EXCITON DIFFUSION IN NANOCRYSTAL SOLIDS

Natalia Kholmicheva

A Dissertation

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Committee:

Mikhail Zamkov, Advisor

Ron C. Woodruff
Graduate Faculty Representative

Ksenija Glusac

Alexey Zayak
This dissertation work is focused on exploring the unique optical and electronic properties of several semiconductor nanostructures and devices based on them.

The present research demonstrates the near-field confinement of light achieved through the use of small-diameter Au nanoparticles embedded into a PbS nanocrystal solid. Using this strategy, we developed plasmonic solar cells that can harness the emission of Au nanoparticles by transferring the plasmon energy to band gap transitions of PbS semiconductor nanocrystals. The contribution of Au near-field emission toward the charge carrier generation was successfully proved through the observation of an enhanced short circuit current and improved power conversion efficiency of mixed (Au, PbS) solar cells, compare to PbS-only devices.

Moreover, unique behavior of semiconductor nanocrystals makes them to be promising candidates not only for photovoltaics but for light-emitting applications as well. In light-emitting devices NC solids are designed to have large interparticle gaps that minimize exciton diffusion to dissociative sites. This strategy reduces electrical coupling between nanoparticles in a film, making the injection of charges inefficient. We demonstrated that bright luminescence from nanocrystal solids can be achieved without compromising their electrical conductivity. Our research showed that solids featuring low absorption-emission spectral overlap exhibit slower exciton diffusion to recombination centers, promoting longer exciton lifetimes. As a result, enhanced emission is achieved despite a strong electronic coupling. The inverse correlation between film luminescence and absorption-emission spectral overlap was verified by the
comparison of CdSe/CdS and ZnSe/CdS solids and further confirmed in two control systems (ZnTe/CdSe and Mn$^{2+}$-doped ZnCdSe/ZnS).

Another challenging task in the development of quantum dot based solids lies in the studying the motion of neutral excitons. The nature of the exciton dissociation mechanism as well as exciton diffusion trajectories in nanocrystal solids remain poorly understood. We developed an experimental technique for mapping the motion of excitons in semiconductor nanocrystal films. This was accomplished by doping PbS nanocrystal solids with metal nanoparticles that force the exciton dissociation. By correlating the metal-metal interparticle distance in the film with corresponding changes in the emission lifetime, we could obtain important transport characteristics, including the exciton diffusion length and the exciton diffusivity.
My dissertation is dedicated to my parents, Elena Kholmicheva and Nikolay Kholmichev, for their endless love, support, and encouragement.
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CHAPTER I. PLASMONIC NANOCRYSTAL SOLAR CELLS UTILIZING STRONGLY CONFINED RADIATION


1.1 Abstract

The ability of metal nanoparticles to concentrate light *via* the plasmon resonance represents a unique opportunity for funneling the solar energy in photovoltaic devices. The absorption enhancement in plasmonic solar cells is predicted to be particularly prominent when the size of metal features falls below 20 nm, causing the strong confinement of radiation modes. Unfortunately, the ultrashort lifetime of such near-field radiation makes harvesting the plasmon energy in small-diameter nanoparticles a challenging task. Plasmonic solar cells, that harness the near-field emission of 5-nm Au nanoparticles by transferring the plasmon energy to band gap transitions of PbS semiconductor nanocrystals, have been developed. The interfaces of Au and PbS domains were designed to support a rapid energy transfer at rates that outpace the thermal dephasing of plasmon modes. It has been demonstrated that central to the device operation is the inorganic passivation of Au nanoparticles with a wide gap semiconductor, which reduces carrier scattering and simultaneously improves the stability of heat-prone plasmonic films. The contribution of the Au near-field emission toward the charge carrier generation was manifested through the observation of an enhanced short circuit current and improved power conversion efficiency of mixed (Au, PbS) solar cells, as measured relative to PbS-only devices.
1.2 Introduction

The spatial confinement of light near metal surfaces gives rise to remarkable optical properties that are highly attractive for the development of light-harvesting materials. Of a particular interest are nanoparticles of noble metals, where the per-volume extinction coefficient in the visible range exceeds those of semiconductor quantum dots or organic polymers by at least an order of magnitude (Fig. 1.1 a). These superior light extinction properties arise from an enhanced density of states associated with the surface plasmon (SP) resonance of free carriers, which funnels incident photons into localized “hot spots”. The ability of metal NPs to concentrate light holds strong promise for improving the performance of photovoltaic and photocatalytic materials provided that an efficient strategy for converting the absorbed energy into spatially separated charges is conceived.9-11

Recently, the prospect of incorporating plasmonic materials in solar cell devices has received a great deal of attention. Several strategies for enhancing the cell’s optical extinction either through solution-processing or via vapor-deposition of plasmonic structures have been considered. Au or Ag metals, exhibiting a strong plasmon resonance in the visible range, have been a common choice of plasmonic materials, although the use of Pt, Pd, Al, and Cu has also been explored. Overall, the improvement in the photovoltaic performance of plasmonic devices was attributed to the enhanced optical extinction of an active layer, which allowed decreasing the absorber thickness enabling shorter carrier extraction distances. The benefits of the reduced charge collection path, however, were partly compromised by the decrease in the carrier diffusion length caused by the presence of metal dopants in the film.
The confining geometry of metal nanoparticles plays a critical role in the ensuing mechanism of the plasmon energy conversion. Depending on the size of the metal domain, the operation of plasmonic solar cells can fall into one of the two regimes corresponding to far-field and near-field energy transfer modes. When the size of metal structures is large (> 50 nm), most of the absorbed radiation is scattered into the far field, whereby increasing the effective light path in a film. On the contrary, the employment of small-size metal features invokes near-field scattering of radiation, which leads to a sub-wave confinement of light (Fig. 1.9). The plasmon energy conversion can then undergo via a near-field energy or electron transfer.\textsuperscript{30}

To date, far field scattering of light in plasmonic photovoltaic devices has been a more common choice of the absorption enhancement strategy. An important benefit of this scheme lies in the reduction of the parasitic absorbance through the use of large-size metal features, which couple most of the incident light back into the film (Fig. 1.8). Typically, the location and geometry of plasmonic scatterers can be optimized to form photonic arrays yielding an improved light-harvesting performance. In the absence of the sub-wave confinement of light, the maximum absorption enhancement, $F$, for such far-field scattering mode, is given by the Yablonovitch’s limit\textsuperscript{31} as, $F = 4n^2$ (assuming isotropic emission), where $n$ in the refraction index of the absorber. The actual enhancement from the far-field scattering is substantially lower since not all of the available momentum states associated with free space modes can be filled.
Figure 1.1 (a). Per-volume extinction cross sections of common nanoscale sensitizers. The comparison highlights superior light-harvesting characteristics of Au nanoparticles relative to semiconductor quantum dots and organic polymers (P3HT). (b). Schematic representation of the surface plasmon relaxation in small-diameter Au NPs. The decoherence of SP oscillations takes less than 50 fs leading to the generation of hot carriers, which eventually decay by coupling to phonon modes in 1-5 ps.

A recent breakthrough in understanding photonic materials has shown that the classical $4n^2$ limit of absorbance enhancement in photovoltaic films can be surpassed if the radiation modes are confined (e.g. using a waveguide structure). It was predicted that for a sub-wave light confinement with a 5-nm localization length the enhancement of the absorbance can be
extended to $F=60n^2$, up to 15 times greater than in the case of the geometric far-field scattering. Theoretically, such trapping of radiation can be realized through a near-field emission of surface plasmons in small-diameter metal nanoparticles where far-field scattering is suppressed (Fig. 1.9). The grand challenge lies in converting the absorbed radiation of small-diameter metal colloids into useful energy, as those structures efficiently couple the electronic decay to phonon modes. Indeed, the decoherence of SP oscillations in metal NPs is extremely fast and takes less than 50 fs leading to the production of hot carriers, which, in turn, decay by coupling to phonon modes in 1-5 ps (see Fig. 1.1b). If the plasmon energy or hot carrier population is not transferred away within this short time window, the absorbed radiation will be internalized primarily through the generation of heat. Evidently, such heat production does not contribute to the device photocurrent and is detrimental to the solar cell performance. In order to avoid the thermal dissipation of SP energy, some photovoltaic and photocatalytic schemes have used the energy of hot carriers generated by a dephasing plasmon, which spill over the Schottky barrier and enter the semiconductor phase. This strategy allows collecting some of the plasmon energy before the onset of the thermalization, albeit leading to only a moderate enhancement in the device performance. Nevertheless, the most efficient conversion of the near-field emission is possible when the plasmon energy is picked up via the near-field energy transfer prior to its dephasing (Fig. 1.1b). This type of energy exchange can occur through a transfer of virtual photons rather than electrons and was recently shown to enable a record efficiency in polymer solar cells doped with metal nanoparticles.

For that reason, plasmonic nanocrystal solar cells operating in the near-field energy transfer regime has been developed. The gain in the photovoltaic performance is enabled through a resonant coupling of surface plasmon modes in Au nanoparticles to band gap excitations of
PbS semiconductor nanocrystals. In order to maximize the confinement of light, the size of Au domains was chosen not to exceed 10 nm in diameter. In this configuration, far field scattering of light is strongly suppressed giving rise to the near-field emission of plasmon radiation. The thermal impact of residual heating in Au nanoparticles was mitigated through the use of an all-inorganic film design featuring a crystalline matrix encapsulating an array of Au and PbS nanoparticles.\textsuperscript{45-47} It has been showed that adding Au NPs into the absorber layer dramatically improves the optical extinction of the film, while causing some curbing of the exciton lifetime due to scattering on Au. The overall benefit of the near-field absorption enhancement strategy was evidenced through a moderate improvement of the solar cell efficiency. For instance, doping the PbS nanocrystal film with 0.3\% of Au NPs (by volume) caused an increase in the average power conversion efficiency (PCE) from 4.0 to 4.2\%, with the best performing device exhibiting 4.5\% of PCE. The increased short circuit current (a gain of 41 ± 3\%) was the primary factor contributing to the enhanced PCE, whose effect was partly compromised by a small drop in the open circuit voltage.
1.3 Experimental Section

1.3.1 Materials.

Lead(II) oxide powder (PbO, 99.999% Aldrich), 1-octadecene (ODE, 90% Aldrich), oleic acid (OA, 90% Aldrich), bis-(trimethylsilyl) sulfide ((TMS)$_2$S, Aldrich, synthetic grade), acetone (anhydrous Amresco, ACS grade), hexane (anhydrous, 95% Aldrich), ethanol (anhydrous, 95% Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, 98% Alfa Aesar), sulfur (S$_8$, 99.999% Acros), methanol (anhydrous, 99.8% Aldrich), isopropanol (anhydrous, 99.8% Acros), toluene (anhydrous, 99.8% Aldrich), tributylphosphine (TBP, 97%, Aldrich), 3-mercaptopropionic acid (MPA, 99%, Alfa Aesar), zinc acetate (98+% Acros), silver nitrate (AgNO$_3$ 99%, Aldrich), gold(III) chloride (AuCl$_3$ 99%, Acros Organics), titanium dioxide (DSL 90T, DyeSol), terpineol (MP Biochemicals), titanium chloride (TiCl$_4$, 99.99% Aldrich) and cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O, 99.999%, Aldrich) were used as received without any further purification. Oleylamine (tech., 70%, Aldrich) was pumped for 1 hour at 120 °C and then stored under argon atmosphere prior using. Fluorine-doped tin oxide (FTO, SnO$_2$/F) glass (TEC 15, 12-14 Ohm/sq) was obtained from Pilkington Glass. All reactions were performed under argon atmosphere using the standard Schlenk technique. The centrifuge used for precipitation operated at 7200 rpm.

1.3.2 Synthesis of PbS nanocrystals.

PbS NCs were synthesized according to the procedure reported by Hines$^{52}$. A mixture of 0.49 g PbO, 18 mL ODE, and 1.5 mL OA was degassed in a 3-neck flask at 120°C for 2 hours, switched to argon flow, and kept at 135°C until injection. At the same time, 10 mL of ODE was degassed at 120°C for 2 hours in one-neck flask, switched to argon flow, and kept at room
temperature. Later, 0.21 mL of (TMS)$_2$S was added to ODE at room temperature under argon flow. The resulting (TMS)$_2$S/ODE mixture was injected into the Pb$^{+2}$ precursor solution at 135°C, while stirring. The reaction was stopped after 2 min by removing the flask from the heating mantle and placing it into a cold water bath. Fabricated PbS nanocrystals were isolated from the mixture by precipitating with acetone, centrifuging, and redispersing in hexane. The cleaning procedure has been repeated 2 times, after which nanocrystals were finally redispersed in hexane (~8 ml). The prepared NCs had 1S peak at 1020 nm.

1.3.3 Synthesis of PbS/CdS core/shell NCs through cation exchange.

The NCs were synthesized according to the procedure reported by Pietryga.$^{53}$ A mixture of 0.2 g CdO, 1.5 ml OA, and 6 ml ODE was heated to 235°C under argon until the solution became clear. The reaction mixture was kept at 55°C under argon flow. Then, 4 mL of PbS was injected to the Cd$^{+2}$ precursor and the reaction was immediately quenched by removing the flask from a heating mantle and placing into a cold water bath. The PbS/CdS NCs were isolated by centrifuging with ethanol. The precipitate obtained during centrifuge was dissolved in 2-3 mL of hexane. The cleaning procedure has been repeated 2 times, after which nanocrystals were finally redispersed in hexane (~4 ml). The blue shift was observed in the prepared core/shell NCs with the value of $\Delta \lambda = 50$-$60$ nm (shell thickness $\approx 0.25$ nm).

1.3.4 Synthesis of Oleylamine-Capped Au nanocrystals (NCs).

Au NCs were synthesized according to previously reported methodology.$^{54}$ In a typical synthesis, 0.011g of AuCl$_3$ and 5 mL of oleylamine were loaded in a one-neck flask and allowed to react at 100 °C for 30 min under argon atmosphere. During this time, the reaction mixture’s color changed from transparent yellow to orange (indicating the formation of Au-oleate
complexes), and then finally to purple (indicating the formation of oleylamine-capped Au NPs). The reaction was stopped by removing the flask from the heating mantle and allowed to cool to room temperature. Then, the solution was transferred from the flask into centrifuge tubes and precipitated with ethanol. After the centrifugation, the supernatant was discarded and the pellet was dissolved in chloroform. The cleaning cycle was repeated one more time and the final product was re-dispersed and stored in 5 ml of chloroform. The final product contained Au NPs with an average diameter of 5 nm and a surface plasmon resonance (LSPR) peak at $\lambda \approx 525$ nm.

1.3.5 Synthesis of Oleylamine-Capped Au/Ag core/shell NCs.

The growth of Ag shell was performed according to the procedure adopted by Shore. Approximately a quarter of Au NPs from the previous step were mixed with 5 mL of oleylamine. The mixture was heated to 120°C while stirring. At this point, $1.05 \times 10^{-2}$ M aqueous solution of $\text{Ag}^+$, prepared by sonication $0.089 \text{g AgNO}_3$ in 5 mL of deionized water was injected stepwise into the Au-seed reaction flask (0.2 mL every 10 minutes). The average thickness of the Ag shell surrounding the Au NPs was tracked by the position of the localized surface plasmon resonance (LSPR) peak. After every 10 minute of the shell growth period, a sample was taken from the reaction flask for steady-state spectroscopic analysis. The LSPR peak of NPs comprised strictly of Au was centered about $\lambda_{\text{Au}} \approx 525$ nm, and this peak blue-shifted closer to the position of pure Ag NP’s LSPR peak ($\lambda_{\text{Ag}} \approx 415$ nm for Ag NPs of similar dimensions) as the Ag shell grew in thickness. After observing the desired LSPR peak at 455 nm ($\Delta \lambda = 70$ nm), the reaction mixture was cooled down to the room temperature by removing the flask from a heating mantle. The synthesized Au/Ag nanocrystals were isolated from the mixture by precipitating with ethanol, centrifuging, and redispersing in chloroform.
1.3.6 Synthesis of Au/Ag\textsubscript{2}S NCs from Au/Ag.

The Au/Ag\textsubscript{2}S NCs were synthesized according to the procedure adapted from Zhang.\textsuperscript{56} Briefly, a solution of sulfur precursor, which was prepared by sonication of 0.005g S\textsubscript{8} powder in 2 mL oleylamine, was injected into a 25 mL two-neck flask containing the entire amount of Au/Ag solution fabricated in the previous step. The sulfur precursor was added in 0.2 mL increments to the solution of Au/Ag core/shell NCs, which were under argon and being vigorously stirred, and then left to react for 10 minutes. After 10 minutes, a sample was taken for spectral analysis. Sulfur was added in this way until the LSPR absorption peak had red-shifted to ~630 nm. The NCs were then cleaned once by adding 10 mL ethanol to the reaction solution and centrifuging the solution. Under argon, the precipitated NCs were then suspended in 4 mL of toluene.

1.3.7 Synthesis of Au/CdS NCS from Au/Ag\textsubscript{2}S.

Au/CdS NCs were fabricated using a procedure inspired by Zhang.\textsuperscript{56} To this end, a toluene solution of Au/Ag\textsubscript{2}S NCs from the previous step was combined with 1 mL of oleylamine, placed in a two-neck flask and heated up to 60 °C under argon atmosphere. The cadmium precursor, which was prepared in a glass vial by sonication 0.12 g (0.39 mmol) Cd(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O in 1 mL of methanol, was quickly injected into a reaction flask and solution was allowed to stir at elevated temperature for 10 minutes. To initiate the cation exchange reaction, 0.1 mL TBP was added to the mixture and solution was left for 2 hours at 60 °C under vigorous stirring. The growth of the shell was accompanied by the blue-shift of the LPSR peak. To isolate final product, 10 mL of methanol was added to the reaction mixture, which was subsequently centrifuged. The precipitate was then dissolved and stored in hexane.
1.3.8 Preparation of the 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 isopropyl alcohol for 5 min in each solvent.

1.3.9 Fabrication of nanocrystal solids.

The fabrication of all-inorganic NC films (SMENA) was performed using previously reported methodology. For each layer, the solution of PbS/CdS NCs in hexane (concentration 20 mg/ml) or a mixture of PbS/CdS and Au/CdS NCs was deposited on the glass substrate and spin at 3000 rpm for 10 seconds. Subsequently, 7-10 drops of MPA/Methanol solution (ratio 1:3) 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 hexane in the same manner. Upon the deposition of 2 layers, the films were annealed at 140-150°C for 15 min. The total amount of layers was varied from 3 to 4. Ratios of PbS/CdS to Au/CdS were calculated using a volume fraction of each material in the mixture (see Supporting Information).

