PHOTOCHEMICAL ENERGY CONVERSION IN METAL-SEMICONDUCTOR HYBRID NANOCRYSTALS

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A Dissertation

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My dissertation work focuses on several aspects in nanoscale materials for photocatalysis. Several nanostructured architectures were explored as detailed below.

The present work demonstrates a general strategy for coupling the near field (NF) radiation of surface plasmons to long-lived optical excitations in semiconductor nanocrystals (NCs) was investigated. A unique signature of the plasmon to exciton energy transfer was observed in photoexcitation measurements that unambiguously correlate the increase in the CdSe exciton population with the excitation of plasmon modes in Au domains. That scheme for harvesting the NF radiation of metal nanoparticles presents an excellent opportunity for extracting the evanescent emission of surface plasmons.

Furthermore, an experimental strategy was developed for monitoring the time-dependent monomer concentration during the hot-injection synthesis of Ag nanocrystals. The present approach employs Au nanoparticles as chemical probes of the Ag monomer build-up in the reaction flask. The precipitation of Ag on the surface of Au nanoparticles is diffusion–limited and results in a blue-shift of the plasmon resonance which is used to gauge the Ag monomer concentration, [Ag⁰]. In particular, it was shown that the nucleation rate is independent of the reaction temperature but is highly sensitive to the concentration of free ligands in solution.

Eventually, a general strategy for the synthesis of colloidal semiconductor nanocrystals (NCs) exhibiting the size dispersion below 5% was demonstrated. That approach relies on the sequential deposition of fully saturated cationic and anionic monolayers onto small-diameter clusters, which leads to focusing of nanocrystal sizes with the increasing particle diameter. The
present synthesis is amenable to different types of semiconductor nanocrystals and can potentially offer a viable alternative to traditional hot-injection strategies of the nanoparticle growth.
I dedicate this thesis to my family, my Mom, my Grandfather and my Grandmother, who helped me become who I am, for their endless love and support.

Dreams always come true.
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My dissertation work would not have been possible without the help of so many people. First of all, I would like to express my deepest appreciation to my advisor, Dr. Mikhail Zamkov, who has the attitude and substance of a genius: he guided me during all four years conveying adventure spirit in regard to research and teaching. Without his support and encouragement this dissertation would not have been possible.

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Finally, I would like to thank people that were working with me during my stay in BGSU especially our group members, for their experience, friendship and support.
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CHAPTER I

EXCITON GENERATION IN SEMICONDUCTOR NANOCRYSTALS VIA THE NEAR-FIELD PLASMON ENERGY TRANSFER.¹

1.1 ABSTRACT

The plasmon resonance of small-diameter metal nanoparticles has an exclusive decay character, as it produces almost no far field scattering. Instead, most of the absorbed light is emitted in the near field (NF), phenomenon also known as strong field localization. Such non-radiative emission is short lived and decays primarily via the production of heat, which prevents efficient harvesting of the NF energy. Here, a general strategy was demonstrated for coupling the NF radiation of surface plasmons to long-lived optical excitations in semiconductor nanocrystals (NCs). This concept was manifested through the observation of an enhanced exciton generation in CdSe NCs coupled to 5-nm Au nanoparticles. To distinguish the plasmon antenna effect from photoinduced charge transfer processes, both Au and CdSe nanoparticles were encapsulated into insulating CdS or ZnS matrices. A unique signature of the plasmon to exciton energy transfer was observed in photoexcitation measurements that clearly correlate the increase in the CdSe exciton population with the excitation of plasmon modes in Au domains. The demonstrated scheme for harvesting the NF radiation of metal nanoparticles presents an excellent opportunity for extracting the evanescent emission of surface plasmons that can find practical applications in photovoltaic or photocatalytic technologies.

1.2 INTRODUCTION

The surface plasmon (SP) resonance of metal nanoparticles (NPs) gives rise to exceptional optoelectronic properties that make easier an advanced control of optical energy on the
nanoscale. Among those, enhanced optical absorbance resulting from high density of SP modes in noble metals is of particular interest. Due to the spatial confinement of free carriers in the conduction band, the extinction coefficients of plasmonic NPs comprised of Au and Ag metals become particularly large, surpassing those of semiconductor nanocrystals (NCs) and molecular dyes by several orders of magnitude. This presents an outstanding opportunity for utilizing the energy of plasmonic NPs in light-harvesting applications through photocatalytic or photovoltaic conversion processes.  

The confining geometry of metal NPs plays an important role in the ensuing mechanism of the plasmon energy conversion. According to Mie theory, far-field scattering of light is common in large-diameter NPs (d > 50 nm), which absorb only a small fraction of incident radiation. With diminishing NP size, absorbance of light increases while scattering becomes suppressed. This situation is illustrated in Fig. 1.1a, showing that the ratio of scattering to absorption cross section in spherical Au NPs approaches zero when the particle size falls below 15 nm. Due to the enhanced light scattering in large metal NPs, many plasmonic materials have been developed using large-diameter colloids (d = 100-150 nm) or lithographically patterned substrates with an average feature size exceeding 100 nm. Meanwhile, small-diameter plasmonic NPs represent a particularly promising venue, as these colloids produce strongly confined electromagnetic field (near-field) associated with a particularly high density of states. Such sub-wave confinement of light offers an advanced control over the absorbed energy. For instance, recent works have shown that the classical limit of absorbance enhancement in photovoltaic films can be enhanced 15-fold if a near-field scattering strategy is employed. In particular, it was predicted that when the incident radiation is confined to a
localization length of 5 nm, the enhancement of the absorbance in a film can be extended from $4n^2$ (far-field scattering limit)\textsuperscript{21} to $60n^2$,\textsuperscript{18} where $n$ is the refraction index of the absorber.

Even with the predicted benefits of NF radiation in photovoltaic devices, the conversion of such strongly localized field into useful energy is quite challenging, as it efficiently couples to phonon modes.\textsuperscript{16} This is caused by a fast decoherence of plasma oscillations that dephase in less than 50 fs\textsuperscript{22,23} giving rise to a hot carrier population. The latter decays through the excitation of phonon modes within 1-5 ps.\textsuperscript{24-26} If the plasmon energy or hot carrier population are not transferred away from the metal NP within this short time window, the absorbed radiation will be internalized primarily through the generation of heat. One potential solution for harvesting the NF energy is to rely on hot carriers that fall into the semiconductor phase over the Schottky barrier.\textsuperscript{27-32} However, to take the full advantage of the sub-wave light trapping scheme, the plasmon energy has to be picked up prior to its dephasing, preferably through the near-field energy exchange. This process can occur \textit{via} the transfer of photons rather than electrons, as long as the separation between surfaces is much larger than the electron de-Broglie wavelength.\textsuperscript{33} To date, only a few experimental works have observed the signature of such a near-field energy transfer (ET).\textsuperscript{17,34,35} For instance, a recent study by Forrest, et al.\textsuperscript{17} has demonstrated an energy transfer between an organic polymer and ultrasmall Ag NCs mediated \textit{via} near-field radiation. It was shown that optical field intensity in the vicinity of a chain of metallic nanoclusters ($d=2.5$ nm) can be increased by up to a factor of 100 when compared with the incident light intensity. This enhancement covered a wide spectral range and extended to distances of up to 10 nm. Similar enhancement was observed by other studies utilizing small-diameter Au or Ag NPs.\textsuperscript{36,37}

In that project it was demonstrated that the near-field (evanescent) radiation of surface plasmons in Au nanoparticles can be harnessed through the energy transfer to semiconductor
nanocrystals. A combination of the photoexcitation and fluorescence (FL) lifetime spectroscopy was employed to confirm that the exciton production in CdSe NCs was strongly excitation correlated with the plasmon in nearby Au NPs. These results indicate that, in the absence of both far-field scattering and the field-enhanced stimulated emission, small-size metal NPs (diameter < 15 nm) can yet efficiently transfer the excitation energy through near-field coupling to absorbing transitions in semiconductor NCs. To enhance the population of excitons induced by the antenna emission of Au NPs, two important design features were introduced. First, the band gap of the semiconductor domain was tuned to fall below the resonant energy of plasmon modes in order to suppress the backwards energy transfer from CdSe into Au (Fig. 1.2a). Detuning the donor-acceptor energies has also allowed reducing the rate of stimulated emission from CdSe in the presence of the plasmon EM field. Second of all, both Au and CdSe domains were encapsulated within insulating matrices to suppress the processes of the interparticle charge transfer. This strategy allowed positioning CdSe NCs in the vicinity of Au NPs, where the incident radiation is enhanced by up to 3 orders of magnitude.\textsuperscript{38,39} Notably, owing to its wide band gap, the same matrix medium has shielded CdSe excitons from defect states on metal surfaces. As a result, the lifetime of photoinduced electron-hole pairs in CdSe NCs has reached a nanosecond range, thus making these structures potentially suitable for photocatalytic or photovoltaic applications.
Figure 1.1. (a). The ratio of scattering to absorbance cross section in Au NPs versus the NP size. The curve is extrapolated from the numerical data derived from Mie theory and the discrete dipole approximation method in Ref. 13 (b). An illustration of the energy harvesting scheme utilizing Au plasmon absorption. Before their thermal dissipation, the short-lived excitations of metal NPs can be harvested through energy or electron transfer to a semiconductor NC.

1.3 RESULTS AND DISCUSSION

To explore the energy transfer processes, both Au and CdSe NCs were stripped of surface ligands and incorporated into inorganic matrices using a Semiconductor-Matrix-Encapsulated-Nanocrystal Array (SMENA) approach.\textsuperscript{40,41} By using this strategy, ligand-free metal and semiconductor domains can be placed within small distances of each other to promote the enhanced energy transfer rate. Notably, both types of nanoparticles remain electrically “insulated” due to the wide gap of the interstitial matrix (either CdS or ZnS). A detailed strategy for encapsulating Au and CdSe NPs into semiconductor matrices is described in the experimental section. Briefly, both Au and CdSe NPs are coated with a shell of the matrix material, according to the scheme in Fig. 1.3d. The resulting Au/CdS (Au/ZnS) and CdSe/CdS core/shell NPs capped
with oleylamine and ODPA ligands, respectively, are then mixed in hexane and used as “inks” for film processing (Fig. 1.3d). Figure 1.3 shows characteristic TEM images of the CdSe/CdS (a) and Au/CdS (b) core/shell nanostructures that were used as precursors in the film assembly process, while TEM images of ZnS-coated Au NPs are shown in Fig. 1.SF2. The deposition of the CdS layer onto CdSe NCs was accomplished using previously established methods and resulted in the formation of an oblong shell of up to 7 monolayers (ML) in thickness (Fig. 1.3a). Here, the number of CdS MLs was optimized to provide a sufficient energetic barrier to charge injection while enabling a considerable degree of exciton-plasmon coupling via dipole-dipole interaction, as discussed later in the text.

**Figure 1.2.** (a). An illustration of allowed and suppressed energy/charge transfer processes between Au and CdSe NPs when both species are encapsulated into CdS matrices. The matrix semiconductor creates a potential barrier to photoinduced charges in CdSe, which prevents their backward transfer into the Au domain. Likewise, the energy transfer from CdSe to Au is not
favorable. (b). The absorbance maximum of Au NPs is blue-shifted relative to the emission band of CdSe NCs, which facilitates the one-directional Au-to-CdSe ET. (c). The energy diagram showing the relative alignment of band edges between Au and CdSe NCs, as well as those of CdS and ZnS semiconductor matrices.

A shell of the matrix semiconductor (either CdS or ZnS) was grown onto Au NPs using a previously developed non-epitaxial deposition method,\textsuperscript{43} which was adapted\textsuperscript{44} to use non-aqueous reaction solvents. This methodology gave rise to low-stress interfaces between Au and CdS domains, therefore allowing for a uniform deposition of the CdS shell onto a lattice-mismatched core. According to Fig. 1.3b, growth of the CdS shell resulted in a homogeneous, non-segmented placement of the semiconductor material around the Au center which was consistent with a low lattice strain at the core/shell interface. As illustrated in Fig. 1.6d, the growth of the CdS or ZnS semiconductor shell was accompanied by a red-shift of the plasmon resonance from $\lambda_{\text{Au}} = 520$ nm to $\lambda_{\text{Au/CdS}} = 575$ nm ($\lambda_{\text{Au/ZnS}} \approx 570$ nm) due to changes in the surrounding dielectric constant. The presence of both Au and semiconductor domains in the core/shell structures was confirmed through the observation of characteristic Bragg peaks in XRD measurements (see Fig. 1.SF1a). Overall, the shapes of Au/CdS (Au/ZnS) NPs were fairly uniform featuring a standard size deviation of 8.1% and contained less than 2% of CdS (ZnS) small-diameter nanoparticle impurities.

The diameter of CdSe NCs was chosen to fall between 4.1 and 4.5 nm to guarantee that the exciton energy is slightly lower than the energy of SP electromagnetic modes (see Fig. 1.2b). Under these conditions, both carriers are expected to exist the CdSe phase (Fig. 1.2c) leading to the spatial confinement of excitons (type I carrier confinement). Additionally, the Au-to-CdSe energy transfer (ET) is expected to be downhill and favorable while the backward ET process
should be suppressed. According to Fig. 1.2b, this condition was clearly satisfied for isolated Au 
\( E_{\text{pl}} = 2.36 \text{ eV} \) and CdSe \( E_{\text{ex}} = 2.01 \text{ eV} \) nanoparticles. In the case of CdS- or ZnS-encapsulated 
Au NPs, the plasmon excitation energy was red-shifted to \( E_{\text{pl}} (\text{Au/CdS}) = 2.15 \text{ eV} \) and \( E_{\text{pl}} 
(\text{Au/ZnS}) = 2.2 \text{ eV} \) due to higher dielectric constants of the matrix semiconductors, which caused 
at least a partial overlap of plasmon and exciton energy bands. Under these conditions, 
fluorescence quenching in CdSe due to the energy transfer into metal\(^{45}\) was possible but 
expectedly weak. Lastly, the use of wide gap CdS or ZnS semiconductor matrices facilitated the 
suppression of the backward charge transfer into Au (Fig. 1.2c), whereby extending exciton 
lifetime.
Figure 1.3. (a). TEM images of ODPA-capped CdSe/CdS core/shell NCs used as soluble precursors for the development of (Au, CdSe) SMENA films. The insert scale bar is 1 nm. (b). TEM images of oleylamine-capped Au/CdS core/shell NPs. The insert scale bar is 1 nm. (c). A TEM image of mixed Au/CdS and CdSe/CdS core/shell NPs used for film deposition. (d). An illustration of the key steps involved in the development of SMENA films. These stages include colloidal synthesis of CdSe/CdS and Au/CdS core/shell NPs (step 1), the spin coating of nanoparticle films (step 2), the exchange of bulky ligands with thermally degradable MPA molecules, and (step 3) crystallographic fusion of core/shell NCs performed using a layer-by-
layer deposition. The pores of the resulting matrix are in-filled with additional CdS (step 4). (e). A SEM image of a (Au, CdSe) NP film.

