship between the interparticle charge transfer rate and the $R_{\text{edge}}$ distance in the film. It is assumed that the charge tunneling rate has a single exponential dependence on the width of the potential barrier separating neighboring nanocrystals. According to Wentzel–Kramers–Brillouin (WKB) approximation, this rate is proportional to $\Gamma \sim \exp(-2(2m\Delta E / h^2)R_{\text{edge}})$, where $\Delta E$ is the height of the potential barrier between electron or hole states in adjacent NCs. The regime of strong charge localization is achieved when the coupling energy $\beta = \hbar \omega \Gamma$ drops below $kT$, known as Mott insulator regime. Since the carrier localization is more pronounced in dots with a larger core size (Fig. 4.2a), the characteristic $R_{\text{edge}}$ distance at which such transition occurs diminishes with the growing diameter of the PbS domain. This trend is clearly seen in Fig. 4.2b through the comparison of the inter-dot coupling energy for the cases of 4-nm and 6-nm diameter PbS NCs embedded into CdS matrices. For example, the value of $R_{\text{edge}}$ associated with the insulator transition in 4-nm-PbS/CdS solids is about 2 times greater than that of 6-nm-PbS/CdS. We note
that while x-axis in Fig. 4.2b is given only in relative units of scale, it preserves the correct lengths ratio corresponding to insulator transitions between different dot diameters.

**Figure 4.2** (a). Energy diagram showing a relative alignment of conduction and valence band edges in 4.0-nm PbS/CdS and 6.0-nm PbS/CdS core/shell nanocrystals. (b). Wentzel–Kramers–Brillouin tunneling approximation of the coupling energy dependence on the interparticle distance ($R_{edge}$) for the two material systems shown in (a). The colored areas indicate the regime of strongly localized charges.
According to Fig. 4.2b, achieving a strong localization of photoinduced charges in small-diameter PbS NCs requires growing a thick CdS shell needed to compensate for a shallow potential barrier to electrons in PbS (see Fig. 4.2a). A possible drawback of this strategy is the propensity of thicker shells to cause an excessive interfacial strain, which typically relaxes through the formation of defects, whereby introducing additional non-radiative decay channels.42-44 Alternatively, the width of the potential barrier separating adjacent PbS NCs could be increased by replacing a portion of PbS NCs with CdS dots of the same diameter, as illustrated in Fig. 4.1b. Such strategy would result in a sufficient interparticle separation needed for a strong carrier localization without the need for an additional shell growth. Within this approach, the balance between the filling factor (ff) and the emission quantum yield of embedded PbS NCs can be controlled by varying the ratio of PbS/CdS to CdS nanoparticle precursors in the mixture. For instance, increasing the volume fraction of PbS NCs embedded into CdS matrices leads to the reduction of an average $R_{\text{edge}}$ distance between neighboring PbS domains. This results in the enhancement of the filling factor and a concurrent drop in fluorescence (FL) quantum yield due to an incomplete localization of excited carriers in electrically coupled PbS cores. Conversely, a low volume fraction of PbS NCs should promote a greater emission QY due to an enhanced carrier localization but would lead to a relatively low filling factor.

To explore the effect of the interparticle separation, $R_{\text{edge}}$, on the PbS exciton decay, we have fabricated two sets of nanoparticle solids representing two different strategies for tuning the value of $R_{\text{edge}}$. In the first approach, the $R_{\text{edge}}$ distance was controlled through a conventional SMENA technique, by adjusting the thickness of the CdS shell in PbS/CdS core/shell nanocrystal precursors. For the second set of films, we have used a modified-SMENA strategy
wherein the value of $R_{\text{edge}}$ was adjusted by introducing a tunable fraction of CdS nanoparticles. Core/shell PbS/CdS NCs used in both sets of experiments were fabricated using a cation exchange approach. This method benefits from a precise control of the shell thickness, a parameter, which determines the ultimate value of $R_{\text{edge}}$ in both film architectures. A characteristic TEM image of core/shell PbS/CdS NCs featuring a 2.7-nm PbS core capped with a 1.3-nm CdS shell is shown in Fig. 4.3a and 4.3b. A uniform placement of the CdS shell around the PbS core is evident in high resolution TEM images of PbS/CdS NCs (Fig. 4.3b and Fig. 4.SF6).

**Figure 4.3** (a,b). High resolution TEM images of 2.7-nm PbS nanocrystals coated with a 1.3-nm CdS shell. (c). The mixture of PbS/CdS core/shell NCs and 5.0-nm CdS NCs prior to the deposition on a glass substrate. Scanning electron microscope (d) and photo (e) images of a CdS-encapsulated PbS NC film.