1.3.10 Preparation of TiO$_2$ electrodes.

The deposition of the TiO$_2$ layer was performed using a previously reported approach. To this end, dry and clean SnO$_2$/F-coated glass substrates were immersed in a 75mM solution of TiCl$_4$ in deionized water and allowed to soak at 70 °C for 30 min. The substrate was then rinsed with deionized water, dried under argon, heated to 450 °C for 1 h, and then allowed to cool to room temperature. Meanwhile, the mixture of TiO$_2$ DyeSol paste and
terpineol (1:3 ratio by weight) was sonicated until solution became homogeneous. Three drops of the freshly prepared TiO$_2$ solution was placed in the center of a dry TiCl$_4$-treated SnO$_2$/F-coated glass slide and spun for 6 s at 700 rpm and for 1 min at 2900 rpm. The substrate was then annealed outside the glovebox (ambient oxygen environment) at 450-500 °C to remove organic matter.

1.3.11 Deposition of mixed (Au, PbS) nanoparticle films from solution.

For the SMENA solar cells fabrication the nanocrystals were deposited using an aforementioned approach (see Fabrication of Nanocrystal Solids). The total 8-10 layers were deposited on the TiO$_2$ electrode. MPA-linked NC films were deposited using a layer-by-layer spincoating process under argon atmosphere. Each layer of nanocrystals was deposited by placing 3-5 drops of the mixture on the spinning substrate (3000 rpm) with subsequent treatment with MPA solution (i.e. MPA:Methanol = 3:1) and rinsing the film with methanol and hexane. The total of 6-8 layers of the NCs were deposited. Ratios of PbS to Au were calculated using a volume fraction of each material in the mixture (see Supporting Information).

1.3.12 In-filling of SMENA pores with ZnS.

For the pore-filling process, the successive ionic layer adsorption and reaction (SILAR) method was applied. Briefly, the deposition of additional layers of ZnS was conducted by sequential soaking of the annealed NC films in methanol solutions of Zn$^{2+}$ and S$^{-2}$ 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 Na$_2$S•9H$_2$O in 20 mL of methanol. One SILAR cycle included 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. 2-6 cycles of pores filling process was applied for all-inorganic films followed by annealing at 150 °C for 15 minutes.

1.3.13 Deposition of Au/Pd counter electrodes.

To complete the cell assembly, 60-90 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 cm².

1.3.14 Characterization.

Absorbance spectra were recorded using a CARY 50 scan and Shimadzu UV-3600 UV-vis-NIR spectrophotometers. Photoluminescence measurements were performed using Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy (TEM) measurements were carried out using JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of NP solution in organic solvent onto a carbon-coated copper grid and allowing it to dry in air. I-V data was measured using a Keithley 2400 source-meter under ambient conditions. Characteristics were performed under AM 1.5 G (100 mW/cm²) solar simulator on the I-V data acquisition system from PV Measurements, Inc. X-ray powder diffraction (XRD) measurements were carried out on a Scintag XDS-2000 X-ray powder diffractometer. FL 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, and 750nm.
1.3.15 Photoexcitation.

Steady-state photoexcitation spectra were measured using a PTI QuantaMaster spectrofluorometer with a Xenon lamp light source. Excitation scan was performed in the range 510-735 nm with the detection on PbS band gap emission at 750 nm. The spectra were collected at 45° for the solid films and integrated for 10 seconds per nanometers for better noise to signal ratio.

1.4 Results and Discussion

Theoretical aspects of photovoltaic absorbers utilizing a strong confinement of optical modes have been discussed in a recent work of Yu. In a simplified interpretation of this model, the absorbance enhancement in thin films is inversely proportional to the light-confinement length, $d$, such that $F \sim M/d$, where $M$ is the number of resonances in the film. Consequently, increasing the density of optical modes in the film through the enhancement of the light localization should lead to the greater enhancement of optical extinction (Fig. 1.8). Near-field emission of small-diameter metal NPs satisfies these conditions, offering a practical way for achieving a strong localization of light in semiconductor solids. With these considerations in mind, the photovoltaic architecture developed in this work was targeted toward supporting an efficient energy transfer from the surface plasmons of 5-7 nm Au NPs to band gap and impurity excitations of 3.2-nm PbS nanocrystals.

The solar cell morphology comprising small-diameter Au NPs represents a fundamentally interesting case. On one hand, the suppression of far field scattering in these films should enable a near-field emission with typical length scales comparable to the size of a plasmonic nanoparticle. In this arrangement, the confined optical modes can stimulate the production of
excitons in semiconductor films leading to an increased device photocurrent. On the other hand, the extraction of the radiative energy from small-diameter metal NPs is more challenging than in the case of large-diameter structures due to a rapid decay of near-field evanescent waves (< 50 fs). One of the goals of this work is to evaluate the very expediency of harvesting such near-field radiation through the generation of excitons and excited carriers in a photovoltaic absorber. Because of the fundamental character of this investigation, the conclusions drawn from experiments are built on qualitative comparisons, which allow omitting some of the device optimization steps.

Enabling an efficient energy transfer between semiconductor and metal nanoparticles is the key to avoiding energy losses associated with electron-phonon scattering. This requirement places several stringent criteria on the design of plasmonic films. First, as discussed above, the size of metal NPs should be sufficiently small to minimize the far field scattering (Fig. 1.9). Second, the energy of the plasmon resonance should be somewhat greater than the band gap of the semiconductor absorber in order to promote a fast, one-directional energy transfer while minimizing the phonon generation from above the gap (intraband) vibrational relaxations. Third, to prevent the transfer of photoinduced charges from semiconductor into metal, the two domains should be insulated by a potential barrier. The latter condition becomes particularly important for interfaces of small-size nanoparticles where Schottky barriers may not exist. Finally, since some fraction of SP energy in metal NPs undergoes electron-phonon relaxation, causing heating of the local environment, the plasmonic solar cell needs to have a greater thermal stability than a non-plasmonic equivalent. With these considerations in mind, we have chosen an all-inorganic active layer morphology comprising Au and PbS nanoparticles as energy transfer partners. To this end, both types of nanocrystals were encapsulated into CdS matrices using a previously developed
Semiconductor Matrix Encapsulated Nanocrystal Array (SMENA) approach with a minimal Au-PbS spacing, $R_{\text{Au-PbS}}^{\text{min}}$ of $\approx 2$ nm.

The details of the matrix-encapsulation assembly technique are described in the Experimental section. In brief, to fabricate a mixed (Au, PbS) absorber film, both Au and PbS NCs were coated with a shell of the matrix material, according to the scheme in Fig. 1.2a. The resulting Au/CdS, and PbS/CdS core/shell NPs were then mixed in octane at predefined ratios (see below) and used as “inks” for processing film layers. The original bulky ligands on the nanoparticle surfaces were exchanged with thermally-degradable MPA molecules during each cycle of the layer-by-later (LbL) deposition process. After each three cycles, the film was heated to approximately 140-150 °C to remove MPA ligands and promote crystallographic fusion of neighboring CdS shells. In the final step, additional ZnS material was deposited into the pores of the interfused nanoparticle solid by means of the successive ionic layer adsorption and reaction (SILAR) method. This step was designed to further passivate charged surfaces as well as to enhance the refractive index of the film.
Figure 1.2 (a). Illustration of the key steps involved in the development of plasmonic solar cells. The colloidal synthesis of PbS/CdS and Au/CdS core/shell NCs is followed by spincoating of the Au/CdS and PbS/CdS nanocrystal mixture onto TiO$_2$-modified FTO substrate, the exchange of long-chain ligands with thermally degradable MPA molecules, and crystallographic fusion of core/shell NCs performed using a layer-by-layer deposition. (b, d). Transmission electron microscope (TEM) images of PbS/CdS core/shell NCs used as soluble precursors for the development of the absorber layer. (c, e). TEM images of Au/CdS core/shell NCs.

Figure 1.2 shows characteristic Transmission Electron Microscope (TEM) images of Au/CdS (c,e) and PbS/CdS (b,d) core/shell nanostructures that served as colloidal precursors for the assembly of photovoltaic films. The growth of the CdS shell onto PbS NCs was carried out using previously established protocols, thorough a Pb$^{2+} \rightarrow$ Cd$^{2+}$ cation exchange.$^{53}$ Here, a 0.25-
nm CdS shell was employed to provide some degree of quantum confinement for photoinduced carriers in PbS NCs, while enabling interparticle tunneling of charge carriers. In the case of Au NPs, the thickness of the CdS shell was allowed to grow up to 2 nm in order to provide a sufficient potential barrier to both carrier types, whereby shielding PbS electrical charges from the excited states in metal. In this geometry, the rate of carrier tunneling between adjacent PbS domains is expected to be much greater than the rate of PbS to Au charge transfer, thus suppressing carrier scattering on Au domains. The formation of a thick (ΔH ≈ 2 nm) CdS shell on Au nanocrystals is evident in a high resolution TEM image of a characteristic Au/CdS core/shell structure (Fig. 1.2e). The uniform placement of the CdS semiconductor around the Au core manifests the absence of an interfacial strain between the two domains, which is a distinct advantage of the cation-exchange growth strategy. As illustrated in Fig. 1.10, the deposition of CdS or ZnS semiconductor shell was accompanied by a red-shift of the plasmon resonance from λ_{Au} ≈ 520 nm to λ_{Au/CdS} = 575 nm resulting from the changes in the surrounding dielectric constant.

A potential issue concerning the performance of plasmonic solar cells is a trade-off between the enhanced absorbance of a mixed (Au, PbS) nanoparticle film and the reduced photoconductivity of a solid due to carrier scattering on Au domains. If a near-field energy transfer (Au to PbS) is not efficient, the absorber film would require a high concentration of Au NPs in order to reach a sizable “plasmonic” effect. At such high levels of Au doping, however, carrier diffusion length may become too short. This would cause the current density to decrease, compromising an overall benefit of the plasmonic light-harvesting scheme. Along these lines, one of the overarching goals of this work was to understand whether the plasmon-exciton (near-
field) energy transfer mechanism is efficient enough to avail the device performance despite adverse effects of metal nanoparticles in the absorber layer.

We first look into the effect of Au doping on the optical density of mixed (Au, PbS) nanocrystal films. Since the per-volume extinction coefficient of Au NPs is about 30 times greater than that of PbS NCs (see Fig. 1.1a), only a small fraction of Au needs to be introduced for a sizable absorption enhancement. To estimate the concentration of Au NPs in the mixed solid, we have quantified the relationship between molar concentrations of both nanoparticle types in precursor solutions and their respective partial number densities. To this end, precursor solutions of mixed (Au, PbS) nanoparticle colloids were deposited onto a TEM grid and analyzed. The ratio of each nanoparticle type (Au/CdS core/shell versus PbS/CdS NCs) can be easily obtained by identifying the corresponding populations of each dot in the TEM specimen as shown in Fig. 1.3a and 1.3b. The ratio of Au to PbS particles on a TEM grid, \( n_{\text{TEM}} \), is then converted to a Au volume fraction, \( v_{\text{Au}} \), according to the following equation (see Supporting Information for details of calculation):

\[
v_{\text{Au}} = \frac{4/3 \pi R_{\text{Au}}^3}{(\sqrt[n_{\text{TEM}}]{D_{\text{PbS}}} + D_{\text{Au}})^3}
\]

(1)

where \( D_{\text{PbS}} \) and \( D_{\text{Au}} \) are the average diameters of PbS/CdS and Au/CdS NCs, respectively, and \( R_{\text{Au}} \) is the average radius of the Au core domain (without the CdS shell).

According to Figs. 1.3 and 1.11, a noticeable enhancement in the optical extinction of mixed metal-semiconductor films can be achieved with just a small percentage of Au nanoparticles in a solid. For instance, a visible range optical density of a nanoparticle film doubles when the Au volume fraction reaches 0.5%. The TEM images of colloidal “inks” used
for film processing are shown in Figs. 1.3a and 1.3b. The corresponding volume fractions of Au for these samples ($\nu_{\text{Au}} = 0.5\%$ (a); $\nu_{\text{Au}} = 0.18\%$ (b)) were determined using Eq. 1. The average Au-to-Au interparticle distance, $R_{\text{Au-Au}}$, which establishes in a solid after the crystallographic fusion of colloidal precursors was estimated to be $R_{\text{Au-Au}} = 23$ nm for a nanoparticle mixture in Fig. 1.3a and $R_{\text{Au-Au}} = 34$ nm for that displayed in Fig. 1.3b (see the Supporting information section for details of calculation).

Figure 1.3. Illustrating the effect of Au nanoparticles on optical properties of a nanocrystal solid. (a,b). TEM images of the two nanoparticle mixtures (Au/CdS + PbS/CdS core/shell NCs) corresponding to Au:PbS nanoparticle ratios of 1:55 and 1:270. (c,d). The steady-state absorption spectra of mixed nanoparticles samples.
As Fig. 1.3 indicates, a sizable enhancement in the film extinction coefficient is reached by using 0.2-0.5% of Au NPs which corresponds to a $R_{\text{Au-Au}}$ range of 23-34 nm. To understand whether this level of Au doping can noticeably shorten the carrier diffusion length in a solid, we have measured the FL lifetime of several mixed films. The FL intensity decay of NC solids has been previously shown to exhibit two distinguishable components, the fast and the slow, corresponding to the exciton dissociation and free carrier recombination processes, respectively (see Fig. 1.11). Such bi-exponential character of the PbS emission decay can be identified in present measurements of PbS-only matrices, shown by the red curve in Fig. 1.4. Upon addition of Au NPs at a 0.3% volume fraction level, the slow decay component decreases from 17.9 to 11.1 ns (blue curve), which implies a reduction in the carrier diffusion length, $l_{\text{diff}} \sim \sqrt{\tau_{\text{slow}}}$, (assuming that the carrier mobility remains the same). Since the diffusion length is inversely proportional to the film resistance, one can expect a reduction of the current density arising just from the effect of additional scattering in a mixed film. The reduction in the fast component of the FL decay (from 1.68 to 1.13 ns) may imply a greater rate of exciton dissociation in a mixed film induced by Au scattering. For instance, if the diffusion length of an exciton (not to be confused with the free carrier diffusion length) in the PbS film is greater than $R_{\text{Au-Au}}$, one can expect a noticeable effect of Au doping on the exciton splitting rate, as reflected by the changes in the fast decay component.
Figure 1.4. The effect of Au doping on carrier diffusion length in (Au, PbS) nanocrystal solids estimated using the fluorescence lifetime technique. The inclusion of Au NPs into a PbS nanocrystal array leads to the reduction of the slow decay component of the PbS band gap emission, which mirrors the decrease in the carrier diffusion length. Meanwhile, the decline of the fast decay component in (Au, PbS) nanocrystal solids reflects an increase in the rate of exciton dissociation.

To observe an experimental signature of the Au-to-PbS energy transfer, photoexcitation (PLE) measurements have been performed. Within this approach, one can unambiguously distinguish between the contributions of Au and PbS domains into the exciton generation. To this end, the excitation of Au-doped PbS films featuring small-diameter \((d = 2.3 \text{ nm})\) PbS NCs was
performed in the 500-735 nm range, covering both Au and PbS absorption bands, while the emission detector was set at the peak of the PbS band gap fluorescence. According to Fig. 1.5b, the observed photoexcitation profile of the Au-doped films (red curve) exhibits a clear contribution of the plasmon resonance, which is absent in PbS-only devices (black curve). Likewise, the observed PLE feature of Au correlates well with the plasmon shoulder in the film’s absorption spectrum (Fig. 1.5a, red curve). This is clearly seen through the comparison of the absorption and photoexcitation enhancement factors, obtained by dividing the corresponding spectra of Au-doped films with their PbS-only “baselines”. According to Fig. 1.5c, the maximum of the plasmon contribution into PbS exciton generation falls close to the absorption enhancement maximum (dotted line). Based on these results, we can conclude that a sizable portion of PbS excitons arises due to the plasmon absorption of doped films.

Photovoltaic characteristics of plasmonic films were explored using depleted heterojunction solar cell architecture, schematically illustrated in Fig. 1.2a. In this geometry, the p-n junction is formed at the boundary of a (Au, PbS) nanoparticle absorber and a TiO$_2$ layer, which separates the photoinduced charges between Fluorine-doped tin oxide (FTO) and Au/Pd electrodes. To fabricate a photovoltaic cell from nanoparticle solutions, a matrix-encapsulated (Au, PbS) solid containing 0.3% of Au by volume was deposited on top of a TiO$_2$ film followed by sputtering of 20-60 nm of Au/Pd electrodes. The development of a TiO$_2$ film was performed by spincoating the DyeSol TiO$_2$ nanoparticle precursor onto FTO-coated glass (resistance = 12 $\Omega$/sq) followed by annealing at 450-480 °C to remove organic traces (see the Experimental section). Preparation of the light-absorbing layer involved spincoating a mixture of Au/CdS and PbS/CdS core/shell NCs, capped with original ligands, onto a TiO$_2$ layer using 8-10 LbL cycles, totaling 350-400 nm. The film was heated to 150 °C for ~15 min after every three cycles. Upon
completion, the pores of the resulting solid were further filled with additional ZnS (typically 4 SILAR cycles), and the film was capped with Au/Pd electrodes through a shadow mask. The area of each metal pixel was 0.03 cm².

Figure 1.5. The effect of Au doping on the PbS exciton generation in plasmonic films. (a). The comparison of the optical absorption between (0.3%-Au, PbS) and PbS-only solids (d_{PbS} ≈ 2.3 nm). (b). The photoexcitation spectrum of a (0.3%-Au, PbS) solid (red curve) is compared to that of PbS-only films. The FL signal was measured at λ = 750 nm. (c). The fluorescence enhancement factor (red curve) calculated by dividing the normalized photoexcitation spectrum of a mixed matrix (Au, PbS) by that of a PbS-only film. The corresponding absorption
enhancement factor obtained by dividing the red by the black curve in (a) is shown for comparison (dotted line).

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<th>MPA-linked PbS-only</th>
<th>MPA-linked (0.3%-Au, PbS)</th>
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Table 1.1 The summary of photovoltaic characteristics for four types of investigated nanocrystal solar cells, including matrix-encapsulated PbS, matrix-encapsulated (Au, PbS), MPA-linked PbS, and MPA-linked (Au, PbS). The plasmonic devices contained 0.3% of Au by volume.