The final step in the development of a mixed (Au, CdSe) nanoparticle film involved a low-temperature fusion of core/shell NCs into an inorganic solid. To this end, the original bulky ligands on NC surfaces were exchanged with thermally-degradable MPA molecules on each cycle of the layer-by-layer (LbL) deposition process. After every three cycles, the film was heated to approximately 140-150 °C to promote ligand desorption. The thermal removal of ligands was confirmed by FTIR. The presence of CdSe NCs in the film was clear through the characteristic band gap emission of fabricated solids at λ = 620 nm (Fig. 1.4b, red curve). Meanwhile, the trace of Au NPs in thermally treated films was manifested by the plasmon emission at λ = 600 nm (Fig. 1.4a), which resonance was somewhat redshifted from its colloidal value. A characteristic SEM image of the resulting NP film on a glass substrate is shown in Fig 1.3e.

The strength of exciton-plasmon coupling in a mixed (Au, CdSe) nanoparticle film depends on the distance between Au and CdSe domains, $R_{Au-CdSe}$. The minimal gap between the two materials is given by: $R_{Au-CdSe, min} = \Delta h_{Au} + \Delta h_{CdSe}$, where $\Delta h_{Au}$ and $\Delta h_{CdSe}$ correspond to the thickness of the shell in Au/CdS (Au/ZnS) and CdSe/CdS NPs, respectively. Beyond the nearest neighbor interaction, a given CdSe NC can also be coupled to non-adjacent Au spheres, with the total number of Au-CdSe coupled pairs being proportional to the volume fraction of Au/CdSe NPs. As a result, the average strength of the plasmon-exciton interaction across the film is ultimately determined by the ratio of Au/CdS (Au/ZnS) to CdSe/CdS NPs in initial precursor solutions. When the fraction of Au NPs is low, the plasmon-assisted exciton generation is
expected to be reduced due to a smaller percentage of CdSe dots being coupled to a SP radiative field. On the other hand, solids that feature a large fraction of Au NPs are expected to have an enhanced near-field exciton generation. Notably, the emission intensity in the latter case does not proportionally increase with the growing number of Au NPs since the lifetime of band gap excitations diminishes due to CdSe-to-Au charge and energy transfer.⁴⁶

**Figure 1.4.** (a). The absorption profile of a mixed (Au, CdSe) NC film on a substrate (green curve) (b). The absorption and emission spectra of colloidal CdSe/CdS NCs used as precursors for film deposition. The red curve shows the emission spectrum of CdSe NCs encapsulated in CdS matrices. The FL lifetime of CdSe NCs in solution is shown in the insert.
The strength of the plasmon-exciton interaction in a mixed (Au, CdSe) nanoparticle film is proportional to the average separation between Au and CdSe domains, $\overline{R_{Au-CdSe}}$. This distance was estimated from the fraction of Au NPs in a TEM image of a colloidal mixture, which was used for film processing. To this end, mixed solutions of Au/CdS and CdSe/CdS nanoparticle precursors were deposited onto a TEM grid whereby creating a two-dimensional snapshot of the nanoparticle distribution. The ratio of each NP type (Au/CdS core/shell NPs versus CdSe/CdS NCs) was obtained by identifying the corresponding populations of each dot in the TEM specimen. Au/CdS (Au/ZnS) core/shell NPs were distinguished from all-semiconductor NCs by their darker shading and larger radii, as evidenced by characteristic TEM images in Figs. 1.3c and 1.SF2. Since the concentrations of each colloid were known prior to TEM sampling, the number density of each NC type in a film could be accurately estimated. The ratio of Au to CdSe dots was then used to determine the volume fraction of Au nanoparticles in the film, $v_{Au}$, according to the following equation (see Supporting Information for details of calculation):

$$v_{Au} = \frac{V_{Au}}{V_{total}} = \frac{4}{3} \pi R_{Au}^3 \frac{1}{(D_{Au/CdS} + \sqrt{n_{TEM}D_{CdSe/CdS}})^3}$$

where $n_{TEM} = N_{CdSe}/N_{Au}$ is the ratio of semiconductor to metal NPs on a TEM grid, and $R_{Au}$ is the average radius of the Au core domain in Au/CdS core/shell NCs.

It was expected that the lifetime of excitons residing in CdSe domains is likely to be reduced due to the photoinduced charge transfer into Au NPs. In principle, nano-interfaces of Au and CdS domains should promote the formation of Schottky barriers that shield excited carriers from entering into metal. Unfortunately, the height of such barriers in nanoscale interfaces may be too shallow. Here, the suppression of the backward charge transfer from CdSe NCs into Au
domains was achieved by using wide gap CdS or mixed CdS/ZnS semiconductor matrices. As illustrated in Fig. 1.2c, a CdS matrix provides a sufficient potential barrier to photoinduced holes in CdSe but enables only a partial localization of electrons. In contrast, matrices of the wide gap ZnS semiconductor provide a desirable large potential barrier to both charge types but are more challenging to grow synthetically. Indeed, the deposition of the ZnS shell onto CdSe NCs creates epitaxial bonds, which causes significant interfacial strain (CdSe/ZnS mismatch ≈ 12%) resulting in a poor quality of the ZnS lattice. On the other hand, the growth of a ZnS shell onto Au is fairly straightforward, as the lattice mismatch between the core and shell domains of non-epitaxial Au/ZnS NPs does not affect the quality of the shell. Thus, to fabricate better–insulating ZnS matrices, ZnS shells were grown only onto Au NPs, while the shell material on the surface of CdSe NCs was always CdS. For such solids, CdSe/CdS and Au/ZnS NP precursors were combined to form a mixed CdS/ZnS interstitial phase.

As mentioned above, the scattering-to-absorption ratio in small-diameter gold NPs (< 15 nm) is close to zero (see Fig. 1.1a), which implies that almost no far-field radiation is emitted from these nanostructures. As a result, the near-field enhancement becomes the primary mechanism of the virtual photon-mediated energy transfer from Au to CdSe domains. To understand whether ultrafast dephasing of Au plasmons was accompanied by the concurrent generation of excitons in CdSe NCs, a set of photoexcitation experiments was performed. It was designed to distinguish the ET contribution to the CdSe emission. To this end, the excitation wavelength selected from the Xenon lamp was varied in the 450-615 nm range, covering both off- and on-resonance plasmon excitation regimes. Meanwhile, the emission detector was set at the peak of the CdSe band gap fluorescence (see the insert in Fig. 1.5). The key advantage of this approach over a
more common strategy based on FL intensity enhancement lies in the spectral correlation of the
increased FL signal with the onset of the plasmon excitation.
Figure 1.5. (a). The photoexcitation spectra of CdS-encapsulated CdSe films (black) and CdS-encapsulated (Au:CdSe = 1:4, vAu = 2%) films (red), showing the contribution of plasmon excitation into the emission of CdSe NCs. The FL signal was measured at λ = 620 nm. (b). The
fluorescence enhancement factor (red curve) calculated by dividing the normalized photoexcitation spectrum of a mixed matrix (Au, CdSe) by that of a CdSe-only film. The plasmon absorption profile of a mixed (Au, CdSe) film is shown for comparison (green curve).

Figure 1.5 shows a characteristic excitation spectrum of CdS-encapsulated CdSe NC films containing no Au ($R_{\text{CdSe-CdSe}}^\text{min} \approx 3.2$ nm, red curve) and 2% of Au NPs by volume ($R_{\text{Au-CdSe}}^\text{min} \approx 3.1$ nm, black curve). The photoluminescence of both films was measured at the maximum of the CdSe band gap emission peak (see Fig. 1.4b), $\lambda \approx 620$ nm. The FL profile of the Au-doped film shows an enhancement relative to the no-Au solid when the excitation wavelength lie in the range of the plasmon resonance ($\lambda \approx 575$ nm), which strongly suggests that surface plasmon modes of Au NPs contribute to the emission of CdSe NCs. Based on the narrow-band profile of the (Au, CdSe) solid emission (see Fig. 1.SF3), it was established that the enhancement in the FL intensity arises from the increased population of CdSe band gap excitons. Also, present measurements (Fig. 1.5b) indicate only a relative increase in the exciton generation (as compared to no-Au films) and not the absolute FL enhancement. The emission of (Au, CdSe) solids was typically scaled by a factor ranging from 1.2 to 3.5, in order to match the emission of CdSe films in the off-resonance range ($\lambda \approx 460$ nm). The spectrally integrated emission of Au-doped films is, in fact, a factor of 1-2.5 lower than that of all-semiconductor films. This reduction is likely due to the fact that the enhanced exciton generation was outweighed by a substantial decrease in the exciton lifetime as a result of backward charge transfer (see Fig. 1.6) and, to a lesser degree, the effects of the backwards energy transfer and CdSe stimulated emission (radiative rate enhancement). That said, the observed relative enhancement provides a clear indication of the plasmon contribution into the exciton generation.
The relative emission enhancement in Fig. 1.5b reaches its maximum at $\lambda \approx 575$ nm, which matches with the maximum of the plasmon resonance for matrix-encapsulated Au NPs. The photoexcitation profiles of CdSe-only and mixed-(Au, CdSe) solids appear to be same when the excitation wavelength is on the high energy side of the plasmon resonance ($\lambda < 510$ nm), as can be inferred from the “plateau” interval in the FL enhancement spectrum for $450 \, \text{nm} < \lambda < 510$ nm (Fig. 1.5b). This indicates that high energy (hot) photoinduced carriers in gold do not contribute significantly to the exciton generation.
Figure 1.6. (a). The FL enhancement factors for several nanoparticle solids illustrating the dependence of plasmon-exciton coupling on the matrix morphology. The FL enhancement in CdSe NCs is recorded for three different conditions: a CdS-encapsulated (Au, CdSe) matrix with $R_{Au-CdSe}^{\text{min}} \approx 3.1\text{nm}$ (green curve), a CdS/ZnS-encapsulated (Au, CdSe) matrix with $R_{Au-CdSe}^{\text{min}} \approx 3.1\text{nm}$ (blue curve), and a CdS-encapsulated (Au, CdSe) matrix with $R_{Au-CdSe}^{\text{min}} \approx 1.8\text{nm}$ (red curve). (b). The photoexcitation spectra of CdSe/CdS NCs (blue curve) and a mixture of Au/CdS and CdSe/CdS
NCs (red curve). Their ratio, plotted in the insert, shows the FL enhancement due to far-field scattering of Au plasmons. (c). The dependence of the FL enhancement on the size of a Au domain. The enhancement factors are plotted for 5-nm and 36-nm Au NPs (both CdS-encapsulated), with the films featuring the same volume ratio of Au to CdSe. A TEM image of 36-nm Au NPs is shown in the insert. (d). The absorbance spectra of Au (black curve), Au/ZnS (red curve), and Au/CdS (black curve) NPs in a colloidal form.

To check whether there is any contribution from far field scattering of 5-nm Au NPs into the exciton production, Au and CdSe nanoparticles were mixed in solution. Figure 1.6b shows the two “colloidal-based” photoexcitation spectra corresponding to CdSe/CdS NC-only (blue curve) and a mixed Au/CdS and CdSe/CdS (1:4 by nanoparticle count, red curve) specimens. The ratio of the two, shown in the insert of Fig. 1.6b, reveals a small contribution of the plasmon resonance to the CdSe emission with the highest FL enhancement of less than 1.1. Therefore, the contribution of far-field scattering from 5-nm Au NPs to CdSe excitons is significantly less than that of near-field enhancement, shown in Fig. 1.5b.

The effect of Au-CdSe interparticle distance on the emission of (Au, CdSe) films can provide further insights into the nature of the exciton generation. It is well known that the efficiency of the non-radiative energy transfer is distance dependent and could be expressed within Dexter or Förster resonance energy transfer (FRET). Here, these expectations are found to be in general agreement with the photoexcitation measurements of the two films featuring different interparticle distances, $R_{\text{Au-CdSe}}^{\text{min}} \approx 3.1$ nm (green) and $R_{\text{Au-CdSe}}^{\text{min}} \approx 1.8$ nm (red), which correspond to Au-to-CdSe, center-to-center distances of 7.6 and 6.3 nm, respectively. According to Fig. 1.6a, the solids with a smaller Au-CdSe separation exhibited a greater relative enhancement factor.
The enhancement in the energy transfer rate for $R_{min}^{Au-CdSe} \approx 1.8$ falls short of FRET scaling, as can be expected due to non-dipolar contributions into local field of large-diameter nanoparticles and enhanced rates of backward charge transfer in films with smaller interparticle distances. Such backward flow of charges increases the rate of exciton dissociation, causing a complex R-dependence of the FL enhancement.

To further understand the character of the energy transfer processes between Au and CdSe domains, the photoexcitation spectra of ZnS/CdS- and CdS-encapsulated (Au, CdSe) matrices have been compared. The Au-CdSe interparticle separation was set even for both films, such that the changes in the observed excitation profiles (Fig. 1.6a) resulted primarily from the difference in the band gap value of the matrix material. According to Fig. 1.6a, both CdS- and ZnS/CdS-encapsulated films exhibited an enhancement of the band gap emission when the excitation wavelength fell within the spectral range of the plasmon resonance. The comparison of the two spectra reveals that the relative FL enhancement is nearly independent of the matrix medium, with a slightly brighter emission observed for ZnS/CdS-encapsulated NCs. This behavior is consistent with the energy transfer pathway of exciton generation, which is independent of the matrix band gap and is determined only by the interparticle separation. A slightly brighter emission from ZnS/CdS-encapsulated films could be attributed to the improved suppression of the backward transfer of CdSe electrons into gold, as expected due to a large potential barrier of ZnS (see Fig. 1.2c). In the case of CdS-only matrices, the backward charge transfer is likely to be faster due to the delocalization of negative charges in the conduction band.