The fluorescence (FL) lifetime of PbS nanocrystal solids assembled using a conventional SMENA strategy (Fig. 4.4a) increases with the growing interparticle separation in the film, which is consistent with a diminishing probability of exciton dissociation through charge and
energy transfer processes. It was previously shown that the characteristic timescale for such interparticle transfer is given by the fast component of the FL intensity decay, as illustrated in Fig 4 SF1, while the slow component represents charge trapping on surfaces of unpassivated CdS matrices. The fast exponent of the film emission is therefore limited to charge and energy transfer processes that result in non-emissive states. Notably, the two transfer mechanisms have distinctly different $R_{\text{edge}}$ dependences. According to WKB approximation, the rate of charge tunneling between resonant states decays exponentially with $R_{\text{edge}}$, while the rate of energy transfer diminishes as $R_{\text{edge}}^6$ in accordance with the nonradiative dipole–dipole coupling approximation (Förster resonance energy transfer). The comparison of experimentally measured $\tau_{\text{fast}}^{FL}$ with the WKB ($\sim e^{\alpha R_{\text{edge}}}$) and FRET ($\sim r^6$) model curves in Fig. 4b reveals that charge transfer is a more likely mechanism to contribute into exciton dissociation. Indeed, the observed transfer times exhibit a nearly single-exponential dependence on $R_{\text{edge}}$, which is characteristic of a charge tunneling process, and not the energy transfer, which is strongly affected by small changes in $R_{\text{edge}}$. This suggests that the charge transfer between adjacent dots in the matrix is the primary mechanism responsible for the formation of non-emissive states.

Figure 4.4 (a). Fluorescence intensity decay of conventional SMENA films representing different $R_{\text{edge}}$ values. (b). Measured exciton lifetimes for CdS-encapsulated PbS NCs and their
fitting by a model according to Wentzel–Kramers–Brillouin (charge transfer) and dipole–dipole coupling (energy transfer) approximations.

In the case of a conventional SMENA approach, the fluorescence lifetime of matrix-encapsulated nanocrystals did not exceed $\tau = 190$ ns, which is far below the 2.8 microsecond lifetime observed for the same nanocrystals in solution (see Fig. 4.SF2). Even with further increases in the shell thickness beyond 3-4 monolayers, the emission lifetime remained roughly the same. Taking into account a significant suppression of the interparticle charge transfer for such large values of $R_{\text{edge}}$, the short lifetime has been tentatively attributed to a continuous build-up of the interfacial strain, manifested by the growing ratio of the trap state to band gap emission (see Fig. 4.SF3).$^{33}$ Decay of trapped carriers creates a broad band emission, which overlaps with the PbS FL peak. Subsequently, despite an enhanced exciton localization in solids featuring large interparticle distances, strong emission within a narrow spectral band cannot be reached through a conventional SMENA architecture. On the contrary, the modified SMENA approach allows enhancing the interparticle separation without the need for an epitaxial growth of large shells. By including CdS nanoparticles within PbS/CdS matrices, we aim to facilitate the suppression of charge and energy transfer between adjacent PbS nanoparticles, while preventing the formation of rate-limiting defects.

To explore optical properties of modified-SMENA solids comprising a mixture of CdS and PbS/CdS NC precursors, we have fabricated several films featuring an increasing fraction of CdS to PbS nanoparticles. The volume fraction of PbS NCs in these solids was calculated based on the known ratio of PbS to CdS particle absorbance. Namely, when CdS and PbS/CdS core/shell colloids are fused into a film, the average interparticle distance, $R_{\text{edge}}$, becomes greater than twice the thickness of the CdS shell as the distance between the PbS dots is now enhanced
by the presence of interstitial CdS domains. To determine the relationship between molar concentrations of both nanoparticle types and the partial number density of these nanocrystals in a mixture, precursor solutions of mixed nanoparticles were deposited onto a TEM grid and analyzed.