Figure 1.6 compares the photovoltaic performance of plasmonic (Au, PbS) and semiconductor-only nanocrystal solar cells configured to have similar optical densities in the visible range ($\lambda \approx 550$ nm). The overall trend observed for several plasmonic films was an enhanced short circuit current, $J_{sc}$ (gain of 41 ± 3%) as measured relative to PbS-only devices and a somewhat lower value of an open circuit voltage, $V_{oc}$ (drop of 15 ± 0.5%). The latter outcome can be attributed to pinning of the PbS Fermi level at defects forming along the Au/semiconductor interface.
Figure 1.6. (a). The comparison of J-V characteristics obtained from a plasmonic (Au, PbS) and a non-plasmonic (PbS-only) nanocrystal solar cells. Both devices were fabricated by sandwiching a CdS-encapsulated nanoparticle layer (~350-400 nm) between a Au/Pd counter electrode and a 300-nm TiO\textsubscript{2} layer, under the requirement that both solids exhibit similar optical densities. On average, Au-doped cells (red curves) showed greater $J_{SC}$ but lower $V_{OC}$ values relative to PV cells containing PbS-only absorber (black curves). The overall performance of Au-doped cells was slightly greater than those of PbS only devices, with the best cell showing PCE of 4.5\% . (b). Scanning electron microscope image of a plasmonic (Au, PbS) nanocrystal film in a fabricated solar cell.
The observed enhancement of the short circuit current in (Au, PbS) devices can be attributed to two possible factors: better carrier extraction from a thinner absorber and an enhanced exciton generation due to near-field Au-to-PbS energy transfer. Since the average $J_{SC}$ of PbS-only devices utilizing a thinner absorber (at 80% optical density of a regular cell) was lower than those tested in Fig. 6a, the difference in the absorber thickness alone cannot explain an enhanced current density in plasmonic films. Furthermore, a greater value of $J_{SC}$ was achieved despite the reduced carrier lifetime in Au-doped cells (see Fig. 1.4). This fact strongly suggests an increased carrier density in plasmonic solids, which is sufficient to overcome additional trapping losses resulting from Au scattering. The enhanced $J_{SC}$ in Au-doped devices has contributed to the overall growth in the average efficiency of nanocrystal solar cells from 4.0% (PbS-only) to 4.2% (Au, PbS). The cumulative gain in PCE reflects a combined effect of the enhanced exciton generation in mixed Au+PbS solids and a lower photovoltage resulting from Fermi level pinning.

To stress the importance of Au encapsulation in plasmonic solar cells, we have replaced an insulating shell of CdS on Au surfaces with low-potential barrier 3-mercaptopropionic acid (MPA) ligands. These molecules facilitate the charge transfer between nanoparticles in a solid leading to the best performing nanocrystals devices reported to date. In this work, the absorber layer was fabricated through a conventional ligand-linking strategy, via processing of OLAM-capped Au NPs and OA-capped PbS NCs into MPA-linked (Au, PbS) solids. The J-V characteristics of these devices comprising 0.3% of Au NPs by volume are shown in Fig. 1.7. The comparison with non-plasmonic cells utilizing MPA-linked PbS NC films reveals a significant performance reduction associated with the addition of Au. Notably, the same level of Au doping in matrix-encapsulated devices has resulted in a 4.2% of PCE, but yielded only 0.32% in the case of MPA-linked cells. The inferior performance of MPA-linked (Au, PbS) films
implies an increase in the rate of carrier scattering processes for solids where Au doping produces just a moderate, 30-40% enhancement of the optical density. Such a considerable effect of Au dopants on the carrier diffusion length necessitates the use of an insulating shell on metal surfaces that reduces the semiconductor-to-metal charge transfer rate.

Figure 1.7. Photovoltaic performance of plasmonic solar cells fabricated by linking PbS and Au nanoparticles with MPA ligands. J-V characteristics of a plasmonic (Au, PbS) device are compared to those of MPA-linked PbS nanocrystal solar cells, fabricated using the depleted heterojunction architecture depicted in Fig. 2a. The PCE of Au-doped cells (black curves) is significantly lower than that of PbS-only device (red curves). The low photoconductivity is attributed to enhanced carrier trapping in Au NPs, which shortens the carrier diffusion length.
1.5 Conclusions

In conclusion, we have explored the feasibility of utilizing near-field energy transfer as an absorption enhancement strategy in plasmonic nanocrystal solar cells. The use of strongly confined radiation of surface plasmons can increase the optical density of photovoltaic devices beyond the theoretical limit of far-field scattering. In this work, the near-field confinement of light was achieved through the use of small-diameter Au nanoparticles embedded into a PbS nanocrystal solid. The absorber layer was fabricated using a matrix encapsulation scheme, which offers two important benefits: reduced carrier scattering on Au centers and improved stability of heat-prone plasmonic films. The contribution of the near-field emission in Au nanoparticles towards the charge carrier generation was manifested through the observation of an enhanced short circuit current and improved power conversion efficiency of prototype (Au, PbS) solar cells, as measured relative to PbS-only devices. Conceptually, this work demonstrates the possibility of utilizing near-field emission of surface plasmons for improving the performance of photovoltaic devices, which could be harnessed as a novel strategy of solar energy conversion.
Figure 1.8. Illustration of absorption enhancement strategies for PV devices. The theoretical enhancement factor, $F$, is the greatest for the case of strongly-confined radiation (near-field evanescent EM waves). The insert shows the ratio of scattering (far-field) to absorbance (near-field) cross section in Au NPs versus the NP size.
Figure 1.9. The ratio of scattering to absorbance cross section in Au NPs versus the nanoparticle size. The curve is extrapolated from the numerical data derived from Mie theory and discrete dipole approximation method.\textsuperscript{59}
Figure 1.10. The absorbance spectra of Au (black curve), Au/ZnS (red curve), and Au/CdS (black curve) nanoparticles in a colloidal form.
Figure 1.11. The absorbance of mixed (Au, PbS) solids. The ratio of Au to PbS NCs in a mixture is growing from 1:270 to 1:10.
Figure 1.12. Fluorescence intensity decay of CdS-encapsulated PbS nanocrystals. The fast and the slow decay components correspond to exciton dissociation (via charge tunneling) and charge trapping processes, respectively.
Figure 1.13. (a). Absorbance profiles of matrix-encapsulated PbS-only and (Au, PbS) films on FTO substrates. (b). Absorbance profiles of colloidal PbS NCs (red) and PbS/CdS core/shell NCs that form as a result of Pb$^{2+} \rightarrow$ Cd$^{2+}$ cation exchange.
Volume fraction calculations. Suppose that on average a unit length of the mixed (Au, PbS) nanoparticle film contains $N_{\text{PbS}}$ of PbS/CdS and $N_{\text{Au}}$ of Au/CdS core/shell nanocrystals. A unit volume of such film be given by $V = (N_{\text{PbS}} D_{\text{PbS}} + N_{\text{Au}} D_{\text{Au}})^3$, where $D_{\text{PbS}}$ and $D_{\text{Au}}$ are the average diameters of PbS/CdS and Au/CdS NCs, respectively. The Au-Au nearest neighbor distance in such film will then be given by:

$$R_{\text{Au-Au}} = \sqrt[3]{\frac{V}{N_{\text{Au}}^3}} = \frac{N_{\text{PbS}} D_{\text{PbS}} + N_{\text{Au}} D_{\text{Au}}}{N_{\text{Au}}} = n D_{\text{PbS}} + D_{\text{Au}}$$

$n = N_{\text{PbS}}/N_{\text{Au}}$ is estimated along a one-dimensional projection (unit length). It is related to a volumetric nanoparticle ratio (which is typically sampled by TEM measurements where a colloidal drop is being projected onto a 2D grid) as: $n_{\text{TEM}} = (N_{\text{PbS}}/N_{\text{Au}})^3 = n^3$, consequently:

$$R_{\text{Au-Au}} = \sqrt[3]{n_{\text{TEM}}^3} D_{\text{PbS}} + D_{\text{Au}}$$

where $n_{\text{TEM}}=N_{\text{PbS}}/N_{\text{Au}}$ is the ratio of PbS to Au nanoparticles on the TEM grid.

The volume fraction of Au NPs is give by:

$$\nu_{\text{Au}} = \frac{N_{\text{Au}}^3 \times \frac{4}{3} \pi R_{\text{Au}}^3}{V} = \frac{N_{\text{Au}}^3 \times \frac{4}{3} \pi R_{\text{Au}}^3}{(N_{\text{PbS}} D_{\text{PbS}} + N_{\text{C}} D_{\text{C}})^3} = \frac{\frac{4}{3} \pi R_{\text{Au}}^3}{(n D_{\text{PbS}} + D_{\text{Au}})^3} = \frac{\frac{4}{3} \pi R_{\text{Au}}^3}{(\sqrt[3]{n_{\text{TEM}}^3} D_{\text{PbS}} + D_{\text{Au}})^3}$$
where \( R_{Au} \) is the average radius of the Au core domain (without the CdS shell).

1.7 References


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CHAPTER II. ENHANCED EMISSION OF NANOCRYSTAL SOLIDS FEATURING SLOWLY DIFFUSIVE EXCITONS


2.1 Abstract

Solution processing of semiconductor nanocrystal (NC) solids represents an attractive platform for the development of next–generation optoelectronic devices. In search of enhanced light-emitting performance, NC solids are typically designed to have large interparticle gaps that minimize exciton diffusion to dissociative sites. This strategy, however, reduces electrical coupling between nanoparticles in a film, making the injection of charges inefficient. This study has demonstrated that bright emission from nanocrystal solids can be achieved without compromising their electrical conductivity. It has been shown that solids featuring a low absorption-emission spectral overlap ($J$) exhibit an intrinsically slower exciton diffusion to recombination centers, promoting longer exciton lifetimes. As a result, enhanced emission is achieved despite a strong electronic coupling. The observed phenomenon was found consistent with a decreased resonant energy transfer in films exhibiting a reduced $J$ value. The positive correlation between film luminescence and $J$ was revealed through a comparative analysis of CdSe/CdS and ZnSe/CdS solids and further confirmed in two control systems (ZnTe/CdSe and Mn$^{2+}$-doped ZnCdSe/ZnS). Exceptionally slow exciton diffusion (~ 0.3 ms) and high brightness were observed for Mn$^{2+}$-doped Zn$_{1-x}$Cd$_x$Se/ZnS NC films exhibiting a nearly vanishing $J$ parameter. It is expected that the demonstrated combination of electrical coupling and bright
emission in nanocrystal solids featuring low $J$ can benefit the development of nanocrystal light-emitting technologies.

2.2 Introduction

Semiconductor nanocrystals (NC) solids represent an important class of nanoscale materials displaying unique optical, electrical, and thermal behavior. Similar to molecular crystals, NC solids are processed from solutions, while their excitonic properties allow additional integration of size-tunable optical characteristics. Despite slightly higher material costs relative to organics, inorganic nanoparticle assemblies offer better electrical performance, a wider range of spectral tuning, and greater photostability. In the last decade, these unique characteristics have allowed successful introduction of NC solids to the technology arena evidenced through the development of light-emitting\textsuperscript{1-9} and photovoltaic devices\textsuperscript{10-19} that often approach or even surpass the commercial standards.\textsuperscript{8,20,21}

A unique advantage of nanocrystal assemblies over organic molecular solids lies in the tunable electrical coupling between nanoparticles in a film, which can be controlled through the use of different binding motifs. The variable degree of interparticle coupling plays an important role in device engineering as it allows adjusting both the length and the rate of exciton diffusion across the solid. For instance, in light-emitting applications of NC films, the motion of excitons is typically restricted to a small volume in order to prevent exciton migration towards luminescence-quenching film boundaries.\textsuperscript{20} Conversely, the diffusion of excitons to charge-separating interfaces in nanocrystal solar cells is vastly beneficial as it leads to photocurrent generation.\textsuperscript{22} Along these lines, the ability to tune the exciton diffusion length in artificial solids of semiconductor NCs represents a unique tool for enhancing their specific functionalities.
Here, it has been demonstrated that nanocrystal solids featuring a low absorption-emission spectral overlap ($J$) exhibit an intrinsically slower exciton diffusion to recombination centers, which promotes longer exciton lifetimes. As a result, enhanced emission is achieved despite a strong electronic coupling. The role of spectral overlap in exciton dynamics was investigated through a side-by-side comparison of CdSe/CdS and ZnSe/CdS NC films featuring type I (high-$J$) and type II (low-$J$) carrier confinement, respectively. It was found that excitons diffuse up to 3 times slower in films of ZnSe/CdS (core/shell) NCs leading to a relatively brighter emission (Fig. 2.1), which was attributed to a slower diffusion of excitons to dissociative defects. This premise was further confirmed in a control experiment utilizing solids of low-$J$ ZnTe/CdSe core/shell NCs, where the exciton diffusion rate was found to be correlated with the value of $J$ in a predictive manner. A vivid demonstration of the slowed energy migration was subsequently provided by Mn$^{2+}$-doped Zn$_{1-x}$Cd$_x$Se/ZnS solids featuring a nearly vanishing value of $J$ integral. The exciton diffusivity in this case was found to be $10^5$ times slower than in CdSe/CdS films, leading to an exceptionally high emission quantum yield (QY). The observed correlation between the exciton diffusion rate in a solid and the magnitude of the absorption-emission spectral overlap was explained within existing energy transfer models.
Figure 2.1. Comparison between difference in the emission intensity of type I (CdSe/CdS) and type II (ZnSe/CdS) solids fabricated from equally emissive nanoparticle solutions. Slower diffusion of excitons in type II nanocrystal solids increases the probability of their radiative recombination, leading to a brighter emission. Both films were fabricated by using oxalic acid as a linking molecule and feature similar interparticle gaps. The use of such short interparticle linkers ($\approx 0.45$ nm) resulted in relatively low emission quantum yields for the two solids ($QY_{ZnSe/CdS} = 3.8\%$; $QY_{CdSe/CdS} = 1.3\%$), however, amplifying the optical differences between the two samples.
The observed slow diffusion of energy in type II and metal-doped nanocrystal solids can be used to facilitate the development of light-emitting devices and materials. At present, quantum dot light-emitting diodes (QD-LEDs) rely almost exclusively on type I films of CdSe/CdS or CdSe/ZnS core/shell NCs (or equivalent graded alloys)\(^2,4,8,23-26\) which utilize a CdSe core capped with a wide-gap CdS or Cd\(_x\)Zn\(_{1-x}\)S shell. Maximizing the electroluminescence yield in such solids typically requires the use of large interparticle gaps comprising a combination of a semiconductor shell and long-chain ligands.\(^8,20,23\) Large interparticle distances suppress the diffusion of excitons to charge transporting layers, thereby preventing their premature dissociation. Unfortunately, the presence of large gaps in nanocrystal assemblies also complicates charge injection into CdSe, because the carrier tunneling rate is also reduced. As a result, the electroluminescence yield can be maximized only in sub-monolayer NC films (e.g. CdSe/Cd\(_{1-x}\)Zn\(_x\)S NC\(^8,26\)) featuring short injection lengths. The present work demonstrates a practical pathway for reducing injection barriers without compromising the radiative yields of NC solids.

2.3 Experimental Section

2.3.1 Materials.

Oleylamine (tech., 70%, Aldrich), sulfur (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), octadecylamine (ODA, 90%, Fisher), oleic acid (OA, tech., 90%, Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), tri-n-octylphosphine oxide (TOPO, 99%, Aldrich), n-octadecylphosphonic acid (ODPA, 98%, PCI Synthesis), n-hexylphosphonic acid (HPA, 98%, PCI Synthesis), Hexadecylamine (HDA, tech., Fluke), 1,2-hexadecane diol (TCI), 11-mercaptoundecanoic acid (MUA, 95%, Aldrich),
platinum(II) acetylacetonate (97%, Aldrich), tellurium powder (Te, -200 mesh, 99.8%, Aldrich), diethylzinc (Et$_2$Zn, 15% wt., 1.1 M solution in toluene, Aldrich), selenium powder (Se, 200 mesh, Acros), hexane (anhydrous, 95%, Aldrich), methanol (anhydrous, 99.8%, Aldrich), ethanol (anhydrous, 95%, Aldrich), tert-butanol (99.7%, Aldrich), and toluene (anhydrous, 99.8%, Aldrich) were used as purchased. All reactions were performed under argon atmosphere using standard Schlenk techniques unless otherwise stated.

2.3.2 Synthesis of ZnSe nanocrystals.

ZnSe core NCs were fabricated according to a procedure adapted from Cozzoli. Briefly, 7 g of ODA was degassed under vacuum at 130 °C for 1 h, after which it was heated to 300°C under argon flow. Se precursor was prepared by sonicating 0.063 g of Se powder in 2 ml of TOP followed by degassing at 120°C for 1 hour and injecting it into ODA solution. 1 ml of diethylzinc was injected into the reaction mixture at 300°C. Upon injection, the temperature dropped to $T_{gr} \approx 265$ °C and was maintained at this level throughout the entire synthesis. The reaction was stopped (in 3-5 min) when the desired particle size was reached by removing the heating mantle. The nanocrystals were precipitated with methanol and redispersed in chloroform.

2.3.3 Synthesis of ZnSe/CdS core/shell nanocrystals.

For the shell deposition, injection stock solutions were prepared at a concentration of 0.04 M in 1-octadecene. Cadmium was obtained by dissolving 0.030 g (0.24 mmol) of cadmium oxide in 0.6 mL of oleic acid and 5.4 mL of ODE in a 25 mL flask under argon by heating it to 280 °C while stirring. After the solution became clear, it was cooled to 60 °C. The sulfur injection solution was prepared from 0.0077 g (0.24 mmol) of sulfur dissolved in 6 mL of ODE by heating the mixture to 200 °C under argon flow. Injections of Cd and S stock solutions into a reaction vessel containing previously prepared ZnSe nanocrystals dispersed in 1.5 g of ODA and
6.3 mL of ODE at 240 °C were made sequentially every 20 min starting with Cd ions. Aliquots of the reaction mixture were taken at 7–10 min intervals for UV–vis and PL spectral characterization. When the desired size of NCs was obtained the reaction was stopped by removing the heating mantle. The nanocrystals were precipitated with ethanol and redispersed in chloroform.28

2.3.4 Synthesis of Oleylamine-Capped Au nanocrystals.

Au NCs were synthesized according to previously reported methodology.28 In a typical synthesis, 0.011g of AuCl₃ and 5 mL of oleylamine were loaded in a one-neck flask and allowed to react at 100 °C for 30 min under argon atmosphere. During this time, the reaction mixture’s color changed from transparent yellow to orange (indicating the formation of Au-oleate complexes), and then finally to purple (indicating the formation of oleylamine-capped Au NPs). The reaction was stopped by removing the flask from the heating mantle and allowed to cool to room temperature. Then, the solution was transferred from the flask into centrifuge tubes and precipitated with ethanol. After the centrifugation, the supernatant was discarded and the pellet was dissolved in chloroform. The cleaning cycle was repeated one more time and the final product was redispersed and stored in chloroform.