The effect of a metal nanoparticle size on the FL intensity of CdSe nanocrystals provides further insights into the nature of the plasmon-exciton energy transfer. Recently, the Hupp group
reported a 20-fold enhancement of the CdSe emission placed in the near-field of 40-nm Ag NPs. Optimal ET conditions were achieved in that work by tuning the thickness of an Al$_2$O$_3$ spacer, which was placed between the metal surfaces and CdSe NCs. In the present work, ET optimization was not easily accessible since only 10-30% of CdSe NCs are coupled to Au NPs. However, to draw a relative comparison between a NP size and the ensuing FL enhancement, the effect of 36-nm Au NPs on CdSe NC emission has been explored. The concentrations of large- and small-diameter Au NPs in the film were normalized by matching the extinction coefficients of the precursor solutions (Au/CdS + CdSe/CdS) at the plasmon resonance. Since the extinction cross section of a metal NP grows as a complex function of its volume, it was estimated that the density of Au NPs in a solid with a fixed optical density scales as $R^\alpha$, where $3 < \alpha < 6$. The latter limit refers to the scattering-only portion of the extinction cross section. The comparison of the two films in Fig. 1.6c reveals a slightly larger plasmon-induced enhancement of the CdSe NC emission in the presence of 36-nm Au NPs. The observed difference is comparable to the experimental uncertainly, indicating that the enhancement factor of the two nanoparticle types (scaled by their extinction coefficient) is approximately the same. With similar enhancement factors, the benefit of employing small-diameter Au NPs lies in the superior confinement of light, which could lead to greater density of states.
Figure 1.7. FL intensity decay data, illustrating the effect of the external environment on the dissociation rate of CdSe excitons. The following scenarios are shown: CdSe/CdS colloidal NCs (black), CdS-encapsulated CdSe NCs (red), and CdS-encapsulated NPs with R\textsubscript{Au-CdSe} of 3.1 nm (green) and 1.8 nm (blue). The excitation wavelength was set at \( \lambda = 420 \) nm in all cases.

The spatial overlap of excited state wave functions between metal and semiconductor NPs leads to an increased rate of exciton dissociation and/or quenching. In the presence of Au, the dissociation of CdSe excitons can occur via a number of non-radiative channels, including the CdSe-to-Au charge transfer and carrier trapping on metal-semiconductor interfaces. The dynamics of these processes can often be inferred from the multi-exponential FL intensity decay of excitons in a nanocrystal solid, as described in Ref. 53. Here, the nature of exciton relaxation...
processes was investigated by exploring the effect of Au nano-domains on the rate of FL intensity decay in CdSe. Without Au co-precursor, CdSe/CdS solids exhibit a 4.1 ns FL lifetime which is substantially reduced from the corresponding lifetime value of CdSe/CdS NCs in solution (Fig. 1.7, red and black curves, respectively). The observed reduction reflects the onset of interparticle charge transfer processes (between neighboring CdSe NCs), which promote exciton dissociation. The addition of Au NPs \( (R_{\text{edge}} = 3.1 \text{ nm}) \) results in a further reduction of the FL lifetime from 4.1 ns to 1.1 ns, which can be attributed to either charge or energy transfer from CdSe into Au. The charge transfer process causes splitting of an exciton into a free electron-hole pair while the energy transfer from CdSe to Au leads to non-radiative quenching of an exciton. Since the plasmon energy exceeds the band gap value of CdSe, the charge transfer process appears to be the primary mechanism of FL quenching in this case. This assignment is corroborated by the decrease in the FL lifetime \( (1.1 \text{ ns} \rightarrow 0.75 \text{ ns}) \) upon further reduction of the Au-CdSe interparticle distance to 1.8 nm (blue curve), and is also consistent with the fact that the transfer of either charge type into Au (or semiconductor/metal interfacial traps) is energetically favorable (Fig. 1.2c).

In conclusion, it was demonstrated that the short-lived, antenna emission of Au nanoparticles (strong field localization) can be harvested via the production of excitons in CdSe semiconductor nanocrystals. This phenomenon was confirmed in photoexcitation experiments of mixed (Au, CdSe) nanoparticle solids that unambiguously correlate the increase in the CdSe exciton population with the excitation of plasmon modes in Au NPs. The observed near-field energy transfer from small-diameter metal nanoparticles can be utilized for converting the energy of strongly confined radiation (evanescent waves) into long-lived excitations, which is useful for photovoltaic or photocatalytic applications.
1.4 EXPERIMENTAL SECTION

1.4.1 Chemicals. Acetone (ACS, Amresco), cadmium (II) nitrate tetrahydrate (Cd(NO₃)₂:4H₂O, 99.999%, Aldrich), cadmium (II) oxide (CdO, 99.99%, Aldrich), chloroform (anhydrous, 95%, Aldrich), ethanol (anhydrous, 95%, Aldrich), gold (III) chloride (AuCl₃, 99% Acros Organics), n-hexylphosphonic acid (HPA, 98%, PCI Synthesis), 3-Mercaptopropanic acid (MPA, 95%, Aldrich), methanol (anhydrous, 99.8%, Aldrich), 1-octadecene (ODE, tech., 90%, Aldrich), n-octadecylphosphonic acid (ODPA, 98%, PCI Synthesis), oleic acid (OA, tech., 90%, Aldrich), silver (I) nitrate (AgNO₃, 99%, Sigma-Aldrich), sulfur (S, 99.999%, Acros), stearic acid (SA, 97%, Acros), selenium powder (200 mesh, Acros), tributylphosphine (TBP, 97%, Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), tri-n-octylphosphine oxide (TOPO, 99%, Aldrich), toluene (anhydrous, 99.8%, Aldrich), and zinc (II) acetate dihydrate ((CH₃COO)₂Zn·2H₂O, 98+%, Acros) were used as purchased. Oleylamine (tech., 70%, Aldrich) was degassed using vacuum pump for 1 hour at 120 ºC and then stored under argon atmosphere prior using. Fluorine-doped tin oxide (FTO) 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 5400 and 7200 rpm.

1.4.2 Synthesis of oleylamine-capped Au NCs. Au NCs were synthesized using a one-pot procedure developed in our previous work.⁵⁰ In a typical synthesis, 0.011 g of AuCl₃ and 5 mL of oleylamine were loaded in a one-neck flask and allowed to react at 100 ºC 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 ~4 mL of toluene. The cleaning cycle was repeated one more time and the final product was re-dispersed and stored in toluene. 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.

1.4.3 Synthesis of oleylamine-capped Au/Ag Core/Shell NCs. An Ag shell layer was grown using a procedure inspired by Ref. 51. 0.25 mL of a standard Au NP sample (synthesis described above) was placed in a 50 mL three-neck flask. This solution was placed under argon and 5.0 mL of oleylamine was injected into the flask. The temperature of the flask’s contents was raised to 120 °C. While the Au NP solution was being stirred vigorously, either 0.2 mL or 0.4 mL injections of 0.1 M aqueous AgNO3 (0.089 g in 5 mL water) were added dropwise to the reaction flask. After each injection, the NPs were left to grow a shell for 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 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 blueshifted 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 the desired blueshift was attained, the flask containing the Au/Ag nanoparticles was taken off of the heating mantle. After the contents of the reaction flask had cooled, the raw Au/Ag NP solution was distributed evenly between two centrifuge tubes and precipitated with ethanol. After centrifugation the solution was discarded and the precipitate was
re-dispersed in toluene. The purification process was repeated one more time. The final Au/Ag pellet was dissolved and stored in toluene.

1.4.4 Conversion of Au/Ag to Au/Ag\textsubscript{2}S core/shell NCs. The following methodology was first reported by Zhang et al.\textsuperscript{47} 0.005g of S\textsubscript{8} powder was dissolved by sonication in 2 mL of oleylamine and injected into a 25 mL two-neck flask containing the entire amount of Au/Ag solution fabricated in previous step. The reaction mixture was stirred at room temperature and every 10 min samples were taken for spectroscopic analysis. After the LPSR peak of Au/Ag\textsubscript{2}S NPs stopped redshifting, the solution was placed in centrifuge tubes and cleaned by the precipitation with EtOH, centrifugation and redispersion in toluene.

1.4.5 Conversion of Au/Ag\textsubscript{2}S to Au/CdS (Au/ZnS). The fabrication of the semiconductor shell was performed using cation exchange methodology.\textsuperscript{47} To this end, metal salt (Cd(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O or Zn(OAc)\textsubscript{2}·2H\textsubscript{2}O) was dissolved in 1 mL of methanol and injected into a two-neck flask containing the mixture of entire amount of Au/Ag\textsubscript{2}S in toluene and 1 mL of oleylamine at 60 °C under argon atmosphere. The amount of metal salt was calculated based on the amount of silver nitrate which was used in the second step. Typically, for the successful cation exchange we used 1.5 times more moles of the metal salt compared to AgNO\textsubscript{3}. The reaction solution was allowed to stir at elevated temperature for 10 minutes, and then 0.1 mL TBP was added to the mixture. Depending on the metal type, the reaction time of the cation exchange and the crystallization of the shell varied from 2 (for CdS) to 20 (for ZnS) hours. The growth of the shell was accompanied by the blue-shift of the LPSR peak. The contents of the flask were then cooled to room temperature. 10 mL of methanol was added to the reaction mixture, which was subsequently centrifuged. The precipitate was then dissolved and stored in hexane.
1.4.6 Synthesis of CdSe nanocrystals. CdSe NCs were grown using a previously reported technique.\textsuperscript{52} In a three-neck flask, stearic acid (0.67 g), ODE (7.1 mL), and CdO (0.078 g) were heated to 200 °C under argon atmosphere until the solution turns clear indicating the formation of cadmium stearate. Then the reaction mixture was allowed to cool to room temperature (RT) at which point 4.5g ODA and 1.5g TOPO were added. The flask was reheated to 280 °C under vigorous stirring and selenium solution, prepared under argon by dissolving 0.461 g of selenium powder via sonication in TBP (2 mL) and further diluting it with 5.2 mL of ODE, was quickly injected. The temperature was set at 250 °C and the reaction continued until the absorption peak was red-shifted to $\lambda \approx 600$ nm, at which point the reaction was quenched by removing the flask from the heating mantle. Once the flask’s contents had cooled to 60°C, chloroform (10 mL) was injected into the flask to prevent solidification. To remove the unreacted material the contents of the flask were centrifuged and the precipitate was discarded. Acetone (6 mL) was added to the supernatant, and the solution was centrifuged again. The final precipitate was stored in toluene (4 mL).

1.4.7 Synthesis of CdSe/CdS core/shell NCs. CdSe/CdS core/shell NCs were synthesized using a previously reported protocol.\textsuperscript{53,46} For this procedure an additional cleaning of TOP was required. To this end, 3 mL of the commercial TOP solution was injected into a three-neck flask under argon. The solution was then connected to the vacuum pump and degassed at 120 °C for 1 hour. A clean TOP solution was stored at RT under argon prior to the utilization. In a separate flask, a mixture of TOPO (3.00 g), ODPA (0.29 g), HPA (0.08 g), and CdO (0.06 g) was degassed under vacuum at 150°C for 1 hour, switched to argon and heated to 350 °C. At this point, 1mL of the pure TOP from the first flask was injected into the Cd precursor. In a third flask, a solution of the sulfur precursor was prepared by mixing 0.12 g of sulfur powder with 2
mL of purified TOP under argon atmosphere at 200 °C until sulfur was dissolved. The temperature of the solution was decreased to 120 °C and 1 mL of CdSe seed nanocrystals in toluene was injected into the S precursor. For concentration of CdSe refer to ref. 44. Excess toluene was removed from the TOPS/CdSe mixture by degasing the solution under vacuum for 10 min. The flask was then flushed with argon and the entire solution containing the sulfur precursor and CdSe seeds was injected into the solution of Cd precursor. The reaction mixture was kept at 350 °C for 4 to 7 min, depending of the desired CdS shell thickness. After reaction was stopped and cooled down to RT, 6 mL of chloroform was injected into the reaction flask. The nanocrystals were precipitated with ethanol and centrifuged. The red precipitate was separated from the supernatant and re-dispersed in hexane (3 mL).

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

1.4.9 Fabrication of NC films. The deposition of ligand-linked NC films was performed under argon atmosphere inside the glovebox using standard layer-by-layer techniques. All-inorganic NC films (SMENA) were fabricated according to a previously developed protocol. To deposit a layer of all-inorganic CdS-encapsulated NC film onto the FTO/glass substrate, 5-6 drops of the CdSe/CdS core/shell NC solution in hexane (concentration 10mg/mL) were placed onto the glass until the surface was covered and then the film was spun until dry at 3000 rpm for 10 seconds. To replace original ligands with thermally-degradable MPA molecules, 7-10 drops of MPA/Methanol solution (ratio1:4) were deposited on the center of the glass slide, soaked for 10 seconds and spun at 3000 rpm for 10 seconds. After the MPA treatment, the film was washed
by covering with 10 drops of methanol and spinning the slide for 10 seconds, followed by rinsing with octane in the same manner. Upon the deposition of 2 layers, the films were annealed at 140-150°C for 15 min. The total of 6-7 layers were deposited. To fabricate all-inorganic films containing Au/CdS or Au/ZnS NCs, the initial solution of CdSe/CdS NCs was mixed with the Au/CdS solution at various ratios.

1.4.10 Characterization: UV-vis absorption and photoluminescence spectra were recorded using a CARY 50 scan spectrophotometer and a 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. 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), and an id50 avalanche photodiode (Quantique).