Figure 4.5 Fluorescence intensity decay of near-IR emitting PbS nanocrystals (a) d=2.7 nm and (b) d=4.1 nm encapsulated into CdS matrices as a function of increasing $N_{CdS}/N_{PbS}$ “precursor nanoparticle” fraction. (c). Steady-state emission of modified-SMENA films (d$_{PbS}$ = 2.7 nm) featuring $N_{CdS}/N_{PbS}$=0 (blue curve) and $N_{CdS}/N_{PbS}$=12 (red curve). (d). Steady-state emission of modified-SMENA films (d$_{PbS}$ = 4.1 nm) representing $N_{CdS}/N_{PbS}$=0 (blue curve) and $N_{CdS}/N_{PbS}$=4
According to Fig. 4.5e, the ratio of each nanoparticle type (PbS/CdS core/shell versus CdS dot) can be easily obtained by identifying the corresponding populations of each dot in the TEM specimen. The core/shell nanocrystals can be differentiated by their larger radii and darker shading, as indicated by arrows in a characteristic TEM image (Fig. 4.5e), featuring 4.3-nm CdS and 5.2-nm PbS/CdS NCs. Since the initial concentrations of each colloid prior to TEM sampling were known, the number density of each nanocrystal type in a film can be estimated. The ratio of CdS to PbS/CdS dots in the film is then used to estimate the PbS volume fraction, $v_{\text{PbS}}$, according to the following equation (see Supporting Information for details of calculation):

$$v_{\text{PbS}} = \frac{(n+1)^2 \times \frac{4}{3} \pi R_{\text{core}}^3}{(nD_C + D_{P/C})^3}$$

where $n = N_{\text{PbS}}/N_{\text{CdS}}$, and $R_{\text{core}}$ is the average radius of the PbS core domain in PbS/CdS core/shell nanocrystals.

Figure 4.5a shows the FL intensity decay of mixed CdS ($d_{\text{CdS}} = 4.3$ nm) and CdS/PbS ($d_{\text{PbS}} = 2.7$ nm) NC solids fabricated using a modified SMENA approach. As expected from WKB approximation, the FL lifetime increases with growing $R_{\text{edge}}$, reflecting a simultaneous decrease in the cumulative rate of interparticle transfer processes. The fastest decay in Fig. 4.5a ($R_{\text{edge}} = 1.2$ nm) corresponds to a solid containing no CdS NCs (conventional SMENA). A relatively thin CdS shell ($\Delta H \approx 1$ nm) used in this case enabled only a partial localization of charges, leading to a charge transfer-limited lifetime of about 95 ns. The addition of CdS NCs to PbS/CdS precursor nanoparticles increases the interparticle separation from 1.2 to 11 nm (Fig.
4.5a), bringing the maximum $R_{\text{edge}}$ to more than twice the value accessible through a conventional SMENA approach. The enhanced interparticle separation results in a stronger localization of photoinduced charges (as illustrated in Fig. 4.2b), which causes the FL lifetime to increase (Fig 4.5a). A particularly interesting trend was observed for large values of $R_{\text{edge}}$. For these matrices, the lifetime of PbS excitons climbed to an unprecedented 0.98 μs (determined by a 1/e intensity drop), which constitutes a four-fold increase over best-performing NC emitters fabricated through a conventional SMENA approach. We note that the exciton lifetime for these nanocrystals in solution is 2.8μs (Fig. 4.SF2), which implies that a substantial fraction of excitations recombine radiatively, setting the upper limit of the fluorescence quantum yield to nearly $100 \times \frac{\tau_{\text{FL}}}{\tau_{\text{radiative}}} = 10\%$ (although absolute quantum yield was not measured for these samples). Likewise, the observed exciton lifetime was found to be enhanced relative to those of previously reported PbS NC film architectures utilizing hybrid molecular ligands. This phenomenon can be tentatively attributed to a suppressed non-radiative decay in matrix-passivated nanocrystals. The saturation of the FL lifetime in modified-SMENA films emitting at $\lambda \approx 1300$ nm occurs faster than in small-diameter PbS NC films (see Fig. 4.5b), with the longest lifetime of $\tau = 480$ ns. An enhanced lifetime of band gap excitons in mixed PbS NC films is consistent with the reduced volume fraction of PbS NCs in comparison with conventional SMENA solids. Finally, according to Figs. 4.5c,d, the increase in $R_{\text{edge}}$ value gives rise to a < 20 nm redshift of the emission peak, as expected due to the delocalization of the electronic wave functions into the CdS matrix.

An absolute value of the emission QY was determined for films comprising large-diameter PbS nanocrystals ($\lambda_{\text{FL}} \approx 1300$ nm). We note that these films did not yield the best exciton lifetime, however, were more compatible with the experimental setup in use. The
detection methodology was adapted from the one described in Ref. 39, and was designed to eliminate the use of a reference dye and to provide the possibility for simultaneous measurement at excitation wavelength of absorbance, which is corrected to reflectance and scattering losses at integrating sphere. According to these measurements (summarized in Table 4.1), the highest value of the emission quantum yield of QY=3.7% was realized for solids featuring R_{edge} of 7.9 nm. To the best of our knowledge, this value represents the highest reported emission quantum yield for inorganic nanocrystal films emitting in the infrared range. The difference between the observed QY value in a solid and a typical QY range for these nanoparticles in solution (10-30%) is attributed to the onset on non-radiative decay pathways (trapping and charge transfer) upon the transfer of colloidal nanoparticles onto a substrate.