2.3.5 Synthesis of CdSe nanocrystals.

To grow CdSe NCs, CdO (0.0256 g), stearic acid (0.2275 g), and ODE (2.53 mL) were combined in a 50 mL three-neck flask, and then heated to 200 °C under argon to dissolve CdO.29 The solution was then cooled down to room temperature, at which point ODA (1.5 g) and TOPO (0.5 g) were added to the flask. Under argon flow, this mixture was then reheated to 280 °C. When this temperature was reached, a selenium solution, prepared under argon by dissolving Se (0.1579 g) via sonication in TBP (0.58 mL) and further diluting it with ODE (1.73 mL), was
quickly injected. After 3–4 min of growth time, the solution containing CdSe NCs was obtained. At this point, the flask was removed from the heating mantle and upon cooling down the reaction mixture to room temperature, chloroform was added. The contents of the reaction flask were then distributed into tubes and centrifuged. The precipitate was discarded while the reddish clear solution was mixed with acetone and centrifuged again. At this point all nanocrystals precipitated and were subsequently redissolved in chloroform.

2.3.6 Synthesis of CdSe/CdS core/shell nanocrystals.

Synthesis of CdSe/CdS core/shell NCs was performed using an “accelerated” procedure evolved from a previously reported seeded-type growth approach. In a typical synthesis, S (0.120 g) was dissolved in TOP (1.81 mL) at 200 °C, and after cooling down to room temperature was mixed with CdSe nanocrystal solution in chloroform. Separately, a mixture of CdO (0.060 g), TOPO (3.0 g), ODPA (0.290 g), and HPA (0.080 g) in a 50 mL 3-neck flask was exposed to vacuum at 150 °C for ca. 30 min. Subsequently, the system was switched to Ar flow and heated to 300 °C until the solution turned optically clear and colorless. At this point, TOP (0.9 mL) was added to the flask and the temperature was raised to 320 °C. The growth of the CdS shell was initiated with a swift injection of nanocrystal seeds/sulfur mixture at 320 °C. After the initial temperature drop, the reaction temperature was allowed to recover to 300 °C. The overall growth time was 6–7 min. Purification of the CdSe/CdS NCs was carried out by precipitation with ethanol and redispersion with chloroform. This process was repeated two times and the final product was stored in chloroform.

2.3.7 Synthesis of Zn$_{0.87}$Cd$_{0.11}$Mn$_{0.02}$Se nanocrystals.

Nanoparticles were grown with slight modifications to previously reported synthetic methods based on the thermal decomposition of the cluster (NMe$_4$)$_2$[Zn$_4$(SePh)$_{10}$]. A flask
containing 10.8 g of hexadecylamine with 12 mg of MnCl₂·4H₂O and 15 mg of CdCl₂ was first degassed under vacuum at 130 °C for 1 h after which 400 mg of (NMe₄)₂[Zn₄(SePh)₁₀] and 20 mg of Se were added anaerobically. The resulting mixture was again degassed at 130°C for 1 h before ramping the temperature to 270 °C, where it was held for 15 min before cooling slowly to 100 °C. The resulting NCs were twice crashed out with ethanol, separated by centrifuging, and redispersed in toluene.

2.3.8 Synthesis of Zn₀.₈₇Cd₀.₁₁Mn₀.₀₂Se/ZnS core/shell nanocrystals.

ZnS shells were grown by transferring the toluene suspension of Zn₀.₈₇Cd₀.₁₁Mn₀.₀₂Se NCs to a flask containing 3g of oleylamine and 3g of octadecane from which the toluene was removed and the resulting suspension degassed for 1 h at 130 °C. Zn(Oleate)₂ was prepared by reacting 440 mg of Zn(OAc)₂ with 4.4 g of oleic acid and 4.4 mL of octadecene under vacuum at 110 °C until all volatile components were removed. The flask was then put under a nitrogen atmosphere, 36 mg of S dissolved in 3.6 mL of TOP was injected, and the resulting mixture cooled to room temperature. The temperature of the flask containing the NCs was raised to 225 °C and the Zn(Oleate)₂-TOP-S mixture was injected via syringe pump at a rate of 0.5 mL/h. The resulting NCs were again purified by flocculation with ethanol followed by resuspension in toluene.

2.3.9 Synthesis of ZnTe NCs.

ZnTe seeds were synthesized according to a procedure described in Ref.vii. To fabricate a Te precursor, 0.104 g of Te powder was mixed with 4 mL of degassed TOP and sonicated to get an optically clear solution. Subsequently, 5.2 mL of diethylzinc solution was added to the Te solution and the mixture was stirred at room temperature. In the second flask, OA (0.4 ml) was mixed with ODE (15.2 ml), degassed at 120 °C for 1 hour and switched to argon, upon which the
temperature was raised to 260 °C. At this point, the mixture of Zn and Te precursors was injected into the second flask. After 4 minutes of heating the flask was raised from the mantle and cooled in air. When the reaction mixture cooled down to 60 °C, 2 mL of hexane and 15 mL of ethanol was added. The mixture was then centrifuged at 5400 rpm for 10 minutes and the precipitate was washed one more time using hexane/ethanol extraction. The final product was stored in chloroform.

2.3.10 Synthesis of ZnTe/CdSe core/shell NCs.

A thin shell of lattice-matched CdSe was grown onto ZnTe seeds using a procedure described in Ref. vii. In brief, Cd precursor solution was made by dissolving 0.038 g of CdO in 0.6 mL of OA and 6 mL of ODE and degassed at 120 °C for 1, then switched to argon, upon which the temperature was raised to 260 °C. The mixture was cooled to the room temperature once the solution became clear. Se precursor solution was made by dissolving 0.02 g of Se powder in 6 mL of degassed TOP by sonication. Both the Cd and the Se solutions were subsequently combined at room temperature. In another flask, a mixture of 2.4 g ODA and 6.3 mL ODE was degassed at 120 °C for 1 hour and subsequently switched to argon. At this point, 1 ml of colloidal ZnTe NCs, grown in the first stage of the procedure were added into the mixture and the temperature was raised to 240 ºC. The amount of ZnTe seeds for the shell growth step was determined by setting the absorbance of the NC solution at the excitonic peak, λ=473 nm, to 1.0 (as measured using a 1-mm-thick cuvette). When the temperature reached 240 ºC, 0.2 mL of Cd/Se mixture was injected every 10 minutes. The growth of core/shell NCs was monitored using steady-state fluorescence measurements. After the addition of a total of 1.2 mL of the Cd/Se mixture, a strong band gap emission at λ=690 nm was observed and the reaction was stopped. When the solution temperature reached 50 ºC, 16 mL of ethanol were added to the flask.
and the solution was centrifuged to precipitate NCs. After cleaning the NCs one more time, the precipitate was dissolved in chloroform and stored.

2.3.11 Synthesis of CdS shell using ZnTe/CdSe nanocrystal seeds.

Synthesis of CdS shell was carried out using a seeded-type growth, according to Ref. vii. In a typical procedure, a mixture of ODA (0.2g) and ODE (10ml) was exposed to vacuum at 120 °C for 1 hour. Subsequently, the system was switched to argon flow and heated to 240 °C. When the temperature reached 225 °C, 1 ml of ZnTe/CdSe core/shell NCs were injected. The amount of ZnTe/CdSe seeds for the second shell growth step was determined by setting the absorbance of the NC solution at the excitonic peak, λ=680 nm, to 1.2 (as measured using a 1-mm-thick cuvette). S precursor solution was prepared by dissolving S (0.008g) in ODE (6 mL) at 290°C and cooling down to room temperature. Separately, a mixture of CdO (0.030 ml), OA (0.6 ml), ODE (5.4 ml) in a 25 mL 3-neck flask under argon flow was heated to 290 °C until the solution turned optically clear and colorless and cooled to room temperature. At this point, once the mixture of core/shell NCs reached 240°C dropwise injections (2 drops per injection) of Cd and S precursor were made. The growth of second shell was monitored by measuring absorbance and fluorescence profiles until the desire wavelength of fluorescence was reached, upon which the reaction was quenched by raising the flask from the mantle. When the temperature of the reaction mixture reached 60 ºC, 14 mL of ethanol was added and the content was centrifuged. The precipitate was subsequently re-dissolved in 2 mL of hexane and precipitated one more time using 8 mL of ethanol. The final product was stored in hexane.

2.3.12 Fabrication of nanocrystal films.

To fabricate films, colloidal NCs were deposited onto glass substrates using a layer-by-layer spincoating process under argon atmosphere. For each layer, the solution of nanocrystals in
hexane (concentration 20 mg/ml) was dropcasted onto a glass substrate and spun at 3000 rpm for 10 seconds.

2.3.13 Ligand Exchange (OA to OX).

Oxalic acid linked NC solids were fabricated by soaking OA-capped NC films in 0.01 M solution of Oxalic acid in acetonitrile for 5 min. The excess of oxalic acid was removed by rinsing films in acetonitrile.

2.3.14 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. FL lifetime measurements were performed using a time-correlated single photon counting setup utilizing SPC-130 single-photon counting PCI card (Becker & Hickle GmbH), picosecond diode laser operating at 420 nm, as an excitation source (Picoquant), an id50 avalanche photodiode (Quantique), and long pass filter on 420nm. Infrared spectra were collected in a Jasco FTIR-4000 equipped with a single reflection ATR accessory.

2.4 Results and Discussion

The basic steps of the photoinduced energy conversion in NC solids are illustrated in Fig. 2.2. Typically, the absorption of light results in the formation of localized excitons that diffuse through a film at a rate determined by the strength of the interparticle coupling. Similar to
polymer films, a singlet exciton in a nanocrystal solid will “hop” through the thermally accessible energy landscape towards the potential energy minimum. The rate of its diffusion through the solid is given by the diffusivity figure, \( \mu^{\text{exc}} = \frac{e l_{\text{hop}}^2}{6kT \tau} \), where \( l_{\text{hop}} \) is the center-to-center interparticle distance, and \( \tau \) is the exciton lifetime. The subsequent decay of excitons, driven by their recombination (radiative or non-radiative) or dissociation into a free electron-hole pair, is accompanied by the measurable drop in the band-gap emission (fast decay component in Fig. 2.2). Previous studies have shown that for strongly coupled NC solids (shell-to-shell gaps < 1 nm), the fluorescence (FL) intensity exhibits double-exponential decay with the fast component, \( \tau_{\text{fast}} \), being approximately equal to the lifetime of excitons.\(^{35}\) Upon exciton dissociation, the emerging free carriers drift through the solid (Fig. 2.2) with mobilities that depend on the strength of interparticle coupling.\(^{36-38}\) The radiative recombination of these carriers gives rise to the slow component of the FL decay, \( \tau_{\text{slow}} \), the value of which is determined by the complex interplay of trap state density and the excitation fluence.
Figure 2.2. An illustration of energy relaxation processes in photoexcited NC solids. Following photoexcitation, excitons diffuse through the thermally accessible energy landscape towards the potential energy minimum in a film. The subsequent decay of excitons can undergo via their recombination (radiative or non-radiative) or dissociation into a free electro-hole pair. By extracting the fast and slow components of the PL intensity decay, one can determine such important transport parameters as the lifetime of excitons in the solid ($\tau_{\text{fast}}$), the exciton diffusivity, and the free carrier diffusion length, $l = d \times \sqrt{\frac{\tau_{\text{slow}}}{6\tau_{\text{fast}}}}$.

As Figure 2.2 illustrates, the dissociation of excitons into a free electron-hole pair represents an important process through which the optical energy ($\hbar\omega$) absorbed by the film is converted into an electrical energy of separated charges ($eV$). Along these lines, NC solids for which the dissociation is fast are typically desired for photovoltaic applications, while solids...
featuring longer exciton lifetimes are more suitable as light-emitting materials. The efficiency of the dissociation process for a particular film can be estimated from the fluorescence lifetime measurements by using the time ($\tau_{\text{diff}}$) and length ($l_{\text{diff}}$) of the exciton diffusion process. To this end, $\tau_{\text{diff}}$ is extracted as the fast component of the FL intensity decay, $\tau_{\text{diff}} = \tau_{\text{fast}}$, (Fig. 2.2), while the diffusion length is obtained from the reduced FL lifetimes of NC solids doped with randomly distributed fluorescence quenching sites (bulk quenching approach).\textsuperscript{40} In general, the accuracy of this approach can be compromised by the fact that the exciton dissociation is not the only mechanism of fluorescence quenching. Trapping of free carriers, whose recombination results in the band gap emission can also lead to FL intensity reduction in a bulk quenching approach. To avoid this contribution in the present work, we extract the fast component of the FL decay which reflects the dynamics of excitons only.\textsuperscript{35} This component of the band gap emission in nanocrystals is quenched exclusively by the process of exciton dissociation.

Most semiconductor NCs that are used for the development of light-harvesting or light-emitting solids utilize a core/shell architecture (e.g. PbS/CdS, CdSe/CdS, CdSe/ZnS). The outer shell is designed primarily to prevent charge trapping on surfaces of substrate-bound nanoparticles. Meanwhile, the potential barrier of the shell layer can also be explored towards establishing a specific carrier localization pattern. According to the accepted terminology, core/shell heterostructures exhibit either a type I or a type II carrier localization regime if electrons and holes find potential minima in the same or different semiconductor domains, respectively (Fig. 2.3 and Fig. 2.10).\textsuperscript{41-44} Most light-emitting NC solids explored to date represent the type I assembly of the two domains. Meanwhile, the presence of large Stokes shifts
in type II semiconductor hetero-nanocrystals can potentially lead to unique optical properties of their solids.

CdSe/CdS and ZnSe/CdS core/shell nanocrystals were chosen as representative examples of type I and type II systems for the development of respective solids.\textsuperscript{28,41,44-49} The character of the charge localization in these materials has been explored in a number of studies leading to a general consensus that large-core (\(d_{\text{CdSe}} > 4\) nm) CdSe/CdS nanoparticles tend to confine both charges in the core domain,\textsuperscript{7,41,45,50} while ZnSe/CdS efficiently separates core-localized holes from shell-confined electrons as long as the shell thickness exceeds just a few monolayers (Fig. 2.10).\textsuperscript{28,47,48} When the two structures are processed into electrically-coupled solids, the ensuing potential energy landscapes for the CdSe/CdS and ZnSe/CdS films are expected to differ (Fig. 2.2), suggesting that the character of exciton diffusion through these materials might exhibit different dynamics.

In this work, the energy coupling between solid-bound nanoparticles was achieved through the use of short oxalic acid (OX) ligands (shell-to-shell gap, \(d_{\text{gap}} \approx 0.45\) nm, see Fig. 2.4e). Such short interparticle distances accelerate the exciton diffusion across the film, amplifying the corresponding differences in the dynamics of type I and type II systems. For a complete ligand exchange, the oxalic acid treatment was performed on substrates of OA-capped NCs by submerging respective films into a 0.01 M OX acetonitrile solution. Typically, soaking spin-coated films for 1-2 min substitutes nearly all of the original oleate ligands on the surface of nanocrystals by oxalates, as attested by the disappearance of the C-H stretch transitions (2800-3000 cm\(^{-1}\), Fig. 2.4c) and a significant shift of \(v_{\text{as}}(\text{COO}^-)\) and \(v_{\text{s}}(\text{COO}^-)\) bands in the FTIR spectra (Figs. 2.4d,f).\textsuperscript{51} The absence of the carbonyl stretch mode at 1700 cm\(^{-1}\) and hydroxyl signal
around 3000-3600 cm\(^{-1}\) suggests that oxalate ligands are fully deprotonated. This indicates that the adsorbed oxalate probably adopts a bridging geometry as a linker between the two nanoparticles with the estimated interparticle gap of \(d_{\text{gap}} = 0.4-0.45\) nm (see Fig. 2.4e).\(^{52}\)

To compare the rates of exciton diffusion between type I (CdSe/CdS) and type II (ZnSe/CdS) NC solids, the two films were developed to have similar “core” to “core” interparticle distances \((d_{\text{CdSe-Cds}} \approx d_{\text{ZnSe-ZnSe}}, \text{see Fig. 2.10})\). Such similarity is important for a fair comparison of the ensuing exciton dynamics since the interparticle energy transfer rate is strongly affected by the exciton hopping distance. Along these lines, CdSe/CdS and ZnSe/CdS colloids were synthesized to have similar shell thicknesses \((\Delta h_{\text{type I}} = 1.55\) nm, \(\Delta h_{\text{type II}} = 1.4\) nm, see Fig. 2.10) while featuring slightly different core diameters \((d_{\text{ZnSe}} = 2.9\) nm, \(d_{\text{CdSe}} = 4.1\) nm). The total sizes of the ZnSe/CdS and CdSe/CdS core/shell nanoparticles were estimated from TEM measurements (Fig. 2.3) to be \(d_{\text{type II}} = 5.7\) nm and \(d_{\text{type I}} = 7.2\) nm, respectively. In this configuration, the minimum edge-to-edge distances between core domains in OX-linked solids are expected to be 3.2 nm and 3.5 nm for ZnSe/CdS and CdSe/CdS solids, respectively.
Figure 2.3. Top panel: Schematic carrier localization patterns in type I (left) and type II (right) solids. Transmission electron microscope (TEM) images of (a) - ZnSe/CdS core/shell NCs, and (b) - CdSe/CdS NCs core/shell NCs.
High-resolution TEM images in Fig. 2.3 confirm the hetero-epitaxial nature of the core/shell interfaces in both colloids. The thickness of the CdS layer in both structures was estimated from the average diameter of core/shell nanoparticles (determined from TEM images) and the known sizes of the respective core domains. Additionally, to verify that the CdS layer thickness is approximately the same in both nanostructures, we have employed a spectroscopic strategy that relies on the FL lifetime measurements of the hole extraction rate from core domains to surface appended 11-mercaptoundecanoic acid (MUA) molecules. Previous works have shown that the MUA HOMO level is located above the valence hole energies in CdSe and ZnSe NCs,\textsuperscript{53} such that the rate of hole transfer from the nanoparticle core (ZnSe or CdSe) to MUA ligands is strongly dependent on the thickness of the CdS potential barrier. Considering that the hole extraction quenches the band gap emission, the FL lifetime of MUA-capped NCs can be used as a probe of the CdS shell thickness.\textsuperscript{7,54} To this end, the original OA ligands on nanoparticle surfaces were replaced with hydrophilic MUA resulting in a stable solution of nanoparticles in methanol. The MUA/nanocrystal molar ratios used for the ligand exchange process were kept the same for the two colloids to ensure that the density of MUA molecules on the CdS surface was similar for both materials.