1.4.11 Photoexcitation. Steady-state photoexcitation spectra were measured using a PTI QuantaMaster spectrophotometer with a Xenon lamp light source. Excitation scan was performed along CdSe and Au NPs absorption profiles in the range 450-615 nm with the detection on CdSe emission band at 620 nm. The spectra were collected at right angle for the liquid samples and at 45° for the solid films and integrated for 10 seconds per nanometers for better noise to signal ratio.
Figure 1. SF1: (a) X-ray diffraction spectra of Au/CdS core/shell nanocrystals. (b). High-resolution TEM image of a Au/CdS structure confirming the crystallinity of the shell domain.
1.5.1 Volume fraction calculations. Suppose that a unit length of the mixed nanocrystal film contains $N_{Au}$ of Au/CdS and $N_{CdSe}$ of CdSe/CdS core/shell nanocrystals. A unit volume of such film be given by $(N_{CdSe}D_{CdSe/CdS} + N_{Au}D_{Au/CdS})^3$, where $D_{CdSe/CdS}$ and $D_{Au/CdS}$ are the average diameters of CdSe/CdS and Au/CdS NCs, respectively. Therefore the volume fraction of Au in the film can be expressed as:
where \( n = \frac{N_{CdSe}}{N_{Au}} \) 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: \( n_{TEM} = \left( \frac{N_{PbS}}{N_{Au}} \right)^3 = n^3 \), consequently:

\[
\frac{V_{Au}}{V_{total}} = \frac{N_{Au}^3 \times \frac{4}{3} \pi R_{Au}^3}{\left( D_{Au/CdS} + n n_{TEM} D_{CdSe/CdS} \right)^3} = \frac{\frac{4}{3} \pi R_{Au}^3}{\left( D_{Au/CdS} + n D_{CdSe/CdS} \right)^3}
\]

**Figure SF3.** Emission profile of CdS-encapsulated mixed (Au, CdSe) NC films, featuring 2% of Au by volume.
1.6 REFERENCES

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CHAPTER II

MEASURING THE TIME-DEPENDENT MONOMER CONCENTRATION DURING THE HOT-INJECTION SYNTHESIS OF COLLOIDAL NANOCRYSTALS.¹

2.1 ABSTRACT

The shape of colloidal nanoparticles grown via hot-injection routes is largely determined by the reaction-limited rate of monomer nucleation. This offers an important synthetic benefit of tuning the morphology of colloidal nanocrystals simply by controlling the rate of monomer release during the thermal conversion of precursors. Unfortunately, the monomer concentration in colloidal reactions is difficult to track in situ, which obscures the actual effect of the temperature, monomer solubility, and the ligand density on the probability of nanoparticle nucleation. Here, an experimental strategy was developed for monitoring the time-dependent monomer concentration during the hot-injection synthesis of Ag nanocrystals. The present approach employs Au nanoparticles as chemical probes of the Ag monomer build-up in the reaction flask. The precipitation of Ag on the surface of Au nanoparticles is diffusion–limited and results in a blue-shift of the plasmon resonance which is used to gauge the Ag monomer concentration, [Ag⁰]. By measuring [Ag⁰] immediately before the nucleation burst, it was possible to elucidate the effect of several reaction parameters on the nucleation dynamics and the ultimate morphology of Ag nanocrystals. In particular, it was found that the nucleation rate is independent of the reaction temperature but is highly sensitive to the concentration of free ligands in solution.
2.2 INTRODUCTION

Colloidal synthesis of inorganic nanocrystals is a quickly growing area of materials science that holds strong promise for future technological applications.\textsuperscript{2-6} Our ability to control the evolution of nanoparticle shapes in colloidal reactions, however, is still evolving. The grand challenge lies in understanding the effect of reaction parameters, such as the precursor concentration, solvent temperature, and ligand chemistry on the processes of nanocrystal nucleation and growth.\textsuperscript{7-9} Recently, significant advances in modelling the hot-injection synthesis of inorganic nanocrystals have been achieved through clarifying the role of the precursor conversion in the product formation.\textsuperscript{10-15} In particular, it was shown that the thermal monomer release from precursor complexes establishes the primary reaction-limiting step and thus can be explored towards controlling the nanoparticle (NP) morphology. An improved understanding of the colloidal synthesis has allowed reconciling the classical nucleation theory with experimentally observed reaction kinetics\textsuperscript{11} and resulted in the development of new synthetic strategies that enable high nanoparticle yields and narrow size distributions.\textsuperscript{16}

The rate of monomer nucleation during the hot-injection synthesis of colloidal nanocrystals plays an important role in the growth of nanoparticle shapes. Particularly, the time-dependent monomer concentration, \([M_i(t)]\), is considered to be one of the key parameters which determine the path of the colloidal reaction.\textsuperscript{11} Unfortunately, the rate of monomer build-up during the colloidal growth is difficult to measure experimentally. As a result, the exact effect of the reaction parameters, such as the solvent temperature, monomer solubility/diffusion, the bulk monomer concentration, and the free ligand concentration on the process of nanoparticle nucleation, \(nM_1 \rightarrow M_n\), is still poorly understood.
Here, an experimental strategy was developed for monitoring the time-dependent monomer concentration during the hot-injection synthesis of Ag nanoparticles. These colloids were chosen as a model system for studying the nucleation dynamics due to the simplicity of a single-atom monomeric unit. The release of Ag\(^0\) monomers was performed in a controllable manner through the thermal decomposition of silver-oleylamine complexes \([(\text{R-CH}_2\text{-NH}_2)\text{Ag}]^{+}[\text{NO}_3]^-\) formed by dissolving silver salts (AgNO\(_3\)) in oleylamine. Tracking the monomer concentration in the bulk of the solution, [Ag\(^0\)], was then achieved by introducing a small amount of Au nanoparticles into the reaction flask prior to the addition of the silver precursor. The plasmon resonance of Au NPs is highly sensitive to the addition of Ag\(^0\) monomer and is used to measure the Ag monomer concentration. In particular, the precipitation of Ag\(^0\) on the surface of Au nanoparticles is a diffusion–limited reaction, which causes the plasmon resonance of 5-nm Au to gradually blue-shift towards the position of the Ag plasmon resonance (\(\lambda = 415\) nm) at an approximate rate of \(\Delta \lambda = 8.8\) nm per 1 angstrom of the deposited Ag shell (see the Supporting Information section, Fig. 2.SF1). By measuring the plasmon absorbance of isolated Ag nanocrystals (\(\lambda = 415\) nm) and the blue-shifted resonance of Au (\(\lambda = 490 - 525\) nm) simultaneously (see Fig. 2.1a), one can deduce the monomer concentration prior to the nucleation burst. Here, the spectral shift of the plasmon resonance was used to calculate the critical concentration of Ag\(^0\) needed for the silver nanoparticle nucleation, [\(M_{\text{critical}}\)]. By using plasmonic nanoparticles as chemical sensors of the reaction conditions, it was possible to elucidate the dynamics of nanoparticle nucleation during the synthesis. In particular, it was demonstrated that the reaction temperature does not influence the rate of nanocrystal nucleation affecting only the precursor conversion rate. On the other hand, both the nucleation rate and the nanoparticle morphology were found to be strongly dependent on the concentration of free ligand in solution.
2.3 RESULTS AND DISCUSSION

To model the nanocrystal growth, a widely accepted formalism was applied which assigns the rate limiting step to the precursor (P) conversion reaction: $11 \, P \rightarrow M_1$. The growth of nanocrystals can then be described as the addition or dissociation of monomers: $M_n + M_1 \leftrightarrow M_{n+1}$, where the monomer unit is defined as the smallest nanoparticle building block carrying a zero electrical charge. For example, in the case of CdSe semiconductor NCs, such monomer unit is formed via the initial cation-anion binding reaction followed by the cleavage: $^{10,17} \, \text{Cd(OOCR)}_2 + \text{SePR}_3 \leftrightarrow [\text{Cd(OOCR)(SePR}_3])^+\text{[OOCR]}^- \rightarrow \text{M}_1(\text{CdSe}) + \text{OPR}_3 + \text{O(OOCR)}_2$. The hot-injection growth of metal nanoparticles follows a similar scheme. Specifically, the colloidal synthesis of Ag NPs performed through the thermal dissolution of the Ag-oleylamine complexes involves the same precursor conversion steps: $\text{R-CH}_2\text{NH}_2 + \text{AgNO}_3 \leftrightarrow [(\text{R-CH}_2\text{NH}_2)\text{Ag}]^+\text{[NO}_3^- \rightarrow \text{Ag}^0 + \ldots \ldots$. Thus, both semiconductor nanocrystal and Ag nanoparticle nucleation kinetics are driven by similar reaction-limited processes of monomer assembly, which face the energy activation threshold. From the experimental standpoint, however, measuring the nucleation dynamics of metal nanoparticles is less challenging, as this reaction requires the conversion of only one precursor allowing for a more straightforward interpretation of the observed experimental data. Previous works $^{18-23}$ have shown that Ag-oleylamine complexes form immediately upon mixing of silver salt (AgNO$_3$) and oleylamine at room temperature, while the thermal conversion of the $[(\text{R-CH}_2\text{NH}_2)\text{Ag}]^+\text{[NO}_3^- \text{ precursor to a Ag}^0$ monomer occurs slowly at temperatures above $T = 70$ °C. The burst of silver NP nucleation is evident as the onset of the plasmon resonance at $\lambda = 415$ nm, which occurs in nuclei as small as $d = 1.5$ nm in diameter. $^{24}$ The subsequent growth of Ag nanoparticles beyond the critical radius is accompanied by a slight shift of the plasmon resonance towards longer wavelengths.
Figure 2.1. (a). Illustration of the basic strategy for monitoring the concentration of the Ag\textsuperscript{0} monomer during the hot-injection growth of Ag nanoparticles. By introducing a small amount of Au NPs into the growth mixture, one can observe the conversion of the Ag precursor (AgNO\textsubscript{3}) to monomer (Ag\textsuperscript{0}) via the blue-shift of the Au plasmon resonance, corresponding to the precipitation of Ag\textsuperscript{0} on Au surface. The rate of the Ag shell growth is then used to estimate the monomer flux in solution, $D \times [M_L] \times L$, where $D$ is the monomer diffusivity and $[M_L]$ is the monomer concentration. (b). The low concentration of Ag precursor inhibits the Ag NP nucleation, however, causes the Ag shell to grow on the surface of Au NPs, confirming the
diffusion-limited character of this reaction. (c-d). Transmission Electron Microscopy (TEM) images of a typical reaction product containing isolated Ag NPs and large-diameter Au/Ag core/shell dots. (e). High resolution TEM image of a Au/Ag core/shell nanoparticle showing a single-phase lattice structure.

To monitor the relative concentration of Ag\(^0\) monomer in the reaction mixture, a small amount of Au nanoparticles was added to the oleylamine solution of the AgNO\(_3\) precursor. In this case, the thermal conversion of AgNO\(_3\) to Ag\(^0\) was accompanied by the spectral shift of the Au plasmon absorption due to the precipitation of neutral silver on Au surfaces (see Fig. 2.1a). Previous works have shown that the plasmon resonance of Au/Ag core/shell system lies in between of those of isolated Au and Ag.\(^{25-27}\) Specifically, one recent study\(^{25}\) has demonstrated that the spectral position of the Au/Ag NP plasmon resonance is a simple function of the Au volume fraction, \(\nu_{Au}\): \(\lambda_{Au/Ag}^{\text{plasmon}} \approx \nu_{Au} \lambda_{Au}^{\text{plasmon}} + (1 - \nu_{Au}) \lambda_{Ag}^{\text{plasmon}}\). When the thickness of the Ag shell is relatively small, the resonant wavelength, \(\lambda_{Au/Ag}\) can be approximately expressed as a linear fit of the Ag shell thickness, \(\Delta r_{Ag}\): \(\lambda_{Au/Ag}^{\text{plasmon}}(nm) \approx \alpha \times \Delta r_{Au/Ag}(nm)\); \(\alpha = 88\). (see Ref. 24, and Fig. 2.SF1 in the Supporting Information (SI) section). Experimental evidence of both homogeneous and heterogeneous growth of Ag is provided by the characteristic TEM images of a reaction product in Figs. 2.1(c)-(e), which confirms the presence of both isolated Ag NPs and Au/Ag core/shell heterostructures. The two different morphologies are readily discrete by their sizes as well as the darker contrast of a heavier Au phase.

According to Fig. 2.SF1, the rate of Ag\(^0\) addition onto Au is quantifiable as a blue shift of the Au/Ag core/shell plasmon resonance. Particularly, the heterogeneous growth of a silver shell has a relatively low activation energy as lattices of Ag and Au fcc phases are nearly matched (strain
Therefore, it was expected that the Ag shell growth is diffusion-limited, such that Ag\(^0\) monomers start to attach to the surface of Au NPs as soon as the AgNO\(_3\) precursor conversion begins. To confirm this statement, Au nanoparticles were heated in the presence of the silver precursor at concentrations that were significantly below the Ag NP nucleation threshold. Expectedly, the growth of isolated Ag nanoparticles was not observed in this case (Fig. 2.1b). Nevertheless, the plasmon resonance of Au NPs has gradually blue-shifted with the increasing temperature indicating that the precipitation of Ag\(^0\) began simultaneously with the precursor conversion (see Fig. 2.1b). This tendency suggests that the energy activation barrier for the shell growth reaction is small. Further evidence of the “low-barrier” growth of the Ag shell is provided by the TEM images of core/shell heterostructures which confirm a uniform distribution of the Ag shell around the Au core (Figs. 2.1c-2.1e), consistent with a low lattice strain between the two phases.