Another relevant property of modified SMENA films that merits discussion is the linewidth of the emission peak. Application of luminescent films in light-emitting technologies often benefits from a spectrally narrow emission profile. Our estimates show that the peak width of modified-SMENA films (FHWM = 165 nm, @λ = 970 nm) increases compared to that of OA-capped PbS nanocrystals in solution (FHWM = 120 nm, @λ = 950 nm). However, the fusion of core/shell nanocrystals into a solid doesn’t not seem to contribute much to broadening of the emission profile, as OA-capped PbS/CdS nanocrystals in solution exhibit FHWM of 160 nm. Indeed, the primary enhancement of the peak width occurs as a result of the shell growth, an important step, which also results in the improvement of the fluorescence quantum yield.
In order to reduce the density of dangling bonds in nanocrystal matrices, interparticle gaps between fused core/shell structures were partly filled with additional CdS. To this end, several SILAR cycles were applied resulting in a deposition of 3-4 CdS monolayers. Previous works have shown\textsuperscript{34} that such treatment increases the refractive index of the nanocrystal film through partial filling of void areas. According to Fig. 4.6, application of 6 SILAR cycles to a CdS-encapsulated PbS NC film featuring $R_{\text{edge}}$ of 1.5 nm results in a 55% increase in the FL lifetime. In particular, the slower component of the FL intensity decay, which is associated with charge tapping has increased from $\tau_{\text{FL, slow}} = 90$ to $\tau_{\text{FL, slow}} = 150$ ns, reflecting the reduction in the rate of carrier trapping.

**Figure 4.6** Suppression of charge trapping on the surface of PbS/CdS SMENA films ($R_{\text{edge}} = 1.5$ nm, $d_{\text{PbS}} = 2.7$ nm) by additional SILAR passivation. The red curve represents an increased exciton lifetime following the SILAR treatment.
**Figure 4.7 (a).** Temporal evolution of the band-edge emission peak area for CdS-encapsulated PbS NC arrays ($R_{\text{cgde}} \approx 2.8$ nm) fabricated using a modified-SMENA approach. (b,c). Comparison of the thermal stability of OA-capped (c) and CdS-encapsulated (b) PbS NC arrays, fabricated using a modified-SMENA approach. (d,e). Temporal evolution of the emission peak.
for films exposed to T=170 °C in air. The comparison is drawn between CdS-encapsulated PbS NC arrays (d) and OA-capped PbS/CdS core/shell NCs on a substrate (e).

Improving the thermal stability of NC solids is important for their deployment in light-emitting devices, as many of those applications are subject to the generation of heat. In the present approach, the presence of heteroepitaxial bonding between NC surfaces and the matrix semiconductor is expected to prevent low-temperature oxidation, deferring the thermal degradation of NCs to occur only at higher temperatures via the phase transition of the lattice. Here, we test this hypothesis by comparing thermal stability of modified-SMENA films (R_{\text{edge}} = 2.8 nm, SILAR treated) with that of oleic acid (OA)-capped PbS NC films. To this end, the intensity of band edge emission in both solids was plotted versus the substrate temperature. According to Figs. 4.7b,c, heating of matrix-encapsulated (b) and OA-passivated (c) PbS NCs in air results in a gradual drop of the emission intensity, which was taken as a sintering temperature of PbS. In the case of CdS-encapsulated PbS NCs, sintering occurred at T \approx 200 °C, which is 90-100 °C above that of OA-capped PbS NC solids. Interestingly, the thermal stability of modified-SMENA PbS solids does not arise merely from the presence of the CdS shell on PbS surfaces. According to Figs. 4.7d,e, oleic acid-capped PbS/CdS NCs (\Delta H_{\text{CdS}} = 1.2 nm) placed on a hot substrate undergo a much faster degradation of the band gap emission then modified SMENA films fabricated from the same core/shell nanoparticles. This result strongly suggests that the crystallographic fusion of core/shell precursors into a solid is essential for enhancing the stability of encapsulated PbS NCs. In the final stability test, we have looked into the temporal degradation of the film versus time by recording the changes in the emission intensity after the heat was applied to the substrate. The two curves in Fig. 4.7a, illustrate the reduction in the emission
intensity of matrix-encapsulated PbS NCs for films kept in argon (red) and air (blue). A slightly faster decay of the latter curve suggests that oxidation is partly responsible for the loss of emission at elevated temperatures. These experiments demonstrate an enhanced heat resistance of matrix-encapsulated PbS SMENA solids as compared to organic-interlinked nanoparticle films.