The FL lifetimes of ZnSe/CdS (Fig. 2.4a) and CdSe/CdS (Fig. 2.4b) colloidal NCs featuring original OA ligands were measured to be $\tau_{\text{ZnSe/CdS}} = 18$ and $\tau_{\text{CdSe/CdS}} = 14$ ns (with an associated FL quantum yields of 27\% and 36\%, respectively). Upon OA → MUA ligand exchange, the FL decay of both colloids becomes dramatically shorter (red curves in Figs. 2.4a,b), consistent with the expected process of photoinduced hole removal by surface anchored MUA. The nearly identical decay rates observed in the two samples whose surfaces were exposed to the same concentration of the incoming ligand ($\tau_{\text{ZnSe/CdS}} = 0.25$ and $\tau_{\text{CdSe/CdS}} = 0.20$ ns)
supports the fact that the thickness of the CdS layer in ZnSe/CdS and CdSe/CdS NCs is approximately the same.

Figure 2.4. (a,b). FL lifetime of OA- and MUA-capped nanocrystals. A substantial drop in the lifetime of MUA-capped nanoparticles implies rapid scavenging of photoinduced holes by surface anchored MUA. The nearly identical decay times observed for MUA-capped ZnSe/CdS (τ_{fast} = 0.25 ns) and CdSe/CdS (τ_{fast} = 0.2 ns) NCs indicate similar shell thicknesses in the two heterostructures. (c,d,f). FTIR spectra of ZnSe/CdS nanocrystals featuring oleic acid (blue) and oxalic acid (red) ligands. The magnification of the C-H stretch region (2800-3000 cm\(^{-1}\)) suggests a successful removal of OA molecules, while the 1600-2300 cm\(^{-1}\) range indicates the attachment of deprotonated oxalic acid, consistent with an interparticle bridging geometry with one example of such configuration sketched in (e).
To compare the character of the exciton decay between the two solids, one needs to
determine both the length ($L_{\text{diff}}$) and the duration ($\tau_{\text{diff}}$) of the exciton diffusion process. The first
parameter - exciton lifetime ($\tau_{\text{diff}}$) was obtained from time-resolved fluorescence measurements
as the fast component of the biexponential decay, $\tau_{\text{diff}} = \tau_{\text{fast}}$. According to Fig. 2.5, the
relaxation rates of the band gap emission in OX-linked ZnSe/CdS and CdSe/CdS NC solids
become noticeably shorter than their respective “solution” values as a result of the coupling-
induced recombination and dissociation processes. Remarkably, upon ligand exchange, the two
solids were found to exhibit substantially different rates of the FL decay despite similar lifetimes
of these colloids in solution. The fast component of the ZnSe/CdS film emission was almost 3
times greater than that of type I CdSe/CdS films ($\tau_{\text{fast}} = 2.6$ nm and $\tau_{\text{fast}} = 0.85$ ns, respectively),
suggesting a similar ratio of the corresponding exciton diffusion times, $\tau_{\text{diff}}(\text{type II})/\tau_{\text{diff}}(\text{type I}) \approx 3$. This outcome is rather unusual in light of the fact that the type II solids fabricated here exhibit
the smaller interparticle gaps ($d_{\text{ZnSe-ZnSe}} = 5.7$ nm vs $d_{\text{CdSe-CdSe}} = 7.2$ nm), which should promote a
greater diffusivity and therefore shorter decay times, contrary to the observed dynamics. A
visibly brighter emission of ZnSe/CdS solids compared to CdSe/CdS films (see Fig. 2.1)
provides further evidence in support of enhanced excitons lifetimes in the type II NC assemblies.
Notably, the two solids in Fig. 2.1 were developed from nanoparticle solutions exhibiting similar
FL intensity levels with associated FL quantum yields of 27% and 36%, respectively (Fig. 2.1
upper panel).
Figure 2.5. (a). FL lifetime of OA-capped ZnSe/CdS NCs in solution (blue curve) and in OX-linked solids (red curve). The fast component of the FL lifetime for the two solids ($\tau_{\text{ZnSe-ZnSe}} = 2.6$ ns and $\tau_{\text{CdSe-CdSe}} = 0.85$ ns) is approximately equal to the exciton lifetimes in these solids. (b). FL lifetime of OA-capped CdSe/CdS NCs in solution (blue curve) and in OX-linked solids (red curve).

The enhanced exciton lifetime in ZnSe/CdS films can be attributed to two possible factors: a larger diffusion volume (e.g. due to fewer exciton-dissociating defects) and/or a slower diffusion rate. To compare the diffusion volumes of ZnSe/CdS and CdSe/CdS NC solids, we have measured the average exciton diffusion lengths in both materials using the bulk quenching strategy. This technique relies on doping of NC solids with randomly distributed Au nanoparticles that serve the role of exciton quenching sites (see Fig. 2.6b). By blending small-diameter Au nanoparticles into nanocrystal films, we were able to restrict the motion of excitons to a smaller volume defined by the average Au-Au interparticle distance ($R_{\text{Au-Au}}$), such that excitons diffusing beyond $R_{\text{Au-Au}}$ become quenched, causing the lifetime of excitons in Au-doped solids to become shorter with increasing Au concentration. A previously developed formalism was used to relate the Au nanoparticle fraction in the film to the exciton diffusion length, as
illustrated in Figs. 2.6a and 2.6c. Considering that the exciton diffusion in NC solids obeys the three-dimensional random walk approximation (Wiener formula), one can use the observed reduction in the FL lifetime of Au doped films to calculate the exciton dissociation probability per single hop, \( p_1(\text{diss}) \), as illustrated in Figs. 2.6a-2.6c (see the supporting information for details of calculation and Fig. 2.11). The resulting probability of the exciton “survival” after diffusing to a length, \( l \), is plotted in Fig. 2.6d for both solids.

Based on the bulk quenching analysis, we conclude that the exciton dissociation probabilities per single interparticle hop in ZnSe/CdS and CdSe/CdS solids are nearly equal (\( p_1(\text{ZnSe/CdS}) = 0.07 \) and \( p_1(\text{CdSe/CdS}) = 0.06 \)), indicating similar exciton diffusion volumes in both solids. A slightly shorter diffusion length in ZnSe/CdS (8.5 nm \textit{versus} 10.8 nm in CdSe/CdS, see Fig. 6d) reflects a somewhat smaller diameter of these nanoparticles, as the mean number of interparticle (pre-dissociation) hops for both solids are nearly the same (\( n_{\text{hop}}(\text{ZnSe/CdS}) \approx 10 \) and \( n_{\text{hop}}(\text{CdSe/CdS}) \approx 12 \)). The observed parity of exciton diffusion lengths in both solids is consistent with the fact that the surfaces of both nanoparticles were developed using similar procedures. Indeed, the dissociation of excitons in strongly coupled NC solids is believed to be driven by charge tunneling to surface defects,\textsuperscript{57} the densities of which are expected to be similar in the two solids due to their parallel shell and ligand deposition steps.
Figure 2.6. (a). The attenuation of the fast FL decay component in ZnSe/CdS NC solids with increasing concentration of Au NPs can be correlated to the changes in the unshaded area under the exciton population curve (shown in c). By modelling the exciton population $N(p_{diss}(1\text{ hop}))$, we determine the probability of exciton dissociation on each hop in OX-linked ZnSe/CdS and CdSe/CdS NC solids to be 7% and 6%, respectively. (b). Transmission Electron Microscope (TEM) image of a mixed (Au + ZnSe/CdS) nanoparticle sample used for developing (Au, ZnSe/CdS) solids. The apparent ratio of Au to ZnSe/CdS nanoparticles on a grid, $n_{TEM}$, can be used to estimate the ultimate gold-to-gold interparticle distance $R_{Au-Au}$ in a solid:

$$R_{Au-Au} = \left(\frac{n_{TEM}D_{ZnSe/CdS} + D_{Au}}{2}\right).$$

where $D_{ZnSe/CdS}$ and $D_{Au}$ are the diameters of ZnSe/CdS and Au nanoparticles, respectively. (d). The predicted evolution of the exciton population in OX-linked ZnSe/CdS and CdSe/CdS NC solids versus the diffusion length.
The results of bulk quenching analysis and FL lifetime measurements suggest that ZnSe/CdS and CdSe/CdS solids have similar exciton diffusion volumes but exhibit rather different exciton decay rates. This conclusion is supported by an apparent deference in the emission yield of the two solids featuring the same optical density at $\lambda_{CdS} = 420$-430 nm (Fig. 2.1). Based on the similarity of $I_{\text{diff}}$ and the difference of $\tau_{\text{diff}}$ values for the two solids, we conclude that longer exciton lifetimes in ZnSe/CdS are the results of slower exciton diffusion in these materials (lower diffusivity: $\mu_{ZnSe/CdS} < \mu_{CdSe/CdS}$). Slower diffusion of excitons in ZnSe/CdS solids to defect-localized quenching sites explains their increased brightness compared to CdSe/CdS films, where fast diffusion leads to a rapid dissociation.

The slower diffusion of excitons in ZnSe/CdS solids was found to be consistent with the FRET mechanism of energy transfer between adjacent nanoparticles in a film. Recent works$^{58,59}$ have demonstrated that both Förster and Dexter processes can contribute to interparticle energy transfer, however, the rate of the Dexter exchange is significantly lower due to a relatively smaller overlap of electronic wave functions across neighboring nanocrystals. For instance, a recent study by the Kamat group$^{59}$ has shown that the rate of Dexter transfer becomes negligible compared the Förster process when the donor-acceptor distance exceeds 2 nm. Since the nanocrystal solids investigated in this work exhibit 5-7 nm interparticle distances, FRET is expected to be the primary energy transfer process.$^{38,60,61}$ According to the FRET framework, the rate of (non-radiative) energy transfer between neighboring nanocrystals is proportional to the spectral integral, $J = \int_0^\infty A(\lambda)\lambda^4 F(\lambda) \, d\lambda$, which reflects the overlap between the donor emission, $F(\lambda)$, and the acceptor absorption, $A(\lambda)$. It is generally expected that $J$ integral is intrinsically
smaller for type II systems (see Fig. 2.7) due to weaker absorbance by the emissive state in these structures. Consequently, the FRET rate in ZnSe/CdS NCs is expected to be lower than that in CdSe/CdS assemblies (with all other parameters being equal for both solids).

Figure 2.7. Normalized absorption and emission profiles of ZnSe/CdS (a) and CdSe/CdS (b) colloidal nanocrystals showing the respective spectral overlap, $J$ (shaded area). A comparatively lower absorbance-emission overlap in type II systems, $J_{\text{II}} < J_{\text{I}}$, is believed to result in a lower FRET rate in these materials. The absorption profiles of both colloids were set to the same value at the excitation wavelength (~420-430 nm). The emission profiles were normalized according to their respective photoluminescence QYs. The overlap integral, $J$, was scaled relative to $J(\text{CdSe}/\text{CdS})$.

Figure 2.7 provides a graphical comparison of overlap integrals, $J$, for ZnSe/CdS and CdSe/CdS solids. The numerical values of $J$ were determined from photoluminescence quantum efficiency spectra, $F(\lambda)$, (the set of red curves in Fig. 2.7) and subsequently scaled relative to $J(\text{CdSe}/\text{CdS}) = 1$. The resulting value of $J$ for ZnSe/CdS NCs is approximately 3 times lower than that of CdSe/CdS solids, which is expected due to a comparatively lower transition dipole for type II heterostructures. A relatively low value of $J(\text{ZnSe}/\text{CdS}) = 0.31$ could explain the
slower exciton diffusion in the ZnSe/CdS NCs. This could be a universal feature of type II solids, which rely on the FRET mechanism for the energy transfer.

To provide further experimental support to the observed slow exciton diffusion in systems with low absorption-emission spectral overlap, we have examined the optical properties of another type II system comprising CdS-capped ZnTe/CdSe NCs. The compound core of these nanoparticles (ZnTe/CdSe) efficiently separates photoinduced charges between ZnTe and CdSe domains (Fig. 2.13), giving rise to a relatively low emission-absorption overlap (Fig. 2.8a). This should potentially lead to a comparatively slow exciton transport and high emission yield.

Figure 2.8. (a). Normalized absorption and emission profiles of ZnTe/CdSe/CdS colloidal nanocrystals showing the spectral overlap, $J$ (shaded area). (b). The relationship between the exciton lifetime in a solid ($x$ axis) and the normalized absorption-emission overlap ($y$ axis). (c). FL lifetime of OX-capped ZnTe/CdSe/CdS NC solids. The fast component of the FL lifetime ($\tau_{\text{fast}} = 6.1$ ns) approximately equals to the exciton diffusion time. (d). TEM images of ZnTe/CdSe/CdS core/shell NCs.
The rate of exciton diffusion in ZnTe/CdSe/CdS films was obtained from the emission intensity decay of OX-linked solids, as illustrated in Fig. 2.2. Prior to film deposition, the surfaces of ZnTe/CdSe heterostructures were capped with a thin shell of CdS to ensure that solution-processed solids exhibited similar interparticle distances and surface defect densities as in the case of ZnSe/CdS and CdSe/CdS materials. According to Fig. 2.8c, the emission lifetime of OX-linked ZnTe/CdSe/CdS NC films (τ = 6.1 ns) was the longest of the three examined solids. Assuming that the diffusion length of excitons in ZnTe/CdSe/CdS assemblies is similar to those of ZnSe/CdS and CdSe/CdS (based on the similarity of the shell and ligand structure among the three samples), we estimate that the rate of exciton diffusion in ZnTe/CdSe/CdS is lower than that of CdSe/CdS and ZnSe/CdS films by factors of ≈6 and ≈2, respectively. This result is in good agreement with the proposed correlation between the rate of exciton diffusion in NC solids and the magnitude of the spectral overlap, J (Fig. 2.8b).

For a control test of the observed exciton dynamics, we have looked into optical properties of transition metal doped nanocrystals, which are known to exhibit an exceptionally low J. Since the luminescence of Mn$^{2+}$ or Cu$^{+}$-doped semiconductor colloids originates from partially or fully localized excited states, the emission profile of these nanoparticles becomes strongly red-shifted from the absorption edge. Moreover, in the case of Mn$^{2+}$, this emission and the corresponding absorption processes are spin forbidden. These factors reduce the FRET probabilities even further relative to those of the excitonic NCs. The impact of these spectral factors is clearly seen in Fig. 2.9a, which shows a nearly vanishing spectral overlap of the emission and absorption profiles in Mn$^{2+}$-doped Zn$_{1-x}$Cd$_x$Se/ZnS NCs. Consequently, one can expect particularly slow energy diffusion across the film. The Dexter energy exchange between
neighboring nanoparticles is also negligible due to the short-range nature of this process\textsuperscript{59} and the highly localized emissive excited state. The emission lifetime measurements confirm these expectations, revealing a very long excited-state lifetime of OX-linked solids of Mn\textsuperscript{2+}-doped Zn\textsubscript{1-x}Cd\textsubscript{x}Se/ZnS NCs ($\tau_{\text{solid}} \approx 0.3$ ms). Remarkably, even when Au NP quenching sites are introduced to the film, the emission lifetime still remains in the sub-millisecond range, suggesting that most energy simply does not diffuse out of the absorbing nanoparticles. Based on the small drop in the luminescence lifetime of Au-doped films (Fig. 2.9a, green curve), we conclude that the energy diffusion rate is $\approx 10^5$ times slower than in the case of CdSe/CdS NC solids. Along these lines, Mn\textsuperscript{2+}-doped Zn\textsubscript{1-x}Cd\textsubscript{x}Se/ZnS NC nanocrystal films were found to maintain the original brightness upon solution processing into an electrically-coupled film (QY $\approx 70$-80 %), which makes these structures attractive candidates for the development of light-emitting materials.

Figure 2.9. (a). Luminescence lifetime of Mn\textsuperscript{2+}-doped Zn\textsubscript{1-x}Cd\textsubscript{x}Se/ZnS NCs in solution (red curve), and in OX-linked solids (blue curve). The green curve represents a minor reduction of the emission lifetime caused by the introduction of Au NP quenching sites into the film (at an approximate 1:1 particle ratio). (b). Normalized absorption and emission profiles of Mn\textsuperscript{2+}-doped Zn\textsubscript{1-x}Cd\textsubscript{x}Se/ZnS colloidal NCs exhibiting a minimal spectral overlap, $J$ (shaded area). (b). TEM images of Mn\textsuperscript{2+}-doped Zn\textsubscript{1-x}Cd\textsubscript{x}Se/ZnS heterostructured NCs. Scale bar is 20 nm.
2.5 Conclusions

In summary, we demonstrate that the rate of exciton diffusion in nanocrystal solids can be controlled via the absorption-emission spectral overlap integral \((J)\), which offers a novel strategy for enhancing the emission of NC films. In particular, solids with low \(J\) overlap (e.g. type II systems, transition-metal doped nanocrystals), featuring slow exciton diffusion, foster a desirable combination of strong interparticle coupling and bright emission, which makes these films attractive for the development of light-emitting applications. The role of spectral overlap in exciton dynamics was investigated through a side-by-side comparison of CdSe/CdS and ZnSe/CdS NC films featuring type I and type II carrier confinement, respectively. It was found that excitons diffuse up to 3 times slower in films of low-\(J\) ZnSe/CdS (core/shell) NCs leading to a relatively brighter emission (Fig. 2.1), which was attributed to a slower diffusion of excitons to dissociative defects. This conclusion was further supported by two control experiments utilizing solids of ZnTe/CdSe/CdS core/shell and Mn\(^{2+}\)-doped Zn\(_{1-x}\)Cd\(_x\)Se/ZnS NCs. The energy diffusion rates in these solids were reduced in a manner consistent with their respective absorption-emission overlaps. A significant reduction in the energy diffusion rate was observed for Mn\(^{2+}\)-doped Zn\(_{1-x}\)Cd\(_x\)Se/ZnS NC solids featuring a particularly low donor-acceptor spectral overlap. The exciton diffusivity in this case was found to be as much as \(10^5\) times lower than in CdSe/CdS films.
2.6 Supporting Information

Figure 2.10. The energy diagram showing the relative positions of zero-angular momentum excited states for CdSe/CdS (left) and ZnSe/CdS (right). The energy offsets are estimated from Ref. 62,63.