An important question to be addressed by this study is whether the critical monomer concentration required for nanoparticle nucleation, \([M_{\text{critical}}]\), depends on such reaction variables as the solvent temperature and the concentration of free ligands in solution. To this end, a systematic approach was developed for extracting a relative concentration of Ag monomer in solution, \([M_1]\) from the spectral shift of the plasmon resonance in Au/Ag core/shell NPs. To simplify the analysis, it was assumed that prior to the nucleation of Ag NPs, the Ag\(^0\) monomer concentration in solution is sufficiently high to ensure that the growth of the Ag shell is much faster than its dissolution, \(|\Delta_{\text{diss}}|_{\text{Au/Ag}}| \ll |\Delta_{\text{growth}}|_{\text{Au/Ag}}|\). This assumption was confirmed experimentally (see Fig. 2.SF2) and is used here to introduce two important generalizations. First, the reduction in the Ag layer thickness on Au surfaces due to Ag\(^0\) dissolution back into
solvent can be neglected. Second, the monomer concentration in the bulk of the solution, \([M_1]\), and near the surface of the nanoparticles, \([M_r]\), are approximately the same, \([M_1] \approx [M_r]\). As a result, the rate of Au/Ag core/shell nanoparticle growth can be expressed as a linear function of the monomer concentration, \([M_1]\), (see the SI section, Eq. 2.SF4):

\[
\frac{dr}{dt} = D \times [M_1] \times L(r, C^0, \gamma)
\]

which takes into the account the diffusion of the monomer, \(D\), and the monomer concentration in solution, \([M_1]\). The constant \(L\) is a complex function of nanoparticle radius (r), surface tension (\(\gamma\)), and monomer solubility (\(C^0\)), as detailed in the Supporting information section (Eq. 2.SI4).

**Figure 2.2.** (a). Illustration of the experimental strategy for measuring the relative concentration of Ag\(^0\) monomer in solution. If the solvent temperature is kept constant, the pre-nucleation monomer concentration \([M_1]\) increases linearly with time (provided that \([M_1] \ll [P]\), see the SI section). The accumulative growth of the Ag shell on Au, \(\Delta r_{\text{Au/Ag}}\), can then be expressed proportionally to the area under the \([M_1(t)] = k[P]\) curve. (b). The ratio of the two
Δr_{Au/Ag} values corresponding to two different precursor concentration, [P_1] and [P_2] is independent of D and L parameters and is determined only by the nucleation time.

According to Eq. 2.1, the rate of the Au/Ag core/shell nanoparticle growth, dr_{Au/Ag}/dt, is proportional to the monomer concentration at any given moment during the reaction, [M_1(t)].

This approximation is derived using an assumption that rate of Au/Ag NP dissolution during the pre-nucleation reaction stage, t < t_{nucl}, is relatively small and can be neglected. Generally, the shell growth rate, dr_{Au/Ag}/dt, should be calculated from a characteristic blue-shift of the plasmon resonance, $\Delta \lambda_{\text{Au/Ag}}$, during a short time interval, dt: $\lambda_{\text{Au/Ag}}(t + \Delta t) - \lambda_{\text{Au/Ag}}(t)$. As a result, the time-dependent monomer concentration, [M_1(t)], can be obtained at any moment prior to the nucleation event provided that the absorption profile is continuously monitored during the reaction. Experimentally, however, measuring the instantaneous changes in the position of the plasmon resonance can be difficult. As an alternative, a simplified formalism has been developed that allows estimating the relative monomer concentrations [M_1(t)] from the overall shift of the Au/Ag plasmon resonance. This approach is illustrated in Fig. 2.2. Prior to the nucleation of Ag NPs, the monomer concentration [M_1] in solution is steadily growing due to the thermal conversion of the precursor (AgNO_3 → Ag^0). If the solvent temperature is preserved at the same value, the precursor decomposition can be assumed to proceed at a constant rate, k: d[P] = - k[P]dt. In this case, the monomer concentration is expressed as: [M_1] = [P](1 - e^{-kT})^t, or simply \[M_1\]_{t, ccP} = [P]kt during the initial stages of the reaction (see the SI section for details). Over the total reaction time, the accumulative growth of the Ag shell, Δr_{Au/Ag} will be determined by the total flux of Ag^0 monomer to the Au surface which is proportional to the area under the [M_1(t)] curve, as illustrated in Fig. 2.2a. Namely, according to Eq. 2.1:
Therefore, the critical concentration of the monomer can be expressed as a linear function of the plasmon shift: 

\[
M_1^{\text{critical}} \sim \frac{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}}{D \times L \times t_{\text{nuc}}} \ 	ext{\textit{const}}
\]  

(2.2)

Notably, when the critical concentration is investigated through the comparison of the two reactions, A and B, featuring either different temperatures, \(T_A\) and \(T_B\), or ligand densities, the constant \(L\) can be omitted:

\[
\frac{M_1^{\text{critical}}(A)}{M_1^{\text{critical}}(B)} \approx \frac{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}(A)}{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}(B)} \times \frac{D(B) \times t_{\text{nuc}}(B)}{D(A) \times t_{\text{nuc}}(A)} \approx \frac{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}(A)}{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}(B)} \frac{T_B \times t_{\text{nuc}}(B)}{T_A \times t_{\text{nuc}}(A)}
\]  

(2.3)

In the last step, it was assumed that the monomer diffusion \(D\) scales linearly with temperature:

\[
D(T_1)/D(T_2) = T_1/T_2 * (v_2/v_1)
\]

where \(v\) is the viscosity of the solvent.

The validity of Eq. 2.3 can be illustrated through the comparison of the two nucleation reactions, A and B, featuring high and low concentrations of the AgNO\(_3\) precursor, respectively. In both cases, the nucleation of Ag NPs is induced by injecting the AgNO\(_3\) salt, dissolved in a minimal amount of water, into a hot oleylamine \((T = 110 \, \text{C}\)\). If syntheses A and B are run at the same temperature, the nucleation of Ag NPs in flask A (high-concentration) will occur faster due to an earlier built up of the critical monomer concentration (see Fig. 2.2b). Notably, the nucleation is expected to occur at the same value of \([M_1^{\text{critical}}]\) for both reactions,

\[ [M_1^{\text{critical}}]_A = [M_1^{\text{critical}}]_B \]

which follows directly from Eq. 2.1, since \(D_A = D_B\) and \(L_A = L_B\).

Consequently, the shift of the plasmon resonance, according to Eq. 2.3, should be simply proportional to the nucleation time (see Fig. 2.2b):

\[
\frac{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}(A)}{\Delta \lambda_{\text{plasmon}}^{\text{Ag}}(B)} \approx \frac{t_{\text{nuc}}(A)}{t_{\text{nuc}}(B)}
\]  

(2.4)
These expectations are verified by the absorption kinetics of several shell growth reactions (Fig. 2.3), performed at the same solvent temperature (T = 110 °C). By using different concentrations of the Ag precursor for the three cases, it was possible to achieve significantly different times of Ag NP nucleation (Fig. 2.3a-c). The overall shift of the Au/Ag plasmon resonance was then recorded at the time of the nucleation event and plotted versus the nucleation time in Fig. 2.3d. As expected from Eq. 2.4, the blue-shift of the Au/Ag plasmon resonance was found to increase with the nucleation time. Based on a reasonable agreement of the least-square fit to the experimental data in Fig. 2.3d, we conclude that the value of the shift grows linearly with $t_{\text{nucl}}$, as predicted by Eq. 2.4.

**Figure 2.3.** Validating the linearity of the Au/Ag plasmon shift with nucleation time (according to Eq. 2.4). The thermal decomposition of the AgNO$_3$ precursor in the presence of Au NPs is performed at different precursor concentrations: (a). [P] = 0.03 M; (b). [P] = 0.126 M; (c). [P] = 0.2 M; causing the nucleation reaction to occur at different times. All of the displayed reactions were performed at T = 110 °C. Consistently with Eq. 2.3, the blue-shift of the Au/Ag plasmon resonance increases with the increasing nucleation time. (d). Time-dependence of the pre-nucleation blue-shift of the Au/Ag plasmon resonance. A straight line represents a linear fit to the experimental data.
Now it is possible to apply the developed strategy to studying the temperature dependence of the nucleation rate. An important question to be addressed is whether the critical monomer concentration required for nanoparticle nucleation, \( [M^{\text{critical}}_i] \), depends on the reaction temperature. So far, qualitative models of nucleation have limited the temperature dependence to the precursor conversion reaction only\(^{11} \) omitting the secondary effect of the reaction temperature on the probability of nuclei formation. In the meantime, the existence of an activation barrier, \( \Delta E \), for the nuclei growth implies that the nucleation rate may be affected by the solvent temperature depending on the exact balance between the monomer kinetic energy and the height of the activation barrier, \( \exp(-\Delta E/k_BT) \).

To explore the effect of the reaction temperature on \( [M^{\text{critical}}_i] \), the dynamics of Ag nanoparticle nucleation at \( T = 110 \, ^\circ C \) and \( T = 160 \, ^\circ C \) has been compared. Solvent temperatures above 100 °C were chosen to prevent an accumulation of water in oleylamine. The two reaction mixtures containing pumped oleylamine were heated to corresponding temperatures and loaded with equal amounts of Au NPs. A few minutes were then allowed for the evaporation of a Au NP transfer solvent (hexane), which resulted in a recovery of the reaction temperature. The Ag nanoparticle growth was then initiated by injecting a small amount of a concentrated AgNO\(_3\) precursor in water (about 0.2ml), starting the reaction clock. The injection was performed without submerging a needle tip into a hot solvent to help avoiding premature heating of the Ag precursor.

The evolution of the absorption spectra corresponding to the Ag NP nucleation at \( T = 110 \, ^\circ C \) and \( T = 160 \, ^\circ C \) is analyzed in Fig. 2.4. The precursor concentrations for the two reaction mixtures were chosen to promote similar nucleation times (\([P_{110}] = 22 \, \text{mM} \); \([P_{160}] = 0.25 \, \text{mM}\)).
In this case, precursor-to-monomer conversion rates were the same in both flasks: \(k_{110}^D[P_{110}] = k_{160}^D[P_{160}]\) (see Eq. 2.SI6), which allowed excluding the non-linear effects associated with different dynamics of monomer evolution \([M_1(t)]\) at different temperatures. Also, similar reaction times allowed minimizing the potential discrepancy between \(\Delta r_{110}\) and \(\Delta r_{160}\) values, which may arise due to uneven contributions of the shell dissolution processes. According to Fig. 2.4, critical concentrations of the Ag monomer in both reaction mixtures were reached at approximately the same time, \(t_{nucl} \approx 4\) min. Therefore, according to Eq. 2.3, the ratio of the critical monomer concentrations at the two temperatures could be expressed as:

\[
\frac{M_1^{critical}(110\,^\circ\,C)}{M_1^{critical}(160\,^\circ\,C)} \approx \frac{\Delta \lambda_{Ag/Ag}^{plasmon}(110\,^\circ\,C)}{\Delta \lambda_{Ag/Ag}^{plasmon}(160\,^\circ\,C)} \times \frac{433K \times t_{nucl}^{(160)}}{383K \times t_{nucl}^{(110)}} \approx \frac{27nm}{34nm} \times \frac{433K}{383K} = 0.9
\]

\(2.5\)

**Figure 2.4.** Ag nanoparticle nucleation kinetics observed at two different solvent temperatures: (a). \(T = 110\,^\circ\,C\) and (b). \(T = 160\,^\circ\,C\). The concentrations of AgNO\(_3\) precursor were adjusted to \([P_{110}] = 22\,mM\) and \([P_{160}] = 0.25\,mM\) in order to promote similar nucleation times.
(t_{nucl} \approx 4 \text{ min}). In this case the ratio of the critical monomer concentrations at the two
temperatures can be obtained from the absorbance data using Eq. 2.5.

The comparison of the two reactions at T = 110 °C and T = 160 °C reveals an interesting
fact: the spectral shifts of plasmon resonances in the two cases are almost the same despite
markedly different monomer conversion rates, k[P_{110}]/k[P_{160}] \approx 90. The Ag nucleation in the
high-temperature flask was accompanied by a slightly larger plasmon shift (Δλ_{160} = 34 \text{ nm} \text{ versus}
Δλ_{110} = 27 \text{ nm}), which can be attributed to an enhanced monomer diffusion at T = 160 °C :
D_{160}/D_{110} \sim (433K/383K)(v_{110}/v_{160}) reflecting the larger temperature and the decreased viscosity
of the solvent. This data strongly suggests that critical concentrations of the monomer required
for nucleation at T = 110 °C and T = 160 °C are near parity! Indeed,

\[ [M_{1}^{\text{critical}}]_{110}/[M_{1}^{\text{critical}}]_{160} = 0.9 \]
does not take into account the solvent viscosity change, which may
further increase this ratio, bringing it closer to unity. Based on the near matching values of

\[ [M_{1}^{\text{critical}}] \]

it was proposed that the monomer concentration required for nucleation is independent
of the reaction temperature. This result is not immediately apparent from the nucleation theory
(Eq. 2.SI3). Classically, the solvent temperature defines the monomer kinetic energy, which is
used to overcome the activation barrier for changing the solute/nucleus chemical potential. The
observed temperature-independence of \[ [M_{1}^{\text{critical}}] \]
may imply that both reactions occur in the over
barrier region, specifically, monomers carry sufficient kinetic energy to clear the chemical
potential barrier. In particular, it was determined that for T > 110 °C, ΔE_{activation} \ll k_{B}T, such that

\[ k_{nucl}(T > 110 \text{ °C}) = \exp(-\Delta E/k_{B}T) \rightarrow 1. \]

This hypothesis is consistent with the fact that the
nucleation of Ag NPs by reduction can be induced even at room temperatures, indicative of an over barrier regime.

**Figure 2.5.** Comparison of the Ag nucleation dynamics for the two reactions featuring ligand-saturated (OLAM only) and ligand-deprived (OLAM:OA = 1:9) growth conditions. (a,c). Evolution of the Au/Ag plasmon absorption for the OLAM-only synthesis ([P(AgNO$_3$)$_{OLAM}$] = 22 mM, T = 110 °C) results in a large, 27-nm, blue shift of the plasmon resonance and low mean nanoparticle diameter, $d_{av} = 4.9$ nm. (b,d). Evolution of the Au/Ag plasmon absorption for the OLAM/OA synthesis ([P(AgNO$_3$)$_{OLAM/OA}$] = 12 mM, T = 110 °C) results in a much smaller, 3-nm, blue shift of the plasmon resonance and a larger nanoparticle diameter, $d_{av} = 14.6$ nm.
The other question to be addressed by this study what the effect of surface ligands on the critical monomer concentration is. Previous works have demonstrated an important role of the precursor chemistry in the nanocrystal nucleation dynamics. It was shown that low reactive precursors (e.g. phosphonic/phosphinic acid derived metal precursors)) delay the formation of monomers allowing only a small fraction of clusters with sizes above the critical radius to grow. This promotes large nanoparticle diameters and poor size distributions. On the other hand, high reactivity precursors (e.g. bis(trimethylsilyl) chalcogenides and short chain alkyl metal complexes) enable high monomer concentrations which triggers the fast onset of nucleation. This results in low nanoparticle diameters.