4.5 CONCLUSIONS

In conclusion, a novel strategy for processing of PbS nanocrystal solids exhibiting bright infrared emission is demonstrated. The reported methodology benefits from the use of inorganic CdS host matrices to provide a stable passivation of nanoparticle surfaces while preserving some degree of quantum confinement. The morphology of encapsulating matrices was judiciously optimized to induce the suppression of non-radiative decay processes associated with surface carrier trapping and interparticle charge transfer. This allowed extending exciton lifetimes up to 1 microsecond, which constitutes at least a two-fold enhancement over ligand-based passivation strategy. The suppressed carrier trapping has given rise to a high emission quantum yield of $QY_{\text{solid}} = 3.7\%$ in the infrared range, while inorganic matrix medium warranted a superior thermal and chemical stability of fabricated nanocrystal solids.

4.6 SUPPORTING INFORMATION

Volume fraction calculations.

Suppose that on average a unit length of the mixed nanocrystal film contains $N_c$ of CdS and $N_p$ and core/shell nanocrystals. A unit volume of such film be given by \((N_p D_{p/c} + N_c D_c)^3\), where $D_{p/c}$ and $D_c$ are the average diameters of PbS/CdS and CdS NCs, respectively. The
number of PbS cores in a unit volume will be given by

\[ \frac{N_p}{N} \times (N_p + N_C)^3 \],

where \( N = N_p + N_C \), where \( N = N_c + N_p \). Therefore the volume fraction can be expressed as:

\[
\frac{V_{PbS}}{V_{CdS}} = \frac{N_p / N \times (N_p + N_C)^3 \times \frac{4}{3} \pi R_{core}^3}{(N_p D_{p/c} + N_C D_C)^3} = \frac{(n+1)^2 \times \frac{4}{3} \pi R_{core}^3}{(n D_C + D_{p/c})^3}
\]

(4.SE1)

where \( n = N_p / N_c \), and \( R_{core} \) is the average radius of the PbS core domain in PbS/CdS core/shell nanoparticles.

**Figure 4.SF1** Fluorescence intensity decay of CdS-encapsulated PbS nanocrystals. The fast and the slow decay components correspond to charge transfer and charge trapping processes, respectively.
Figure 4.SF2 (top). Steady-state emission of PbS/CdS core/shell NCs in solution (black curve) and encapsulated into a film (red curve). (bottom). Fluorescence intensity decay of OA-acid capped PbS/CdS core/shell NCs in solution.
Figure 4SF3: Steady-state emission of PbS/CdS solids featuring large $R_{edge}$ distances (thick CdS shell). The use of a conventional SMENA methodology leads to excessive trap state emission in the $\lambda=500$-800 nm range.
Table 4.ST1 Quantum yield of CdS-encapsulated PbS NC solids emitting at $\lambda_{\text{PbS}} = 1300$ nm. The relative error of Quantum Yield measurement is about 15%. The effects of self-absorption were neglected due to low optical density of the samples.

<table>
<thead>
<tr>
<th>Sample $(\lambda_{\text{PbS}}=1300$ nm)</th>
<th>PbS volume fraction ($\nu_{\text{PbS}}$)</th>
<th>Optical density @808 nm</th>
<th>Quantum Yield, %</th>
<th>Life time, ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{edge}}=2.5$ nm</td>
<td>0.24</td>
<td>0.032</td>
<td>2.0</td>
<td>105</td>
</tr>
<tr>
<td>$R_{\text{edge}}=6.5$ nm</td>
<td>0.096</td>
<td>0.015</td>
<td>3.3</td>
<td>350</td>
</tr>
<tr>
<td>$R_{\text{edge}}=7.9$ nm</td>
<td>0.07</td>
<td>0.015</td>
<td>3.7</td>
<td>480</td>
</tr>
</tbody>
</table>

Figure 4.SF4 Spectra of laser and PL emission of the solid with $R_{\text{edge}}=2.5$ nm, transmission spectra of longpass and shortpass filters applied for quantum yield.
Figure 4.SF5 Absorption spectra of samples measured with integrating sphere spectrometer.

Figure 4.SF6 High resolution TEM image of PbS/CdS core/shell NCs.
REFERENCES