Exciton diffusion length is related to the exciton lifetime, \( \tau \), according to the following expression:

\[
\tau_{\text{diffusion}} = \sqrt{\frac{d}{D}}
\]

where \( D \) is the diffusion coefficient. A Wiener formula for random walk diffusion in three dimensions is given by

\[
D = \frac{d^2}{6 \tau_{\text{step}}}
\]

where \( d \) is the length of a single hop.
(interparticle distance) and \( \tau_{\text{step}} \) is the time elapsed between two successive steps. Consequently,

\[
I_{\text{diffusion}} = D\tau = d \times \sqrt{n_{\text{hop}} \tau_{\text{step}} / 6\tau_{\text{step}}} = d \times \sqrt{n_{\text{hop}} / 6} .
\]

Determination of the exciton scatter-free length in a Au-doped NC solid.

\[
V_2 (\text{excluding } V_1) = V_3 (\text{excluding } V_1 \text{ and } V_2)
\]

(as explained in the Figure legend)

\[
\frac{4\pi}{3} (r_2^3 - r_1^3) = \frac{1}{2} R_{\text{Au-Au}}^3
\]

\[
I_{\text{free travel}} = r_2 - r_1 = \frac{3}{8\pi} R_{\text{Au-Au}}^3 + r_1^3 - r_1
\]

\[
r_1 = R_{\text{eff}} (\text{Au}) \approx 3.5 \text{ nm}
\]

Figure 2.11. Illustration of the general strategy for determining the effective mean free path of excitons in a Au-doped nanocrystal solid, \( r_{\text{eff}} \). If we assume that a single photon is absorbed by a semiconductor NC in a film, the average scatter free diffusion of the resulting exciton can vary
from 0 to about $R_{\text{Au-Au}}/2$ (minus the diameter of a Au NP) depending on the exact location of the absorbing NC. The statistically averaged distance from the absorbing nanocrystal to the closest Au nanoparticle is defined as the scatter free distance, $l_{\text{free\ travel}}$, for which half of semiconductor NCs are located closer and the other half further away from a Au NP (volumes $V_2$ and $V_3$, respectively). In other words, the total volume of a $V_2$ sphere (excluding the effective volume of a Au nanoparticle) should be equal to the interstitial volume ($V_3$). Given the large number of nanoparticles in the film, the statistical error of estimating $l_{\text{free\ travel}}$ using the aforementioned strategy is expected to be small.
Figure 2.13. Energy diagram comparing the alignment of conduction and valence band edges for ZnSe/CdS (left) and ZnTe/CdSe (right) nanocrystals.
Definition of type I and type II core/shell NC combinations.

Figure 2.14. Definition of type I and type II core/shell NC combinations. Conventionally, a heterojunction of two semiconductor materials can be classified as either type I, where both carriers are confined within the same semiconductor, or type II, where an electron and a hole are spatially separated in two different parts of the heterostructure. Due to highly stable emissions associated with nanocrystals in the first group, their properties are readily utilized in applications that require a coupling of quantum dots to organic moieties, such as in hybrid LEDs or in vivo imaging, where the use of single-phase nanocrystals typically causes an irreversible loss of fluorescence or severe blinking. Heterostructures of the second group benefit from an efficient separation of charges between the core and the shell, which makes them useful in photovoltaic applications, where spatial charge separation reduces an exciton dissociation potential, or QD-based lasers, where an electric dipole of a photogenerated pair Stark-shifts the biexciton level resulting in a desirable linear light amplification regime.

2.7 References


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CHAPTER III. MAPPING THE EXCITON DIFFUSION IN NANOCRYSTAL SOLIDS


3.1 Abstract

Colloidal nanocrystal solids represent an emerging class of functional materials that hold strong promise for device applications. The macroscopic properties of these disordered assemblies are determined by complex trajectories of exciton diffusion processes, which are still poorly understood. With the lacking theoretical insight, experimental strategies for probing the exciton dynamics in quantum dot solids are in great demand. Here, we develop an experimental technique for mapping the motion of excitons in semiconductor nanocrystal films with a sub-diffraction spatial sensitivity and a picosecond temporal resolution. This was accomplished by doping PbS nanocrystal solids with metal nanoparticles that force the exciton dissociation at known distances from their birth. The optical signature of the exciton motion was then inferred from the changes in the emission lifetime, which was mapped to the location of exciton quenching sites. By correlating the metal-metal interparticle distance in the film with corresponding changes in the emission lifetime, it became possible to obtain important transport characteristics, including the exciton diffusion length, the number of pre-dissociation hops, the rate of interparticle energy transfer, and the exciton diffusivity. The benefits of this approach to device applications were demonstrated through the use of two representative film morphologies featuring weak and strong interparticle coupling.
3.2 Introduction

Solution processing of semiconductor nanocrystal solids represents a promising strategy for the development of novel optoelectronic applications. An important advantage of these materials lies in the spectral tunability of their optical properties, which results from the quantum confinement of photoinduced charges. The colloidal stability of semiconductor nanocrystals offers another important benefit, as it enables low-cost solution processing of thin films virtually on any substrate. The electrical conductivity of quantum dot solids is typically rendered through the use of short molecular linkers, or encapsulating matrices that preserve some degree of quantum confinement while promoting an electrical coupling between neighboring nanoparticles. So far, this strategy has been rewarded through the development of high-performance materials for light-emitting and photovoltaic applications. Nevertheless, despite an on-going improvement in the function of nanocrystal-based devices, the electrical transport in semiconductor nanocrystal films remains to be the subject of an active debate. Controversial viewpoints arise from the fact that the basic processes of exciton and carrier diffusion in nanoparticle solids cannot be easily imaged. In light of this limitation, novel experimental tools offering both spatial and temporal sensitivity are in great demand.

It is generally accepted that photoexcitation of nanocrystal films leads to the formation of localized excitons that diffuse into a solid at rates determined by the strength of the interparticle coupling. Similar to the exciton dynamics of polymer films, a bound electron-hole pair in a nanocrystal solid will diffuse until reaching a potential energy minimum, which could result in its recombination or dissociation. The exact mechanism of the exciton decay depends on several morphological parameters and is highly important to the performance of ensuing nanocrystal devices. For example, the exciton diffusion towards film boundaries in quantum dot light-
emitting diodes causes quenching of the luminescence, which limits the device efficiency.\textsuperscript{39} On the contrary, the diffusion of excitons to charge-separating interfaces in nanocrystal solar cells is highly beneficial as it leads to the generation of photocurrent.\textsuperscript{37} These and other examples confirm that the knowledge of exciton dissociation processes is central to the nanocrystal device design.\textsuperscript{35} Ideally, the rates of these processes should be controlled toward improving the desired functionalities of nanocrystal assemblies.

A unique feature of excitons in nanocrystal solids concerns their relatively low binding energy. Unlike polymer films, where the dissociation of excitons occurs only at interfaces of different material phases, the splitting of bound electron-hole pairs in nanocrystal solids can be triggered by less energetic processes, such as charge tunneling between neighboring nanocrystals.\textsuperscript{40} The emerging free carriers will then drift through the solid with mobilities that depend on the strength of interparticle coupling, as was confirmed by numerous studies of charge transport dynamics in nanocrystal solids.\textsuperscript{41-46} Studying the motion of neutral excitons, however, is a far more challenging task. To date, the exciton diffusion in NC solids has been investigated \textit{via} steady-state and time-resolved spectroscopy methods\textsuperscript{36,44,47-52} while their diffraction limited spatial profile has been visualized through optical microscopy.\textsuperscript{35} Despite these efforts, the exact nature of the exciton dissociation mechanism as well as exciton diffusion trajectories in nanocrystal solids still remain poorly understood.

Here, the mapping of the spatial and temporal dynamics of the energy transport processes in PbS nanocrystal solids has been performed by forcing the exciton dissociation at known distances from their birth. This was achieved by doping the nanocrystal film with Au nanoparticles that induce the non-radiative recombination of carriers.\textsuperscript{53,54} Within this approach, the optical signature of the exciton dissociation (splitting) events was inferred from the changes
in the lifetime of the Au-doped PbS NC emission, which was mapped to the location of exciton quenching sites. The experimental data was then compared to the predictions of a random walk diffusion approximation aimed to establish the correlation between the changes in the exciton lifetime and the density of Au domains in a film. By applying this strategy to PbS nanocrystals solids, we found that the probability of the exciton dissociation per single interparticle hop is \( p_{\text{diss}} \) (1 hop) = 9%, if PbS NCs are linked with short-chain 3-mercaptopropionic acid (MPA) ligands, and \( p_{\text{diss}} \) (1 hop) = 3% when longer-chain 8-mercaptooctanoic acid (MOA) molecules are used. In the case of MPA-linked solids (interparticle distance = 0.9 nm), excitons diffused to an average length of 5.7 nm in approximately 12 hops, which corresponded to the diffusion mobility (diffusivity) of 0.012 cm²s⁻¹. Meanwhile, MOA-linked solids (interparticle distance = 1.7 nm) gave rise to a longer diffusion length of 11.4 nm (34 hops) and a lower diffusivity of 0.003 cm²s⁻¹. The observed difference in the dynamics of the two film types was found consistent with the proposed charge-tunneling mechanism of the exciton dissociation.

To reveal the nature of exciton dissociation processes the FL lifetime data was complemented with the steady-state emission measurements of Au-doped PbS NC films. Based on the observed relationship between the density of Au NPs and the ensuing PbS emission wavelength we were able to conclude that the exciton dissociation process is likely to be induced by inter-dot charge tunneling rather than carrier scattering on defects. Another interesting trend was inferred from the comparison of nanoparticle solids utilizing different architectures. Measurements of the exciton diffusion lengths in MPA- and MOA-passivated NC films allowed determining the effect of the interparticle distance on the energy transfer (ET) rate. The observed ET distance dependence suggested a possible deviation from Förster scaling, indicating the presence of the non-dipolar contribution into exciton coupling in nanocrystal films. This
phenomenon was previously observed by Tisdale and others and was ascribed to the effect of a nanoparticle size, which does not conform the point dipole approximation. In addition to studying the exciton diffusion processes, the developed model was complemented with the time-resolved measurements of free carrier recombination, which further contributed to elucidating the energy relaxation dynamics in PbS NC solids.

3.3 Experimental Section

3.3.1 Materials.

Lead(II) oxide powder (PbO, 99.999% Aldrich), 1-octadecene (ODE, 90% Aldrich), oleic acid (OA, 90% Aldrich), bis-(trimethylsilyl) sulfide ((TMS)\textsubscript{2}S, Aldrich, synthetic grade), acetone (anhydrous Amresco, ACS grade), hexane (anhydrous, 95% Aldrich), ethanol (anhydrous, 95% Aldrich), methanol (anhydrous, 99.8% Aldrich), isopropanol (anhydrous, 99.8% Acros), toluene (anhydrous, 99.8% Aldrich), 3-mercaptopropionic acid (MPA, 99%, Alfa Aesar), 8-mercaptooctanoic acid (MOA, 95%, Aldrich), gold(III) chloride (AuCl\textsubscript{3}, 99%, Acros Organics) were used as received without any further purification. Oleylamine (tech., 70%, Aldrich) was pumped for 1 hour at 120 °C and then stored under argon atmosphere prior to using. Fluorine-doped tin oxide (FTO, SnO\textsubscript{2}/F) glass (TEC 15, 12-14 Ohm/sq) was obtained from Pilkington Glass. All reactions were performed under argon atmosphere using the standard Schlenk technique. The centrifuge used for precipitation operated at 7200 rpm.

3.3.2 Synthesis of PbS nanocrystals.

PbS NCs were fabricated according to a procedure adapted from Hines. In a typical synthesis, a mixture of 0.49 g (2mmol) PbO in 18 mL of ODE and 1-16 mL of OA (increasing the amount of OA results in a larger NC diameter) 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 NCs) by removing the flask from the heating mantle and placing it into an ice water bath. Nanocrystals were isolated from the mixture by precipitating with acetone, centrifuging, and re-dispersing in toluene. The cleaning procedure was repeated 2-3 times, upon which nanocrystals were re-dispersed in a minimal amount of hexane (4-5 ml).

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

3.3.3 Synthesis of Oleylamine-Capped Au nanocrystals (NCs).

Au NCs were synthesized according to previously reported methodology.$^{64}$ In a typical synthesis, 0.011g of AuCl$_3$ and 5 mL of oleylamine were loaded in a one-neck flask and allowed to react at 100 °C for 30 min under argon atmosphere. During this time, the reaction mixture’s color changed from transparent yellow to orange (indicating the formation of Au-oleate complexes), and then finally to purple (indicating the formation of oleylamine-capped Au NPs). The reaction was stopped by removing the flask from the heating mantle and allowed to cool to room temperature. Then, the solution was transferred from the flask into centrifuge tubes and precipitated with ethanol. After the centrifugation, the supernatant was discarded and the pellet was dissolved in chloroform. The cleaning cycle was repeated one more time and the final
product was re-dispersed and stored in 5 ml of chloroform. The final product contained Au NPs with an average diameter of 5 nm and a surface plasmon resonance (LSPR) peak at \( \lambda \approx 525 \) nm.

3.3.4 Preparation of the nanocrystal film.

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) or a mixture of PbS and Au NCs was deposited on the glass substrate and spun at 3000 rpm for 10 seconds. Subsequently, 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. Finally, the film was rinsed with methanol and hexane solutions. The total amount of layers varied from 3 to 4. Ratios of PbS to Au were calculated using a volume fraction of each material in the mixture (see the Supporting Information).

MOA-linked NC solids were fabricated using a layer-by-layer spincoating process under an argon atmosphere. After the deposition of 5-7 drops of PbS NCs, or a mixture of PbS and Au NCs, onto a FTO/glass substrate followed by spinning at 3000 rpm for 15 s, the film was immersed into 0.7 M MOA solution in acetonitrile for 1 min and washed with 10 drops of acetonitrile. Overall, 3-4 cycles were required to completely perform the deposition of PbS or PbS/Au NCs. Ratios of PbS with Au for the mixed films were calculated the same way as in case of MPA-linked films.

3.3.5 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 & Hickle GmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), an id50 avalanche photodiode (Quantique), and long pass filters on 400nm, and 532nm.

3.4 Results and Discussion

The fluorescence intensity decay is emerging as a viable tool for “non-contact” measurements of the excited state dynamics in semiconductor nanocrystal solids.\textsuperscript{40,44,48,56-59} To date, this strategy has been used primarily for monitoring the downhill migration of excitons in a film, providing important insights into the carrier recombination dynamics. Recently, the emission intensity decay approach was adapted towards distinguishing between the recombination rates of bound and free carriers in a quantum dot solid. This differentiation was achieved by extracting the fast and the slow components of the FL intensity decay in PbS NC solids containing “insulating” ZnS barriers.\textsuperscript{44} The presence of ZnS dots in the gaps between PbS NCs enabled the suppression of the interparticle charge transfer, which allowed attributing the fast decay component of the PbS-only NC emission to the exciton dissociation process while the slow exponent was ascribed to free carrier trapping on nanocrystal surfaces, as shown in Fig. 3.1.

Despite providing a powerful tool for probing the excited state dynamics in nanocrystal solids, the time-resolved emission alone does not offer the spatial resolution needed for imaging the motion of excitons in a three-dimensional film. As a result, a number of important questions
concerning the energy relaxation pathways in NC solids still remain unanswered. First of all, it is unclear how far an exciton can diffuse into a solid prior to its dissociation into a free electron-hole pair. The expected diffusion length along with possible exciton trajectories is central to the design of photovoltaic materials, since these parameters determine the ultimate p-n junction geometry and the maximum length of the carrier collection path. Secondly, knowing mechanisms that trigger the exciton dissociation is likewise important, as these processes can be controlled for on-demand enhancement or suppression of free carrier generation. While it was hypothesized that tunneling of one of the charges is the primary mechanism of exciton splitting, an alternative explanation based on exciton migrating to trap states or non-emissive potential minima (large-diameter NCs) could not be ruled out.

Figure 3.1. The fluorescence intensity decay of semiconductor nanocrystal solids often contains two distinct decay components. The fast time reflects the rate of exciton dissociation, which is
presumably driven by charge tunneling processes, while the slow exponent is determined by the rate of free carrier trapping on nanocrystal surfaces.

In this work, the sub-diffraction mapping of excitons was achieved by doping PbS nanocrystal solids with a small amount of Au NPs. Due to a high density of states in metals, Au dopants promote a non-radiative recombination of excitons, decreasing their lifetime. By correlating the Au-Au interparticle distance in the film with the corresponding change in the FL lifetime, ΔFL, it is therefore possible to obtain the average length of the exciton diffusion, l_{exc}^{diff}, and the number of interparticle hops made by excitons prior to the dissociation, n_{hop}. These two parameters can then be used to derive other important transport characteristics, including the exciton diffusivity and the dot-to-dot energy transfer rate.

The confirm that Au nanoparticles can be used for quenching excitons in semiconductor nanocrystal solids, we have carefully examined the emission of mixed (Au, PbS) NC films. In these experiments, Au nanoparticles were electrically coupled into the surrounding “matrix” of PbS NCs though the use of ligands that promote the PbS-to-Au charge transfer, causing a non-radiative decay of PbS excitons. We note that quenching of PbS excitons via energy transfer to Au is likely to be slow. Indeed, the energy of PbS excitons (1.4 eV) is lower than that of plasmon excitations (2.2 eV), such that the resonant ET is uphill and therefore suppressed while the non-resonant ET is weakened by the poor spectral overlap of Au and PbS NPs at the PbS band gap energy. To introduce Au “dopants” into a PbS NC film, solution-cast films of oleylamine-capped Au and PbS nanoparticles were treated with short-chain MPA molecules. The ratio of Au to PbS NCs in the resulting (Au, PbS) solids was determined from TEM images of mixed (Au, PbS) nanoparticle solutions prior to deposition (Figs. 3.2a-3.2c). Several films exhibiting the same
optical density (at the PbS exciton feature) were fabricated to determine the effective radius of Au NPs that promotes quenching of PbS excitons. According to Fig. 3.2, the emission of (Au, PbS) films is almost fully quenched when the ratio of Au to PbS falls below 2, and is reduced to about 40% when the ratio of Au to PbS is 1:30. The emission loss in (Au, PbS) films, ΔFL/FL, which represents the fraction of “quenched” PbS NCs was then used to determine the effective radius of Au nanoparticles that promotes quenching (Fig. 3.8 for details). Based on the best model fit (Fig. 3.2d, red curve), we found the effective “quenching” radius to be \( R_{\text{eff}}^{\text{Au}} \approx 3.5 \) nm, which was just slightly larger than the physical size of Au NPs appended with MPA ligands \( R_{\text{physical}}^{\text{Au + MPA}} \approx 3.0 \) nm. The effective “quenching” radius of Au nanoparticles grew to 3.8 nm when longer-chain MOA ligands were used as interlinking molecules.