While the effect of the precursor chemistry on the evolution of nanoparticle shapes has been investigated extensively, the role of ligands in the process of an energy-activated cluster assembly is still unclear. One of the questions that demands attention is whether the concentration of free ligands in solution can affect the monomer nucleation rate. To address this issue, characteristic changes in the value of \( [M_1] \) induced by variations in the primary ligand concentration have been considered. In present tests, the synthesis of Ag NPs is performed in oleylamine (OLAM), which serves the dual role of the reaction solvent and the \( L \)-type (neutral donor) surface ligand. Therefore, the growth reaction is performed in a ligand saturated solution, where neutral monomers Ag\(^0\) can form complexes with OLAM molecules. Reducing the concentration of an OLAM ligand in this case can be achieved by diluting the reaction mixture with a solvent or an X-type ligand. In this work, electron-donating oleic acid (OA) molecules were used, which negative charge ([OOCR]\(^-\)) prevents the formation of monomer-ligand complexes. As a result, OA acts primarily as a high-temperature solvent, such that the
addition of OA to the reaction mixture simply reduces the concentration of the primary ligand (OLAM).

To understand the effect of the ligand concentration on \( [M_{1}^{\text{critical}}] \), the nucleation kinetics of the two reaction mixtures have been compared, which containing ligand saturated (OLAM only) and ligand deprived (OLAM:OA = 1:9) growth conditions. The concentration of Ag precursors were adjusted to \([P(\text{AgNO}_3)_{\text{OLAM}}] = 22 \text{ mM} \) and \([P(\text{AgNO}_3)_{\text{OLAM/OA}}] = 12 \text{ mM} \) to promote similar nucleation times. In this case, the plasmon shift, \( \Delta \lambda_{\text{Au/Ag}} \), becomes proportional to the critical monomer concentration, \( \Delta \lambda_{\text{Au/Ag}}^{\text{plasmon}} \sim [M_{1}^{\text{critical}}] \), which is obtained from Eq. 2.3 assuming that \( T_A = T_B \) and \( t_{\text{nuc}}(A) = t_{\text{nuc}}(B) \).

According to Fig. 2.5a, the nucleation of Ag NPs in a OLAM/OA mixture leads to a comparatively smaller blue-shift of the Au/Ag plasmon resonance (\( \Delta \lambda_{\text{OLAM}} = 27 \text{ nm} \) versus \( \Delta \lambda_{\text{OLAM/OA}} = 3 \text{ nm} \)). The observed difference between the two growth environments is substantial to indicate that the ligand-deprived (OLAM/OA) environment requires a lower concentration of Ag monomer for nucleation. Based on Eq. 2.3, it was found that

\[
[M_{1}^{\text{critical}}]_{\text{OLAM/OA}} = 0.11 \times [M_{1}^{\text{critical}}]_{\text{OLAM}}.
\]

The suppressed nucleation of Ag in OLAM-only reaction can be attributed to excessive binding of OLAM molecules to a neutral monomer, Ag\(^0\). This interaction is possible through a donor-acceptor mechanism, which is facilitated by an apparent oversaturation of OLAM. When the concentration of an L-type OLAM ligand in solution is lowered through the addition of OA, a smaller fraction of monomeric units will be ligated. As a result, cluster nucleation will not require ligand displacement and may go via a simple monomer addition. Likewise, unligated monomers will experience less stearic hindrance, lowering the nucleation barrier.
In addition to affecting the nucleation rate, the concentration of free ligand in solution was found to play an important role in the ultimate morphology of Ag nanoparticles. This was observed by mapping the evolution of Ag NP shapes in OLAM/OA and OLAM-only syntheses. Here, the two reactions were allowed to proceed until the near-complete conversion of the precursor, which was manifested by the saturation of the Ag plasmon absorbance. The two products were then compared using the TEM analysis. According to Figs. 2.5c and 2.5d, nanoparticles grown under ligand deprived (OLAM/OA) growth conditions were larger in size and showed less homogeneity. The observed morphology was consistent with a lower-energy nucleation threshold expected in this case due to a high concentration of unligated, free Ag monomers. On the other hand, a large nucleation threshold corresponding to ligand saturated growth (OLAM-only) lead to a comparatively smaller nanoparticle size (see Fig. 2.5c). In such environment, most surface sites are terminated with OLAM molecules, suppressing the nanoparticle growth.

In conclusion, an experimental strategy have been developed for estimating the monomer concentration during the hot-injection synthesis of Ag nanocrystals. By using metal nanoparticles as plasmonic sensors of the reaction conditions it was possible to elucidate the role of reaction parameters in the nanoparticle growth. In particular, it was demonstrated that the process of monomer nucleation is independent of the solvent temperature. On the other hand, both the nucleation rate and the nanoparticle morphology were found to be strongly affected by the concentration of a free ligand in solution. It is expected that the demonstrated strategy for tracking monomer concentration will facilitate the rational design of hot-injection nanocrystal synthesis.
2.4 EXPERIMENTAL SECTION

2.4.1 Materials. Acetone (ACS, Amresco), chloroform (anhydrous, 95%, Aldrich), ethanol (anhydrous, 95%, Aldrich), gold (III) chloride (AuCl₃, 99% Acros Organics), methanol (anhydrous, 99.8%, Aldrich), oleic acid (OA, tech., 90%, Aldrich), silver (I) nitrate (AgNO₃, 99%, Sigma-Aldrich) were used as purchased. Oleylamine (tech., 70%, Aldrich) was degassed using vacuum pump for 1 hour at 120 ºC and then stored under argon atmosphere prior using. All reactions were performed under argon atmosphere using the standard Schlenk technique. The centrifuge used for precipitation operated at 5400 and 7200 rpm.

2.4.2 Synthesis of oleylamine-capped Au NCs. Au NCs were synthesized using a one-pot procedure developed in our previous work. In a typical synthesis, 0.011g of AuCl₃ and 5 mL of pumped oleylamine were loaded in a one-neck flask and allowed to react at 110 ºC for 30 min under argon. 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 ~ 4 mL of chloroform. The cleaning cycle was repeated one more time and the final product was re-dispersed and stored in chloroform. The final product contained Au NPs with an average diameter of 5 nm and a surface plasmon resonance (LSPR) peak at λ ≈ 525 nm.

2.4.3 Nucleation of Ag NPs in a presence of Au “probe” NPs. Ag NCs were grown using a procedure adapted from Ref. 25. In a typical synthesis, 5 ml of pumped oleylamine were placed
in a 25 mL two-neck flask under argon. The temperature of the flask’s solution was raised to 110-160 °C. When the desired temperature was reached, a known concentration of Au NPs in 0.25 mL of hexane (total weight of purified Au NPs was typically less than 1 mg) was injected into the flask. After hexane had evaporated (2-3 minutes), an aqueous solution of AgNO₃ was added to the reaction flask. The total amount of AgNO₃ depended on experimental conditions and is specified in the text. The Ag shell growth was monitored through a spectral shift of the localized surface plasmon resonance (LSPR) peak. When the desired shell thickness was reached, the flask was taken off of the heating mantle. After cooling, the NP solution was distributed evenly between two centrifuge tubes and precipitated with ethanol. After centrifugation, the solution was discarded and the precipitate was redispersed in chloroform.
2.5 SUPPORTING INFORMATION

Figure 2.SF1. The expected relation between the spectral position of the Au/Ag core/shell plasmon resonance and the thickness of the Ag shell, calculated from Eq. SI1 (d_{Au} = 5 nm). For small values of the Ag shell thickness, the spectral shift of the plasmon resonance is roughly linear.
2.5.1 Blue-shift of the plasmon resonance in Au/Ag core/shell nanoparticles. According to previous works, the spectral position of the Au/Ag NP plasmon resonance can be approximately expressed as a simple function of the Au volume fraction, \( \nu_{Au} \):

\[
\lambda_{Au/Ag}^{plasmon} \approx \nu_{Au} \lambda_{Au}^{plasmon} + (1 - \nu_{Au}) \lambda_{Ag}^{plasmon} = 525 \times \left( \frac{R_{Au}}{R_{Au/Ag}} \right)^3 + 420 \times \left[ 1 - \left( \frac{R_{Au}}{R_{Au/Ag}} \right)^3 \right]
\]

(2.SI1)

For small values of the Ag shell thickness, \( \Delta R_{Au/Ag} \), the shift of the plasmon resonance can be approximated using a linear relationship:

\[
\lambda_{Au/Ag}^{plasmon}(nm) \approx \alpha \times \Delta R_{Au/Ag}(nm); \quad \alpha = 88.
\]

(2.SI2)

**Figure 2.SF2.** Evolution of the plasmon resonance in Au/Ag core/shell nanoparticles corresponding to (a) - growth of the shell in the presence of AgNO\(_3\) precursor (T = 110 C°). (b), - thermal dissolution of the Ag shell (T = 110 C°). The process of dissolution appears to be much slower.
2.5.2 Calculation of the nanoparticle growth rate. The total flux of monomers toward the particle surface is given by:\(^{33}\):

\[
J = \left(\frac{4\pi r^2}{V_m}\right) \frac{dr}{dt}
\]

where \(dr/dt\) is a particle growth rate and \(V_m\) is the molar volume. According to the nucleation framework proposed by Talapin et al., \(^{35}\) the nanoparticle growth rare can be express as:

\[
\frac{dr}{dt} = V_m D \left[ [M_1] - C^0 \exp\left(\frac{\beta \gamma V_m}{rRT}\right) \right] \quad (2.\text{SI}3)
\]

where \(D\) is the monomer diffusion coefficient, \([M_1]\) is a monomer concentration in the bulk of the solutions, \(\gamma\) is the surface energy per unit area, \(C^0\) is the solubility of the monomer, \(k\) is the growth rate constant, \(\alpha\) and \(\beta\) are transfer coefficients.

Prior to nucleation, the monomer concentration is relatively high, such that the negative term in the numerator of Eq. SI3, which reflects the particle dissolution process, can be neglected (see Fig. SF2). This will allow simplifying the expression for nanoparticle growth rate:

\[
\frac{dr}{dt} = D \times [M_1] \times L \quad (2.\text{SI}4)
\]

where \(L = \frac{V_m}{r + (D/k) \exp\left(\frac{\alpha \gamma V_m}{rRT}\right)}\)

2.5.3 Evolution of the monomer concentration \([M_1]\) at a constant temperature. The amount of precursor molecules, \(dN\), which is thermally converted into a monomer during \(dt\) time of the
reaction is: \(dN = -kN dt\), or \(dN/N = -kd t\), where \(k\) is the temperature dependent rate of the precursor decomposition. By integrating both sides of this equation, we obtain the number of precursor molecules, remaining in the flask as a function of time: \(N = N_{(t=0)}e^{-kt}\). Assuming that prior to the onset of nucleation the monomer is not being consumed, the monomer concentration in the reaction mixture can be expressed as:

\[
[M_1(T)] = [P](1 - e^{-k(T)t})
\]  
(2.SI5)

where \([P]\) is the initial concentration of the precursor in the flask. In reactions where the nucleation is achieved with only a small fraction of the converted precursor (high \([P]\)), the rise in the monomer concentration can be expressed as a linear function of time:

\[
[M_1]_{M_1<<P} = [P](1 - e^{-kt}) \approx [P](1 - (1 - kt)) = [P]kt
\]  
(2.SI6)

**Figure 2.SF3.** Evolution of the monomer concentration in the flask prior to the onset of nucleation (\(T = \text{const}\)). The linearity of \([M_1]\) at early times (see Eq. 2.SI6) is highlighted.
2.6 REFERENCES


CHAPTER III

COLLOIDAL SYNTHESIS OF MONODISPERSE SEMICONDUCTOR
NANOCRYSTALS THROUGH SATURATED IONIC LAYER ADSORPTION.¹

3.1 ABSTRACT

A general strategy was established for the synthesis of colloidal semiconductor nanocrystals (NCs) exhibiting the size dispersion below 5%. The present approach relies on the sequential deposition of fully saturated cationic and anionic monolayers onto small-diameter clusters, which leads to focusing of nanocrystal sizes with the increasing particle diameter. Each ionic layer is grown through a room-temperature colloidal atomic layer deposition (ALD) process that employs a two-solvent mixture to separate the precursor and nanocrystal phases. As a result, unreacted precursors can be removed after each deposition cycle, preventing the secondary nucleation. By using CdS NCs as a model system, it was demonstrated that a narrow size dispersion can be achieved through a sequential growth of Cd²⁺ and S²⁻ layers onto starting CdS cluster “seeds”. Besides shape uniformity, the demonstrated methodology offers an excellent batch-to-batch reproducibility and an improved control over the nanocrystal surface composition. The present synthesis is amenable to other types of semiconductor nanocrystals and can potentially offer a viable alternative to traditional hot-injection strategies of the nanoparticle growth.