Figure 3.2. Determining an effective radius of a Au nanoparticle that promotes exciton quenching in a PbS NC solid. (a)-(c). Transmission electron microscope (TEM) images and the corresponding emission profiles of nanoparticle solids featuring different concentrations of Au. (a) – Au:PbS = 1:2 (by nanoparticle count); (b) – Au:PbS = 1:30; (c) – PbS only solids. (d). The effective radius of a Au nanoparticle that results in quenching of excitons is determined by fitting the experimental data (the emission reduction versus Au concentration) with several predicted quenching scenarios, corresponding to \( R_{\text{eff}}^{\text{Au}} = 3.5 \) nm (red curve), \( R_{\text{eff}}^{\text{Au}} = 6 \) nm (blue curve), \( R_{\text{eff}}^{\text{Au}} = 9 \) nm (green curve). Fitting model is described in Fig. 3.8.
The character of exciton diffusion through a uniform nanocrystal solid (prior to Au doping) can be viewed as random provided that the energy disorder in the film does not exceed the room temperature $kT$. In this case, the relation between the exciton diffusion length and the number of interparticle hops, $n_{hop}$, obeys a three-dimensional random walk approximation,

$$l_{diff}^{exc} = l_{hop} \sqrt{n_{hop}/6},$$

where $l_{hop}$ is the average center-to-center spacing between adjacent dots (see Supporting Information). By setting the average probability of exciton dissociation per single hop, $p_{diss}(1 \text{ hop})$ to be a free parameter, we can express the probability of exciton dissociation on its $n^{th}$ hop: $p(n_{hop}) = p_{diss}(1) \times (1 - p_{diss}(1))^{n_{hop}-1}$. The resulting probability distribution (black curve in Fig. 3.3a) reflects the fraction of the exciton population in a solid, $N_{exciton}(n_{hop})$, which remain excited (unquenched) after each hop.

With the introduction of Au NPs into a nanocrystal solid, excitons become forced to dissociate at shorter distances, which are related to the Au-Au interparticle separation, $R_{Au-Au}$. As a result, some of the exciton diffusion volume accessible for PbS-only NC solids will be restricted when Au NPs are added to the film. This leads to the reduction of the emission lifetime due to the forced electron-hole recombination in a metal nanoparticle. Qualitatively, the emission intensity of NC films featuring a relatively small value of $l_{diff}^{exciton}$ will not be altered significantly upon Au doping, since most excitons in this case will dissociate before reaching Au NPs. Conversely, when the exciton diffusion length is large, the motion of most excitons will be interrupted by the premature recombination on Au, leading to a significant reduction in the emission lifetime, as compared to PbS-only films.
Figure 3.3. (a). The experimental strategy for determining the exciton diffusion length in a nanocrystal solid. Assuming that on every hop, excitons have a certain probability of dissociating, $p_{\text{diss}}(1 \text{ hop})$, we can simulate the relationship between the exciton population in a film and the number of interparticle hops. The emission from the film is proportional to the exciton lifetime and therefore to the area under the population decay curve, as shown. Using the Einstein relation for the random-walk diffusion in 3D, we can estimate the exciton diffusion length, $L_{\text{exciton}}^{\text{diff}}(n)$, which is shown in the upper x-axis. (b-c). The decay of exciton population in a solid corresponding to the two values of a single-hop dissociation probability: $p_{\text{diss}}(1 \text{ hop}) = 0.1$ (blue) and $p_{\text{diss}}(1 \text{ hop}) = 0.03$ (red) is shown. If Au NPs are inserted into a PbS solid, the dissociation of excitons will be forced at shorter distances (see text). This will result in the reduction of the fast component of the PbS emission lifetime. By comparing the ratio of the two areas under the exciton population curve, labelled radiative and non-radiative, to the attenuation ratio of FL lifetimes in Au-doped PbS NC films, the exciton dissociation probability can be determined.

From the quantitative perspective, the emission changes in Au-doped PbS NC films convey the sufficient amount of information needed to determine the probability of exciton dissociation per single interparticle hop, $p_{\text{diss}}(1 \text{ hop})$. Due to the fact that the radiative recombination of PbS excitons in a solid occurs spontaneously, the total number of emitted photons from a nanocrystal film will be proportional to the average lifetime of an exciton and, thus, to the total number of hops, $n_{\text{hop}}$, that excitons make prior to splitting or quenching by gold. Consequently, the number of emitted photons from a NC solid, $N_{\text{ph}}$, will be proportional to the total area under the exciton population decay curve, $N(n_{\text{hop}})$, such that

$$N_{\text{ph}}^{\text{PbS-only}} = \int_0^\infty N(n_{\text{hop}})dn_{\text{hop}} \approx \langle N \rangle \langle n_{\text{hop}} \rangle,$$

as shown in Fig. 3a. The emission from a Au-doped film will be reduced due to a restricted diffusion length, $N_{\text{Au-PbS}} = \int_0^{n_{\text{max}}} N(n_{\text{hop}})dn_{\text{hop}}$. We can then express the expected reduction in the number of emitted photons resulting from Au doping as the ratio of “unshaded” to total area under the decay curve (see Figs. 3.3b and 3.3c):

$$\Delta FL_{\text{theor}}(p_1^{\text{diss}}) = \frac{N_{\text{ph}}^{\text{PbS-only}}}{N_{\text{ph}}^{\text{PbS}}} = \frac{\text{Area}_{\text{unshaded}}(p_1^{\text{diss}})}{\text{Area}_{\text{total}}(p_1^{\text{diss}})}$$

(1)
Experimentally, the same reduction can be estimated as the ratio of photons emitted with and without Au present. To distinguish the band gap exciton emission from the contribution of free carriers, we include only the fast decay component of the FL decay into the intensity integration, \( I_{FL} = \exp\left(-\frac{t}{\tau_{fast}}\right) \):

\[
\Delta FL_{\text{exp}} = \frac{N_{\text{Au-PbS}}^{ph}}{N_{\text{PbS-only}}^{ph}} \approx \int \frac{\exp\left(-\frac{t}{\tau_{\text{Au-PbS}}^{fast}}\right)}{\exp\left(-\frac{t}{\tau_{\text{PbS-only}}^{fast}}\right)} dt = \frac{\tau_{\text{Au-PbS}}^{fast}}{\tau_{\text{PbS-only}}^{fast}}
\]  

(2)

By setting the theoretical and experimental emission changes equal to each other, \( \Delta FL_{\text{theor}}(p_{diss}^{1}) = \Delta FL_{\text{exp}} \), we can then determine the probability of exciton dissociation per single step, \( p_{\text{diss}} \) (1 hop).

Figures 3.3b and 3.3c simulate two possible scenarios of the exciton diffusion through a solid following a single excitation pulse and corresponding to a high (\( p_{\text{diss}} = 0.1 \); blue) and low (\( p_{\text{diss}} = 0.03 \); red) dissociation probability per single interparticle hop. The resulting decay population curves (red and blue) show the fraction of undissociated excitons after each hop. The corresponding diffusion length \( l_{\text{diff}}^{\text{exciton}} \) is shown at the top of the plot. The shaded area in Figs. 3.3b and 3.3c represents the exciton population, which is likely to be quenched through a forced recombination with Au nanoparticles. The average scatter-free length of the exciton diffusion, \( l_{\text{free travel}} \), in the presence of Au doping (green dashed line in Figs. 3.3b and 3.3c) will be determined by the average distance between Au NPs in the film, \( R_{\text{Au-Au}} \), and the effective Au radius for exciton quenching, \( R_{\text{eff}}(\text{Au}) \), as illustrated in Fig. 3.5a. The overall lifetime of a
scatter-free diffusion of an exciton in a solid measured between the photoexcitation and the quenching events is given by: 
\[
\tau_{\text{exciton}}^{\text{diss}}(n_{\text{hop}}) = t_{\text{step}} n_{\text{hop}},
\]
where \( t_{\text{step}} \) is the average nearest-neighbor energy transfer time. Experimentally, the total time of the exciton diffusion (with or without Au present) is given by the fast decay component in the FL intensity decay, 
\[
\tau_{\text{exciton}}^{\text{diss}} = \tau_{\text{FL}}^{\text{fast}}.
\]

To determine the exciton diffusion length in ligand-linked PbS NC solids we have fabricated several mixed (Au, PbS) films featuring different concentrations of Au nanoparticles. To this end Au (\( d \approx 5.0 \text{ nm} \)) and PbS (\( d \approx 3.1 \text{ nm} \)) NCs were mixed in octane at predefined ratios and used as “inks” for processing film layers. For better miscibility the surfaces of both nanoparticle types were passivated with long-chain oleylamine ligands. Upon spincasting of a thin layer, the bulky ligands were exchanged with either 3-mercaptopropionic acid (MPA) or 8-mercaptopooctanoic acid (MOA) molecules on each cycle of the layer-by-layer (LbL) deposition process. The two ligand types were designed to promote different degrees of PbS interparticle coupling, associated with different rates of exciton hopping through the solid. Based on previously performed film analysis via grazing-incidence small-angle X-ray scattering (GISAXS) measurements,\(^{13}\) the partial cross linking of short-chain MPA ligands gives rise to an interparticle edge-to-edge distance of approximately 0.9 nm, while MOA molecules result in longer gaps of 1.7 nm. The thickness of fabricated films was ranging between 200 and 300 nm.
Figure 3.4. Transmission Electron Microscope (TEM) image of a mixed (Au + PbS) nanoparticle sample used for developing (Au, PbS) solids. The apparent ratio of Au to PbS nanoparticles on a grid, $n_{TEM}$, can be used to estimate the ultimate gold-to-gold interparticle distance $R_{Au-Au}$ in a solid. $R_{Au-Au} = \frac{1}{3}n_{TEM}D_{PbS} + D_{Au}$, where $D_{PbS}$ and $D_{Au}$ are the diameters of PbS and Au NPs, respectively.

The fraction of Au nanoparticles in a solid was determined by finding the ratio of Au to PbS NCs in solution. To this end, a colloidal mixture of Au, and PbS nanoparticles was deposited onto a TEM grid and analyzed. The ratio of each nanoparticle type (Au versus PbS) could be easily obtained by identifying the corresponding populations of each material in a TEM specimen, as shown in Fig. 3.4. The ratio of Au to PbS particles on a TEM grid, $n_{TEM}$, was then converted to a Au volume fraction, $v_{Au}$, and the average Au-to-Au interparticle distance, $R_{Au-Au}$, assuming a simple cubic packing of nanoparticles (see Supporting Information for details of calculation):
A denser packing order of nanoparticles is possible and may result in the reduction of $R_{\text{Au-Au}}$. In the limiting case of closed packed ordering (face cubic centered – fcc), which could form if oily long-chain ligands are used instead of MPA molecules, Au-to-Au interparticle distance becomes: $R_{\text{Au-Au}}(\text{fcc}) \approx 0.89*R_{\text{Au-Au}}(\text{simple cubic})$, as shown in the SI section. Upon the introduction of Au NPs into PbS films, the scatter-free diffusion length of excitons becomes limited to $l_{\text{free travel}}$ (see Fig. 3.5c and the Supporting Information, Fig. 3.9, for details of calculation), which represents the mean free path of excitons in a PbS NC solid doped with evenly distributed Au NPs.

The FL intensity decay of PbS NC films featuring several concentrations of Au NPs is shown in Fig. 3.5d. The corresponding “quenching” distances, $l_{\text{free travel}}$, were determined from the concentrations of Au in each solid and are given in Fig. 3.5c. Expectedly, the longest emission lifetime (black curve) was obtained for PbS-only films where the exciton diffusion is limited either by charge tunneling (carrier ionization) or exciton trapping at potential minima. The inclusion of Au NPs into PbS NC films resulted in a proportional drop of the FL lifetime, as seen in Fig. 3.5d. Overall, the lifetime of the PbS band gap emission was decreasing in a consistent manner with the growing concentration of Au NPs. A double exponential fit of the FL intensity decay was employed to obtain an accurate estimate of the fast FL component, $\tau_{\text{fast}}^{\text{FL}}$, corresponding to the exciton lifetime in a solid.

To estimate the probability of exciton dissociation per single interparticle hop, $p_{\text{diss}}(1\ \text{hop})$, the measured reduction in the emission lifetime in Au-doped NC solids, $\Delta FL_{\text{exp}}$, was set equal to $\Delta FL_{\text{theor}}$. The value of $p_{\text{diss}}(1\ \text{hop})$ was then determined by finding the best match:
\[ \Delta F_{\text{theor}}(p_{1}^{\text{diss}}) = \Delta F_{\text{exp}}, \] conjoinly for all investigated (Au, PbS) films. This strategy is illustrated graphically in Fig. 5e. The best fit for the observed value of \( \Delta F_{\text{exp}} \) was obtained according to Eq. 2, by requiring that the ratio of unshaded to the total area under the \( N(n_{\text{hop}}) \) curve was equal to the emission lifetime ratio \( \tau_{\text{Au-PbS}} / \tau_{\text{PbS-only}}, \) consistently for all investigated film. The extracted values of \( p_{\text{diss}}(1 \text{ hop}) \) are given in Table 3.1.

Each of the several films fabricated using MPA ligands represents an independent measurement of the exciton diffusion length. In principle, a single-concentration measurement of emission quenching is sufficient for determining the transport characteristics. By employing several PbS films featuring different Au concentrations, we estimate the standard deviation of the exciton dissociation probability to be within 10%, as shown in Table 3.2.
Figure 3.5. Experimental determination of the exciton diffusion length in MPA-linked PbS nanocrystal solids. (a). An illustration of the three characteristic distances in (Au, PbS) solids: the average scatter-free length of the exciton diffusion, $l_{\text{free travel}}$, the Au-Au interparticle distance, $R_{\text{Au-Au}}$, and the effective Au radius for exciton quenching, $R_{\text{eff}}(\text{Au})$. (b). The relationship between $R_{\text{Au-Au}}$ and the PbS:Au nanoparticle ratio (see Supporting Information) for simple cubic and fcc packing orders. (c). The relationship between $l_{\text{free travel}}$ and the PbS:Au nanoparticle ratio (see Supporting Information). (d,e). The attenuation of the fast decay component in the emission of PbS NC solids induced by an increasing concentration of Au NPs (d) can be correlated to the changes in the unshaded area under the exciton population curve (e). By modelling the exciton population curve $N(p_{\text{diss}}(1))$, we determined the probability of exciton dissociation on each hop in MPA-linked PbS NC solids ($d_{\text{PbS}} \approx 3.1$-nm) to be 9%, $p_{\text{diss}}(1 \text{ hop}) = 0.09$. 
For MPA-linked films, the value of the exciton dissociation probability per single interparticle hop was found to be 0.09. Under these conditions the 1/e drop in the exciton population is reached after $\langle n_{\text{hop}} \rangle = 12$ hops, which corresponds to the diffusion length of 5.7 nm. Since the total time of the exciton diffusion is given by $\tau_{\text{fast}}^{\text{FL}}$, we can estimate the exciton diffusivity using the Einstein equation:

$$\mu_{\text{exc}} = \frac{e l_{\text{hop}}^2}{6kT \tau} = \frac{e l_{\text{hop}}^2}{6kT \tau_{\text{fast}}^{\text{FL}} (\text{PbS - only})}$$

where $l_{\text{hop}}$ is the center-to-center interparticle distance, which in the case of MPA-linked films is estimated to be $2R_{\text{PbS}} + 0.9$ nm = 4.0 nm. According to the above equation, the room temperature exciton diffusivity for MPA-linked PbS NC solids is 0.012 cm$^2$s$^{-1}$. Since both the total number of hops ($\langle n_{\text{hop}} \rangle = 12$) and the total diffusion time ($\tau_{\text{fast}}^{\text{FL}} (\text{PbS - only}) = 1.06$ ns) are known, we can estimate the average rate of energy transfer between neighboring PbS nanocrystals:

$$\Gamma_{\text{ET}} = 1/\langle \tau_{\text{hop}} \rangle = \langle n_{\text{hop}} \rangle / \tau_{\text{fast}}^{\text{FL}} = 1/0.089 = 11.3 \text{ ns}^{-1}.$$  

The short-chain MPA linkers are well suited for applications requiring high photoconductivity of a nanocrystal solid. Alternatively, light-emitting properties of nanocrystals are enhanced in solids with larger interparticle gaps. In this work, we explore the exciton dynamics of weakly coupled films by cross-linking PbS NCs with long-chain MOA ligands. For these molecules, the edge-to-edge interparticle gap is 1.7 nm, corresponding to a $l_{\text{hop}}$ value of 4.8 nm. The greater interparticle separation for MOA-linked solids is expected to cause a slower diffusion of excitons throughout the film. Likewise, the dissociation rate of excitons in MOA-linked solids will be reduced compared to MPA-linked films due to an increased potential barrier between adjacent dots. This trend is clearly seen in the FL intensity decay of MOA-linked PbS NC solids. According to Fig. 3.6a, the fast component of the emission lifetime ($\tau_{\text{fast}} (\text{MOA})$}
= 15.1 ns) in PbS-only solids is substantially longer than that of MPA-linked films (τ_{fast(MPA)} = 1.1 ns), reflecting a slower rate of exciton dissociation. With the addition of Au NPs the fast component of the emission lifetime in MOA-linked films (R_{Au-Au} = 24.9 nm; l_{free travel} = 8.8 nm) decreases from 15.1 to 6.7 ns due to quenching. By using the aforementioned strategy (Fig. 3.6b), we estimate the single-hop dissociation probability for MOA-linked films using three concentrations of Au in PbS NC solids (see Table 3.3). The average dissociation probability was found to be \( p_{\text{diss}}(1 \text{ hop}) \approx 0.03 \), corresponding to an average number of interparticle hops, \( \langle n_{\text{hop}} \rangle \), of 34 (see Table 3.1). The associated diffusion length was 11.4 nm.