3.2 INTRODUCTION

Colloidal semiconductor nanocrystals (NCs) have attracted significant attention as possible candidates for the development of novel optoelectronic materials.² ³ Their characteristic sizes fall within the unique length scale where inorganic semiconductors exhibit tunable, molecular-like
properties while retaining a high density of exciton states and a compelling photostability. Unlike molecules, however, colloidal NCs are not chemically uniform. Fabricated through hot-injection routes, these nanostructures tend to exhibit polydisperse sizes, poorly defined ligand coverage, and broad distributions of cation-to-anion ratios across the sample.\textsuperscript{4-10} As a result, their distinct optoelectronic properties cannot always be harnessed into device technologies, leading to only a few successful examples of NC-based applications for which the size dispersion does not directly impact the efficiency (e.g. light-emitting phosphors in panel displays, bio-labels).\textsuperscript{3}

The morphological variety of colloidal nanocrystals affects their ensemble-averaged properties in several ways.\textsuperscript{3} The dispersion of surface compositions in colloidal NCs is restrictive to both the light-emitting applications as the nanocrystal emission yield is dependent on the cation-to-anion ratio\textsuperscript{11-16} and the charge transport characteristics of NC solids,\textsuperscript{17-20} since nanoparticles featuring different surface stoichiometries exhibit different types of trap states\textsuperscript{21-23} and thus cannot be effectively passivated using a cohesive treatment. Such unpassivated sites induce charge localization, shortening the carrier diffusion length in NC films.\textsuperscript{24} The variety of nanoparticle sizes is likewise limiting to the optoelectronic performance of nanocrystal assemblies. The inhomogeneous broadening of the NC band gap emission beyond the natural emission line width\textsuperscript{25} is generally unwanted in applications seeking the color purity. In the case of charge-transport materials, the polydispersity of nanocrystal sizes factors in through an increased energy disorder in a solid, which weakens electrical coupling between neighboring dots, leading to a poor charge mobility.\textsuperscript{26} The energy dispersion exceeding the room-temperature $kT$ can also promote funneling of excitons to the lowest energy site, thus impeding the charge extraction in photovoltaic devices.\textsuperscript{27,28} Therefore, while the present level of nanoparticle homogeneity resulting from hot injection growth strategies (with the standard size deviation of 5-
10%²⁹-³¹ without the selective precipitation²²-³⁴ may be acceptable for phosphor-based applications of semiconductor NCs (e.g. light-emitting diodes,³⁵ bio-labels³⁶,³⁷), it remains inadequate for technologies that rely on the charge or exciton diffusion through nanocrystal solids (e.g. solar cells, photodetectors, light concentrators, and field effect transistors).³⁸,³⁹ In light of these limitations, the development of novel synthetic protocols that give rise to a reduced dispersion of nanocrystals sizes, shapes, and surface compositions is in great demand.

The current project demonstrates a general strategy for the colloidal synthesis of semiconductor nanocrystals that enables a narrow dispersion of nanoparticle sizes. The present approach is exemplified through the growth of monodisperse CdS NCs and is readily amenable to the synthesis of other metal chalcogenide semiconductors. Within this strategy, nanoparticles are synthesized in a step-wise manner through a sequential deposition of fully saturated cationic and anionic monolayers onto molecular cluster “seeds” (Fig. 3.1). Each ionic layer is grown via a room-temperature colloidal atomic layer deposition (c-ALD) approach,⁴⁰ which employs separate solvent phases for precursors and nanocrystals. This allows reaching an ionic saturation of each half-monolayer (either Cd²⁺ or S²⁻) without carrying any unreacted precursors over to the next step.

In addition to a narrow distribution of nanocrystal sizes, the demonstrated Saturated Ionic Layer Adsorption (SILA) synthesis offers a number of useful advantages. First, due to the self-limiting nature of the half-monolayer growth, the synthetic procedure becomes highly reproducible regardless of variations in the solvent temperature, injection concentrations, etc. Second, the surfaces of nanocrystals are rendered to have similar compositions, which is important for unifying an ensemble-averaged response of nanocrystals in a macroscopic sample (i.e. QD solids, hybrid films). Third, nanoparticles are grown using room-temperature ALD⁴⁰
under ambient conditions through a series of copious synthetic steps which could potentially make this strategy amenable to automatization. Lastly, the present synthesis offers a theoretically conceivable opportunity for focusing the nanocrystal size distribution to a fraction of a monolayer, provided that the size variations of original seeds are minimized through the use of well-defined clusters.

3.3 RESULTS AND DISCUSSION

The effectiveness of nanoparticle size focusing via the SILA strategy is determined by several conditions. First, the diameter dispersion of starting nanoclusters for seeding the subsequent monolayer growth should be as small as possible, as the standard size deviation of the seed, $\Delta d_{\text{SEED}}$, is retained as a non-vanishing component of the size dispersion in fully grown nanoparticles: $\Delta d_{\text{FINAL}} = \Delta d_{\text{SEED}} + \Delta d_{\text{SHELL}}$. Second, the deposition of cation and anion half-monolayers should be performed to an ionic saturation. Even in cases when a complete surface coverage with one type of surface ions is not possible due to an uncompensated surface charge, the full-saturation requirement should still lead to a nearly identical morphology of the deposited surface layer across the entire nanoparticle sample.
Figure 3.1. (a). Illustration of the general strategy for growing monodisperse semiconductor nanocrystals *via* the Saturated Ionic Layer Adsorption. Nanocrystals are grown from small-diameter CdS seeds (e.g. 2-nm CdS clusters) by using a sequential c-ALD growth of saturated cationic (Cd$^{2+}$) and anionic (S$^{2-}$) half-monolayers. Since a well-defined number, *n*, of CdS monolayers, *n*(CdS)$_1$, is overgrown, the resulting size dispersion in the final product remains similar to that of the initial CdS clusters: $\Delta d_{\text{final}} = \Delta d_{\text{seed}} + \Delta d_{\text{shell}}$ ($\Delta d_{\text{shell}} \rightarrow 0$). As a result, the standard size deviation of grown CdS nanoparticles is reduced compared to that of original seeds, $\Delta d_{\text{final}}/d_{\text{final}} < \Delta d_{\text{seed}}/d_{\text{seed}}$. The statistical diagrams are simulated to illustrate the size focusing effect. (b). A representative Transmission Electron Microscope (TEM) image of 5.6-nm CdS NCs (size dispersion, $\Delta d/d \approx 3\%$) grown from 2.9-nm CdS seeds *via* the saturated ion layer adsorption technique.
A sequential monolayer growth on surfaces of colloidal nanocrystals is traditionally performed using a hot-injection strategy, known as successive ionic layer adsorption and reaction (SILAR). This method relies on successive injections of charge-neutral precursors into the hot reaction mixture containing “seed” nanoparticles. Over the years, SILAR has become the method of choice for the synthesis of various core/shell systems with a particular success in applications to CdSe/CdS core/shell NCs. The popularity of SILAR is related to an important premise of this strategy that a full monolayer can be grown without a build-up of unreacted precursors in solution. Recent works, however, have shown that during the SILAR synthesis, surface-anchored precursor ions remain in a partial equilibrium with those in solution, such that the surface saturation with either cations or anions can only be achieved at the expense of having an excess of precursors in the reaction mixture (Fig. 3.SF1a). Since unreacted cations/anions cannot be removed, precursors continuously build up causing an expected formation of isolated nanoparticles after just a few cycles (Fig. 3.SF1a).

Colloidal ALD (c-ALD) was recently introduced as an alternative to the SILAR strategy for a stepwise growth of the CdS shell onto CdSe nanosheets. In contrast to the SILAR approach, this technique relies on a sequential transfer of either nanoparticles or molecular precursors between polar and nonpolar phases in order to achieve a convenient phase separation between the product and unreacted precursors. As a result, the secondary nucleation is strongly suppressed, which allows achieving a narrow distribution of shell thicknesses giving rise to high-quality core/shell nanosheet heterostructures. In the present work, the c-ALD strategy has been employed to allow the nanocrystal growth without the phase transfer. To this end, nanoparticles were solubilized in a non-polar solvent (toluene) while precursors were injected into the polar phase (formamide). Upon completion of the reaction, the two phases separate again and
unreacted precursors can be removed via a toluene/formamide extraction rather than product precipitation. This allows a simple monolayer growth cycle that can be repeated multiple times.

Figure 3.2. Evolution of the steady-state absorption and emission profiles of CdS NCs during a single monolayer growth via c-ALD. (a,b). Absorption and emission of the original CdS NC seeds, grown via hot-injections routes. (c,d). Absorption and emission of (CdS)S\(^{2-}\) NC resulting from the reaction of CdS NCs in toluene with Na\(_2\)S in formamide. The surface saturation with sulfur is accompanied by quenching of the surface emission (500 nm < \(\lambda\) < 800 nm). (e,f) Absorption and emission spectra of CdS(CdS)\(_t\) NCs resulting from the reaction of (CdS)S\(^{2-}\).
nanoparticles with Cd(OAc)\textsubscript{2}. The deposition of Cd\textsuperscript{2+} is accompanied by the recovery of the surface emission in CdS.

The strategy for depositing one full (CdS)\textsubscript{1} monolayer onto 3.7-nm CdS NCs, grown via hot injection routes, is illustrated in Fig. 3.2. At the beginning of the synthesis, the top layer of the two-phase growth solution (toluene/formamide) was loaded with CdS seeds, while the bottom, formamide (FA) layer, was infused with the sulfur precursor (Na\textsubscript{2}S). A small amount of oleylamine (OLAM) was added at this stage to the toluene phase for the subsequent ligand displacement (for the exact amount of OLAM and Na\textsubscript{2}S see Figs. 3.3 and 3.SF2). The deposition of the first sulfur layer was performed by agitating the test tube containing the two-solvent mixture (toluene/formamide = 1:1) on a vortex shaker for approximately 30 sec. Upon mixing, the two phases were separated by centrifuging the test tube for 20 seconds (at 5000 rpm). At this stage, most of unreacted Na\textsubscript{2}S was found in the FA phase with the toluene solution showing very little trace of S\textsuperscript{2-} ions (as was verified by mapping the distribution of S\textsuperscript{2-} ions in a nanoparticle-free, two-solvent mixture through the reaction with Cd(OAc)\textsubscript{2}). The concentration of oleylammonium sulfide (NH\textsubscript{4}\textsubscript{2}S in the nonpolar phase was likewise insufficient to cause secondary nucleation at subsequent steps. Any residual S\textsuperscript{2-} in the toluene layer was consequently removed from the (CdS)S\textsuperscript{2-} product by washing with fresh FA. The washing cycles were repeated 1-2 times until the used up FA solution contained no residual S\textsuperscript{2-} (as was confirmed by injecting Cd(OAc)\textsubscript{2} to a phase-separated FA). Upon washing, the toluene solution of (CdS)S\textsuperscript{2-} was centrifuged to remove any aggregates.

The degree of the sulfur layer filling can be estimated \textit{in situ} without the need for time-consuming elemental analysis by measuring the relative yield of the trap state emission in (CdS)S\textsuperscript{2-} NCs. It is well known that the exciton decay in oleic acid (OA)- or OLAM-capped CdS
is primarily driven by the surface defect recombination which has been attributed to sulfur
vacancies on the surface. The addition of sulfur ions passivates these sites causing quenching
of the trap emission, as seen in Fig. 3.2d (red curve). By using a combination of Fourier
transform infrared spectroscopy (FTIR), TEM, and absorption measurements (below), it was
confirmed that full quenching of the surface emission in (CdS)S\(^2^-\) corresponds to a complete
filling of the sulfur half-monolayer. A partial quenching of the surface emission in (CdS)S\(^2^-\) NCs
indicates that a charge-neutrality driven equilibrium between the sulfur-saturated surface and the
solution was established. It should be noted that when the emission of cation- and anion-capped
nanocrystals is not distinguishable, other strategies could be used for monitoring the surface
saturation. For instance, Talapin et. al has recently demonstrated the use of potentiometric
titrations for retrieving the charge and ligand affinity of nanoparticle surfaces. In addition to the
sulfur-induced quenching of the surface (and band gap) emission, the deposition of S\(^2^-\) ions
causes the characteristic changes in the absorption profile of CdS NCs that are manifested in two
distinct ways. First, the lowest energy exciton transition (band edge) red-shifts as a result of an
increased particle volume. The magnitude of such red-shift was found to be consistent with the
known size-scaling of the CdS band gap (see Fig. 3.6b). Second, sulfur capping of nanocrystals
decreases the apparent intensity of the secondary, 1Se-2S\(_{3/2}\)h, absorbing transition (Fig. 3.6a).
This phenomenon is attributed to broadening of the 1Se-2S\(_{3/2}\)h feature rather than the change in
its extinction.

The highest achievable ratio of S to Cd surface ions in sulfur-saturated (CdS)S\(^2^-\) NCs
depends on the availability of passivation schemes that preserve the charge neutrality of these
nanoparticles. The solubility of (CdS)S\(^2^-\) NCs in the non-polar phase suggests binding of OLAM
ligands to reacted nanocrystals. Indeed, without OLAM in the toluene phase, sulfur-capped NCs
readily transfer into formamide upon mixing. Therefore, the surface layer in saturated (CdS)S\(^2^-\) NCs is likely to be a combination of OLAM, S\(^2^-\), [S]\(^2-\)2[Na]\(^+\) and [S]\(^2-\)2[RNH\(_3\)]\(^+\) surface molecules. The steps corresponding to the removal of OA by S\(^2^-\) ions and the subsequent passivation of (CdS)S\(^2^-\) surfaces with OLAM were monitored using Fourier transform infrared spectroscopy (FTIR) in Figs. 3.4a, 3.SF3 and \(^1\)H NMR (Fig. 3.SF6). The exchange of the oleic acid to the S-OLAM complex is attested by the disappearance of the COO\(^-\) oleic acid stretch modes (both asymmetric 1536 cm\(^{-1}\) and symmetric 1437 cm\(^{-1}\) peaks) and the onset of the OLAM NH\(_3^+\) stretch (both asymmetric 1650 cm\(^{-1}\) and symmetric 1565 cm\(^{-1}\)) which is consistent with the formation of the RNH\(_3^+\)- S\(^2^-\) complexes. Notably, RNH\(_3^+\)- S\(^2^-\) capped nanocrystals do not exhibit any N-H stretch transitions (3385, 3294, 1620 and 793 cm\(^{-1}\)) but display two pronounced NH\(_3^+\) features. This pattern suggests that the RNH\(_3^+\)- S\(^2^-\) ligand-ion complex is formed through the protonation of the amine groups.\(^{48}\)

**Figure 3.3.** The effect of Na\(_2\)S concentration in the formamide phase (3 ML) on the S\(^2^-\) monolayer saturation, quantified using a relative intensity of the surface trap state emission. Prior to the addition of Na\(_2\)S precursor, nanocrystals were capped with OA ligands. (b). The effect of Cd(OAc)\(_2\) concentration in the FA phase on the intensity of the surface emission in (CdS)Cd\(^{2+}\) NCs, which is proportional to the cadmium layer filling. The emission amplitude can, in
principle, exceed unity as the ratio of Cd to S in Cd-saturated nanocrystals is greater than that of original OA-capped CdS seeds. (c). Relative filling of the sulfur layer in (CdS)S$_2^-$ NCs (normalized to unity) versus the concentration of OLAM in toluene and Na$_2$S in FA.