Figure 3.6. Experimental determination of the exciton diffusion length in MOA-linked PbS nanocrystal solids. (a). The FL intensity decay of PbS-only (blue) and doped (Au+PbS) NC solids (red). The reduction in the fast decay component due to Au doping (Au:PbS = 1:55 by count) by a factor of 6.7/15.1 is attributed to forced dissociation. (b). Modelling of the exciton population curve (N(\( p_{\text{diss}}(1) \))) corresponding to the experimentally observed reduction in the fast FL decay component. Here, \( p_{\text{diss}}(1 \text{ hop}) \approx 0.03 \).
The increased amount of interparticle hops in nanocrystals solids featuring weaker electrical coupling is consistent with the previously proposed charge-tunneling mechanism of the exciton dissociation. Indeed, if the ionization of excitons is driven by trapping on nanoparticle surfaces, then $\langle n_{\text{hop}}(\text{MOA}) \rangle$ should be significantly smaller than $\langle n_{\text{hop}}(\text{MPA}) \rangle$ since the density of traps is roughly the same for both film types while diffusion in MOA-linked films is much slower. However, if the dissociation event occurs due to tunneling of one of the charges to a neighboring nanoparticle or a remote defect state, $\langle n_{\text{hop}}(\text{MOA}) \rangle$ could, in principle, be greater than $\langle n_{\text{hop}}(\text{MPA}) \rangle$. This scenario is possible when the rate of non-resonant charge tunneling to a different nanocrystal drops faster with an increasing interparticle gap than the rate of resonant energy transfer between neighboring dots. Consequently, the observed increase in the number of interparticle hops upon MPA→MOA ligand exchange provides additional evidence supporting the charge tunneling mechanism of exciton dissociation.

The PbS-to-PbS energy transfer rate for MOA-linked solids was found to be $1/0.44 = 2.3$ ns$^{-1}$ (see Table 3.1), approximately an order of magnitude slower than in the case of short-chain MPA ligands. Notably, the 0.089 → 0.44 ns increase in the hopping time was caused by the 4.0 → 4.8 nm enhancement in the center-to-center interparticle distance. If we assume a power dependence of the ET rate on the donor-acceptor distance $\sim (l_{\text{hop}})^\alpha$, then the best fit is obtained for $\alpha = 8.7$. Given a large uncertainty associated with only two data points ($R_{\text{MPA}}$ and $R_{\text{MOA}}$), it is difficult to tell whether the observed scaling deviates from the $\alpha = 6$ Förster power dependence. However, it should be noted that a possibility of such non-Förster $R$-dependence of the energy transfer in nanocrystal assemblies has been acknowledged in a number of recent reports.36,60
Table 3.1. The summary of exciton transport characteristics for PbS-only nanocrystal solids obtained using the developed forced dissociation approach.

<table>
<thead>
<tr>
<th>Type of PbS NC</th>
<th>$p_{\text{diss}(1 \ \text{hop})}$</th>
<th>$&lt;n_{\text{hop}&gt;}$</th>
<th>$l_{\text{exc. diff.}}$</th>
<th>$\tau_{\text{FL,fast}}$</th>
<th>$\tau_{\text{ET}}$</th>
<th>$\mu_{\text{exc. diff.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td></td>
<td></td>
<td>$(nm)$</td>
<td>$(ns)$</td>
<td>$(ns)$</td>
<td>$(cm^2/s)$</td>
</tr>
<tr>
<td>MPA-linked</td>
<td>0.09</td>
<td>12</td>
<td>5.7</td>
<td>1.1</td>
<td>0.089</td>
<td>0.012</td>
</tr>
<tr>
<td>($R_{\text{edge}} = 0.9 \ \text{nm}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOA-linked</td>
<td>0.03</td>
<td>34</td>
<td>11.4</td>
<td>15.1</td>
<td>0.44</td>
<td>0.003</td>
</tr>
<tr>
<td>($R_{\text{edge}} = 1.7 \ \text{nm}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To further explore the nature of exciton dissociation processes the time resolved data was complemented with the analysis of the steady-state emission in Au-doped films. Due to the diffusion of excitons towards the potential minima, the emission of solid-bound nanocrystals is typically red-shifted relative to the corresponding maximum in solution. By adding Au NPs to the solid, we can controllably lower the diffusion volume of excitons, which should cause the magnitude of the emission red-shift to diminish. This strategy can therefore be used to map the average distribution of excitonic traps – large-diameter PbS NCs that funnel the exciton energy. Notably, the comparison of the emission changes between PbS-only and Au-doped solids provides a more accurate description of energy funneling process than the one obtained through the comparison of emission maxima between nanoparticles in solution and solid forms, since the effect solvent charging and wave function delocalization are excluded.
Figure 3.7 shows the steady-state emission of PbS-only (red) and two mixed (PbS, Au) films cross-linked with MPA ligands. The emission maxima of Au-doped solids are blue-shifted relative to the FL peak of PbS-only films, as expected due to the restricted volume of the exciton diffusion in the former case. The maximum magnitude of the spectral shift is obtained at high levels of Au doping ($R_{\text{Au-Au}} = 14.6$ nm; exciton mean free path, $l_{\text{free travel}} = 6.8$ nm) and equals to $\Delta \lambda = 4$ nm (5.5 meV). Considering that nanocrystals are electrically coupled if the energy disorder in the film is lower than $\Delta E << 2\sqrt{2}\Delta kT \approx 30$ meV, we conclude that the motion of excitons in the investigated PbS NC film is rather random at room temperature. Consequently, quantum funneling is not likely to be prevalent in MPA–linked PbS films featuring a small dispersion of nanoparticle diameters. The lack of a significant energy gradient in PbS NC solids is consistent with the proposed charge-tunneling mechanism of the exciton dissociation. This process is independent of the energy disorder and can lead to the dissociation of excitons even in a solid of identical nanocrystals. Consequently, we can assume that the exciton dissociation probability is the probability of charge tunneling (ionization), as was suggested by the work of Guyot-Sionnest. That is $p_{\text{diss}}(\text{MPA}) = 0.08$ is the probability of electron tunneling per single interparticle hop.
Figure 3.7. (a). The steady-state emission of PbS NC solids doped with Au nanoparticles. The blue shift of the emission is attributed to the forced dissociated in Au-doped films, which shortens the diffusion length whereby preventing excitons from reaching the local potential minima in the film. (b). The excitation power dependence of the FL intensity decay in PbS-only
NC solids. The slow decay component appears to be strongly affected by the excitation intensity, which is consistent with the proposed free-carrier origin of this decay channel.

While the fast component of the FL intensity decay reflects the rate of exciton dissociation processes, the slow exponent has been tentatively attributed to the recombination of free carriers in a nanocrystal solid.\textsuperscript{44} If this assignment is correct, the slow decay component will be shortened as a result of Au doping since metal nanoparticles are likely to absorb the excited charges. From the broader prospective, we expect the decay of photoinduced carriers in Au-doped films to be determined by the two competing processes: radiative recombination, which depends on the concentration of free carriers in a solid, and trapping of charges, which is determined by Au-doping. The contribution of the former process is clearly seen in the comparison of the PbS-only and Au-doped films in Fig. 6a. The slow component of the FL decay decreases from 150 ns to 32 ns upon the addition of Au NPs (\(R_{\text{Au-Au}} = 24.3\) nm), which reflects an efficient consumption of free carriers by Au NPs. Using a previously developed model,\textsuperscript{44} we estimate the average diffusion length of free carriers in terms of the slow and the fast components of the FL intensity decay: \(l_{\text{diff}}^{\text{free carrier}} = l_{\text{step}} \times \sqrt{\tau_{\text{FL,slow}}/6\tau_{\text{FL,fast}}}\). In the case of MPA-linked PbS solids (Fig. 7b, green curve), the value of \(l_{\text{diff}}^{\text{free carrier}}\) is 5.3 nm. Notably, the average mean free path of free carriers in MPA-linked films estimated from the Au-Au interparticle distance, \(l_{\text{free travel}}\), (which in the absence of the electric field will be the same as for neutral excitons) is \(\approx 7\) nm. This value is in a good agreement with the extracted \(l_{\text{diff}}^{\text{free carrier}}\) of 5.3 nm, considering that the former figure is likely to be revised lower when the contribution of intrinsic (non-Au) traps is included. The observed reduction of the \(\tau_{\text{slow}}\) lifetime in Au-doped solids provides additional evidence in support of the proposed free-carrier origin of the slow decay
component in PbS NC solids. This assignment is further confirmed by the excitation power dependence of the $1/\tau_{\text{slow}}$ rate in undoped PbS NC solids. According to Fig. 3.7b, the rise in the excitation power leads to the increase in the rate of the slow decay component while the fast component remains nearly the same. The dependence of $\tau_{\text{slow}}$ on the excitation intensity is consistent with the free-carrier mechanism of the FL decay since the recombination rate of free carriers is strongly dependent on their concentration in a solid.

3.5 Conclusions

In conclusion, a spectroscopic approach for mapping the ultrafast dynamics of excitons in nanocrystal solids with a sub-diffraction spatial resolution has been demonstrated. By introducing Au nanoparticles into nanocrystal films the motion of excitons was restricted to a well-defined volume. The exciton diffusion beyond this volume resulted in quenching of the fluorescence and was detected as a change in the emission lifetime. Here, this strategy was employed for studying the exciton dynamics in two types of PbS nanocrystal solids featuring both strong (MPA-linked) and weak (MOA-linked) interparticle coupling. These measurements allowed determining a number of important transport characteristics including the exciton diffusion length, the rate of energy transfer between neighboring PbS dots, the number of interparticle hops performed by excitons prior to the dissociation and the ensuing exciton diffusivity. In the case of MPA-linked solids excitons were found to diffuse to an average length of 5.7 nm in approximately 12 hops, which corresponded to the diffusivity of 0.012 cm$^2$s$^{-1}$. Meanwhile, MOA-linked solids gave rise to a longer diffusion length of 11.4 nm (34 hops) and a lower diffusivity of 0.003 cm$^2$s$^{-1}$. The observed difference in the dynamics of the two film types was consistent with the proposed charge-tunneling mechanism of the exciton dissociation. The
developed experimental strategy was also extended for imaging the diffusion of free carriers that emerge as a result of exciton diffusion. It is expected that the demonstrated imaging strategy will avail the rational design of nanocrystals devices, where interface-limited diffusion of excitons is critical to the performance. These include nanocrystals solar cells, light-emitting diodes, and photodetectors.

3.6 Supporting Information

Figure 3.8. Illustration of the strategy for determining the effective radius of a Au nanoparticle that promotes exciton quenching, \( R_{eff}^{Au} \). The drop in the emission intensity of a (Au, PbS) solid is
proportional to the fraction of “quenched” PbS NCs, which lie within the $R_{\text{Au}}^{\text{eff}}$ distance of the Au nanoparticle.

**Diffusion length** is related to the exciton lifetime, $\tau$, according to the following expression:

$$l_{\text{diffusion}} = \sqrt{D \tau}$$

where $D$ is the diffusion coefficient. A Wiener formula for random walk diffusion in three dimensions is given by

$$D = \frac{d^2}{6 \tau_{\text{step}}}$$

where $d$ is the length of a single hop (interparticle distance) and $\tau_{\text{step}}$ is the time elapsed between two successive steps. Consequently,

$$l_{\text{diffusion}} = \sqrt{D \tau} = d \times \sqrt{\frac{n_{\text{hop}} \tau_{\text{step}}}{6 \tau_{\text{step}}}} = d \times \sqrt{\frac{n_{\text{hop}}}{6}} .$$

**Volume fraction calculations.** We first assume simple cubic packing of Au and PbS spheres. Suppose that on average a unit length of the mixed (Au, PbS) nanoparticle film contains $N_{\text{PbS}}$ and $N_{\text{Au}}$ nanocrystals. A unit volume of such film be given by

$$V = (N_{\text{PbS}} D_{\text{PbS}} + N_{\text{Au}} D_{\text{Au}})^3 ,$$

where $D_{\text{PbS}}$ and $D_{\text{Au}}$ are the average diameters of PbS and Au NCs, respectively. The Au-Au nearest neighbor distance in such film will then be given by:

$$R_{\text{Au-Au}} = \sqrt[3]{V / N_{\text{Au}}} = \frac{N_{\text{PbS}} D_{\text{PbS}} + N_{\text{Au}} D_{\text{Au}}}{N_{\text{Au}}} = n D_{\text{PbS}} + D_{\text{Au}} ,$$

where $n = N_{\text{PbS}} / N_{\text{Au}}$. 
n = \frac{N_{\text{PbS}}}{N_{\text{Au}}} is estimated along a one-dimensional projection (unit length). It is related to a volumetric nanoparticle ratio (which is typically sampled by TEM measurements where a colloidal drop is being projected onto a 2D grid) as: 
\[ n_{\text{TEM}} = \left( \frac{N_{\text{PbS}}}{N_{\text{Au}}} \right)^3 = n^3, \]
consequently:
\[ R_{\text{Au-Au}} = 3\sqrt[3]{n_{\text{TEM}} D_{\text{PbS}}} + D_{\text{Au}}, \]
where \( n_{\text{TEM}} = \frac{N_{\text{PbS}}}{N_{\text{Au}}} \) is the ratio of PbS to Au nanoparticles on the TEM grid.

The volume fraction of Au NPs is given by:
\[ V_{\text{Au}} = \frac{N_{\text{Au}}^3 \times \frac{4}{3} \pi R_{\text{Au}}^3}{V} = \frac{N_{\text{Au}}^3 \times \frac{4}{3} \pi R_{\text{Au}}^3}{(N_p D_{p/c} + N_c D_c)^3} = \frac{4/3 \pi R_{\text{Au}}^3}{(n D_{\text{PbS}} + D_{\text{Au}})^3} = \frac{4/3 \pi R_{\text{Au}}^3}{(\sqrt[3]{n_{\text{TEM}} D_{\text{PbS}}} + D_{\text{Au}})^3} \]
where \( R_{\text{Au}} \) is the average radius of the Au core domain (without the CdS shell).

If nanoparticles are packed more densely, the volume fraction will be higher. For instance, for face centered cubic (fcc), the volume fraction will be increased by:
\[ \frac{\pi}{3\sqrt{2}} \approx 0.74 \]
\[ \frac{\pi}{6} \approx 0.52 \]

\[ V_{\text{Au}}^{\text{fcc}} = \frac{4\sqrt{2}/3 \pi R_{\text{Au}}^3}{(\sqrt[3]{n_{\text{TEM}} D_{\text{PbS}}} + D_{\text{Au}})^3} \]
and
\[ R_{\text{Au-Au}}^{\text{fcc}} = \left( \sqrt[3]{n_{\text{TEM}} D_{\text{PbS}}} + D_{\text{Au}} \right) / \left( \sqrt{2} \right)^{1/3} \approx 0.89 \times R_{\text{Au-Au}}^{\text{simple cubic}} \]

Determination of the exciton scatter-free length in a Au-doped PbS NC solid
Figure 3.9. Illustration of the strategy for determining the effective mean free path of excitons in a Au-doped nanocrystal solid, \( r_{\text{eff}}^{\text{Au}} \). If we assume that a single photon is absorbed by a PbS NC in a film, the average scatter free diffusion of the resulting exciton can vary from 0 to about \( R_{\text{Au-Au}}/2 \) (minus the diameter of a Au NP) depending on the exact location of the absorbing PbS NC. The statistically averaged distance from the absorbing PbS NC to the closest Au nanoparticle is defined as the **scatter free distance**, for which half of PbS NCs are located closer and the other half further away from a Au NP (volumes \( V_2 \) and \( V_3 \), respectively). In other words, the total volume of a \( V_2 \) sphere (excluding the effective volume of a Au nanoparticle) should be equal to the interstitial volume (\( V_3 \)). Given the large number of nanoparticles in the film, the statistical error of estimating \( l \) scatter-free using the proposed strategy is small.

\[
V_2 \text{ (excluding } V_1) = V_3 \text{ (excluding } V_1 \text{ and } V_2) \\
\text{ (as explained in the Figure legend)}
\]

\[
\frac{4\pi}{3} (r^3_2 - r^3_1) = \frac{1}{2} R^3_{\text{Au-Au}}
\]

\[
l_{\text{free travel}} = r_2 - r_1 = \sqrt[3]{\frac{3}{8\pi} R^3_{\text{Au-Au}} + r^3_1 - r^3_1}
\]

\[
r_1 = R_{\text{eff}}^{\text{Au}} \approx 3.5 \text{ nm}
\]
### Table 3.2. Determining the exciton dissociation probability $p_{\text{diss}(1 \text{ hop})}$ in MPA-linked PbS NC solids from several independent measurements corresponding to different levels of Au doping.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>$&lt;p_{\text{diss}(1 \text{ hop})}&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{Au-Au (nm)}}$</td>
<td>12.3</td>
<td>14.6</td>
<td>17.7</td>
<td>20.7</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>$\Delta FL_{\text{exp}}$</td>
<td>0.32</td>
<td>0.51</td>
<td>0.76</td>
<td>0.83</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{diss}(1 \text{ hop})}$</td>
<td>0.085</td>
<td>0.097</td>
<td>0.098</td>
<td>0.091</td>
<td>0.078</td>
<td><strong>0.089±0.008</strong></td>
</tr>
</tbody>
</table>

### Table 3.3. Determining the exciton dissociation probability $p_{\text{diss}(1 \text{ hop})}$ in MOA-linked PbS NC solids from several independent measurements corresponding to different levels of Au doping.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>$&lt;p_{\text{diss}(1 \text{ hop})}&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{Au-Au (nm)}}$</td>
<td>17.5</td>
<td>24.9</td>
<td>30.1</td>
<td></td>
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<tr>
<td>$\Delta FL_{\text{exp}}$</td>
<td>0.25</td>
<td>0.44</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{diss}(1 \text{ hop})}$</td>
<td>0.035</td>
<td>0.03</td>
<td>0.029</td>
<td><strong>0.031±0.003</strong></td>
</tr>
</tbody>
</table>
3.7 References


(17) Chen, O.; Wei, H.; Maurice A.; Bawendi, M. G.; Reiss, P. MRS Bull. 2013, 38, 696-702.