Figure 3.4b illustrates several possible reaction paths for the four types of ligand binding motifs$^{45}$ on the surface of original CdS seeds upon the reaction with Na$_2$S. Based on the results of previous works$^{49}$ and the present FTIR characterization of (CdS)S$_2^-$ NCs (Fig. 3.4a), it was proposed that the native anionic OA ligands (X type) are fully replaced with (X type) S$_2^-$ anions. Any neutral-donor ligands (L-type) present on the surface of original seeds can be exchanged or displaced with [S]$^{2-}$ 2[Na]$^+$ that forms a dative covalent bond with Cd in the lattice. A Z-type neutral acceptor ligand or a Cd(O$_2$CR)$_2$ carboxylate complex ligand on the surface of original NCs can undergo a L-promoted Z-type displacement to yield a vacant S site (Fig. 3.4b).
Ultimately, most sulfur vacancies on the surface of \((\text{CdS})S^{2-}\) NCs become filled causing the suppression of the surface trap emission.

**Figure 3.4.** (a). FTIR spectra of OLAM-stabilized \((\text{CdS})S^{2-}\) NCs resulting from the deposition of the saturated sulfur layer (red curve). FTIR of OA-capped CdS NCs is included for comparison (black curve). Filling of the sulfur layer is accompanied by the disappearance of the
COO’ OA stretch modes and the onset of the OLAM NH\textsubscript{3}+ stretch transitions. This pattern suggests that OLAM attaches to the surface of (CdS)S\textsuperscript{2-} nanoparticles by forming a RNH\textsubscript{3}+ - S\textsuperscript{2-} complex with the sulfur ion. (b). The proposed surface chemistry modifications of OA-capped CdS NCs resulting from the sulfur layer deposition.

For the deposition of a cadmium half-monolayer, sulfur-saturated (CdS)S\textsuperscript{2-} NCs were re-dispersed in the toluene phase of the toluene/formamide growth solution, while Cd(OAc)\textsubscript{2} was added to formamide. A small amount of oleylamine was injected into the nanocrystal phase to promote nanoparticle stabilization upon cation attachment. The reaction of Cd\textsuperscript{2+} ions with nanocrystal surfaces was carried out by agitating the test tube until the trap state emission (monitored via the UV lamp) was maximized. Upon completion of the cadmium layer growth, the toluene/formamide mixture was phase separated by centrifuging the contents for 20-30 sec and the top layer containing CdS was transferred to a clean test tube. Unreacted Cd(OAc)\textsubscript{2} was discarded through several formamide/toluene extractions which were performed until the used-up formamide solution contained no noticeable traces of cadmium (as verified by inducing the reaction with Na\textsubscript{2}S). Typically 1-2 extractions were sufficient. Following the cleaning step, the nanoparticle layer was centrifuged to remove any aggregates. The absorption of the cleaned product exhibited almost no sub-band gap contribution (A ≈ 0, λ > λ\textsubscript{band edge}, see Fig. 3.2f), which confirmed the absence of any residual aggregates or secondary nuclei.

The degree of the cadmium surface coverage was concluded from the characteristic changes in the absorbance and emission profiles, as illustrated in Figs. 3.2e,f and 3.3b. Naturally, the nanocrystal growth was accompanied by an apparent red-shift of the band edge absorbance (Fig. 3.2e, blue curve), as well as the recovery of the 1Se-2S\textsubscript{3/2}h absorption feature (also evident in the set of darker curves in Fig. 3.6a). Measurements of the trap state emission were concurrently
performed to monitor the saturation of the cadmium layer \textit{in situ}. Typically, the relative yield of the surface trap emission was sharply enhanced upon reacting of \((\text{CdS})\text{S}^2-\) nanocrystals with \(\text{Cd}^{2+}\), ultimately exceeding the intensity level observed in the original NCs (Fig. 3.2f, blue curve). The new maximum in the surface emission yield was expected due to a greater ratio of Cd to S surface ions in Cd-saturated nanoparticles (after the first full monolayer) as compared to the original CdS seeds. Typically, an excessive concentration of the cadmium precursor was used in the formamide layer to ensure a full saturation of the surface. If the aggregation occurred at this step, additional OLAM was added to the toluene phase.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{Changes in the absorbance profile of the \text{CdS}_{318\text{~nm}} clusters upon deposition of the sulfur layer. An increasing concentration of Na\text{S} in the toluene/formamide reaction mixture causes the \text{CdS}_{318\text{~nm}} cluster (with a proposed structure \text{Cd}_{17}\text{S}_4(\text{OA})_{26}) to gradually transform into…}
\end{figure}
the CdS\textsubscript{360 nm} cluster (with a proposed assignment of \([\text{Cd}_{17}\text{S}_{17}(2\text{NH}_4^+\text{S}_2^-)_m(\text{C}_{18}\text{H}_{35}\text{NH}_2)_n])^{15-m}\). In addition to the two aforementioned clusters, evolution of the absorbance profile does not reveal any other intermediate structures. The right panel illustrates the proposed cluster transformation.

The ionic saturation of c-ALD half-monolayers is well illustrated during the deposition of the sulfur layer onto Cd-terminated CdS\textsubscript{318 nm} clusters (Fig. 3.5). Based on the spectral position of the exciton absorbance, which was previously classified for thiol-capped CdS clusters\textsuperscript{33,50-54} and the experimental evidence of the Cd-saturated surface (see Fig. 3.SF4), observed 318-nm absorbance feature was assigned to a Cd\textsubscript{17}S\textsubscript{4}(OA)\textsubscript{26} pyramid-shape cluster. Figure 3.5 shows the evolution of the exciton absorption in CdS\textsubscript{318 nm} clusters upon their reaction with an increasing amount of Na\textsubscript{2}S in the FA phase (as indicated by a vertical arrow). The addition of S\textsuperscript{2-} ions results in a gradual transformation of CdS\textsubscript{318 nm} structures into a superseding CdS\textsubscript{360 nm} cluster architecture, revealing essentially no traces of other intermediate morphologies. Similar cluster growth dynamics was recently observed by Owen’s group\textsuperscript{54} that demonstrated a complete heat-induced transformation of 350-nm CdSe clusters into either CdSe\textsubscript{380} or CdSe\textsubscript{408} superseding cluster morphology.
Figure 3.6. Spectral changes in absorption and emission of CdS nanoparticles accompanying the c-ALD growth of 4 full monolayers onto CdS$_{390\text{ nm}}$ nanocrystal seeds (growth via hot injection routes). (a). Evolution of the absorption profile. (b). Spectral position of the exciton absorption versus the number of deposited monolayers. The blue curve represents a theoretically expected red-shift of the absorbance edge accompanying the deposition of a full monolayer (calculated from Ref. 55). (c). Evolution of the trap state emission yield versus the number of deposited monolayers. (d). Band gap emission and the absorbance profile of CdS$_{378\text{ nm}}$+3(CdS$_{1}$) NCs.

Following the growth of the first CdS monolayer onto CdS seeds, the subsequent monolayers were deposited through a copious procedure using similar “verification” steps. At the beginning of each cycle, CdS nanoparticles were reacted with Na$_2$S until the surface saturation with sulfur occurred. This process was monitored in situ by measuring the kinetics of both the absorption and the emission profiles (Fig. 3.6b,c). The product was then washed with FA until the residue solution contained no traces of Na$_2$S. Subsequently, cadmium layer was deposited until the saturation of trap state emission was reached. Unreacted precursors were removed through toluene/formamide extractions while aggregated nanoparticles were discarded by centrifuging. Due to changes in the total surface area of growing nanoparticles at each step, the saturation of each layer had to be verified after each half cycle. In particular, the sulfur deposition was performed to a minimum of the (CdS)S$^{2-}$ trap emission, while Cd$^{2+}$ was reacted to achieve the maximum of the trap emission intensity (see Fig. 3.6c). The increment in the nanocrystal size upon full monolayer growth was inferred from the red shift of the exciton absorption feature (for small nanocrystal sizes) as well as the TEM analysis (Figs. 3.7 and 3.SF4). Figure 3.6a,b shows the evolution of the absorption profile accompanying the 4 monolayer growth onto d = 2.9-nm
CdS NC seeds. The comparison of the observed red-shift in the exciton absorption with the predicted absorption value (calculated from Ref. 55) confirms that monolayers are grown to nearly a full completion. This conclusion is verified by the Transmission Electron Microscopy (TEM) analysis of fully grown CdS\textsubscript{390nm}+ 4(CdS\textsubscript{1}), shown in Figs. 3.7c,d. An incomplete monolayer filling (typically < 90\%) is tentatively attributed to the competition between OLAM molecules and S\textsuperscript{2-} anions for available surface sites in CdS NCs. As illustrated in the Fig. 3.3c, an excess of OLAM causes an incomplete monolayer growth while OLAM deficiency results in the monolayer saturation (but poor stabilization of nanoparticles in toluene).
Figure 3.7. TEM images of CdS NCs grown by SILA technique. (a). CdS\(_{390\text{nm}+10(CdS_1)}\) NCs grown without full layer saturation. (b-c). TEM images of CdS\(_{390\text{nm}+4(CdS_1)}\) NCs grown to a full
layer saturation (d). Statistical distribution of NCs sizes in (c). (e). X-ray powder diffraction (XRD) spectra of CdS NCs containing 3-ML of SILA grown shell (CdS\textsubscript{378nm}+3(CdS\textsubscript{1}) NCs). The observed diffraction pattern is consistent with the zinc blende crystal structure.

The TEM analysis of SILA-grown CdS NCs fabricated by depositing 4 ALD (CdS\textsubscript{1}) layers onto CdS hot-injection seeds (d = 2.9 nm) shows a narrow dispersion of particle sizes ≈ 3% (sample size = 123 nanoparticles, Figs. 7b-d). This result is consistent with the observation of a spectrally narrow band gap emission in these nanocrystals (\(\Delta E_{\text{FWHM}} = 130\) meV), which is slightly greater than single particle emission linewidth at room temperature (e.g. 60-100 meV for CdSe).\textsuperscript{56} The average diameter of fully grown CdS\textsubscript{390nm}+4(CdS\textsubscript{1}) NCs was determined to be ≈ 5.4 nm (Figs. 3.7d and 3.SF5a). The observed size corresponds to an added monolayer thickness of approximately \(\frac{1}{2} \times (5.4-2.9)/4\text{ML} = 0.32\) nm, which is close to an expected 0.35-nm Cd-Cd distance in zinc blende CdS. Consequently, the full saturation growth leads to about 90% level filling at each ion deposition cycle. Expectedly, when the ionic saturation is not reached at each step the size dispersion increases. This trend is manifested by a larger diameter dispersion (5.5%) of 6.3-nm CdS NCs grown through the deposition of 10 unsaturated (CdS\textsubscript{1}) MLs (with an approximate layer filling of 45%) in Figs. 3.7a and 3.SF5b. CdS NCs grown through a partial layer saturation also appear to be less spherical than the ones grown using a full ionic saturation. The reason for such difference requires further investigation. Perhaps, unsaturated conditions result in lower energy surfaces which are natively faceted for zinc blende nanocrystals. The lattice structure of CdS NCs was investigated by X-ray powder diffraction (XRD). Figure 3.7e shows the diffraction spectrum of CdS NCs fabricated by growing 3 (CdS\textsubscript{1}) monolayers onto 2.9-nm zinc blende CdS NCs. The observed Bragg peaks confirm the crystallinity of the shell, which continues the zinc blende crystal structure of the core domain.
Upon the completion of c-ALD nanoparticle growth, OLAM surface ligands can be exchanged with oleic or other fatty acids through the oleylamine to carboxylate, $L \rightarrow Z$ type displacement. To preserve a narrow distribution of nanoparticle diameters, the reaction is performed under Cd-saturated conditions by inducing a thermally activated substitution of OLAM molecules with carboxylates ($\text{Cd(O}_2\text{C}_R\text{)}_2$)$^{47}$, as illustrated in Fig. 3.8a. To this end, OLAM-capped nanoparticles were loaded into a flask containing pumped ODE, OA, and Cd($\text{O}_2\text{C}_R\text{)}_2$ (for details, please see the Experimental information section). Heating the reaction to $230 \, ^\circ\text{C}$ initiates the ligand exchange/displacement, which is evident through a characteristic red-shift of the exciton absorption (due to an increased volume of carboxylate-appended nanoparticles) and the onset of the $1\text{Se}-2\text{S}_{3/2}$ absorbing transition feature (red arrow in Fig. 3.8a). Notably, the width of the absorption peak remains the same, which indicates that the size dispersion is preserved upon ligand exchange.

To demonstrate the generality of the SILA method beyond the investigated CdS system, the c-ALD growth of CdSe monolayers onto OA-capped 2.4-nm CdSe (hot-injection) seeds have been attempted. To this end, the Se precursor ($\text{Na}_2\text{Se}$) was fabricated via a simple reduction process ($\text{NaBH}_4 + \text{Se (powder)} + (\text{FA/methanol}) = \text{Na}_2\text{Se} + …$, see Ref. 57), and kept under argon. Inert atmosphere was also needed during the layer growth stage due to an elevated sensitivity of $\text{Na}_2\text{Se}$ to air. According to Fig. 3.8b, c-ALD deposition of 2 ($\text{CdSe})_1$ saturated monolayers causes a noticeable decline in the spectral width of the CdSe exciton absorption and band-gap emission features, indicative of the reduction in the nanoparticle size dispersion.
Based on the known size-scaling of the CdSe band gap,\textsuperscript{55} it was determined that 60\% filling of each \((\text{CdSe})_1\) ML on average was reached.

\textbf{Figure 3.8.} (a). Changes in the absorption profile of c-ALD grown CdS NCs caused by the OLAM\textrightarrow{}OA ligand exchange. The attachment of carboxylic complexes results in the onset of the \(1\text{Se}-2\text{S}_{3/2}\)h peak (indicated by a red arrow), as well as a slight red-shift of the \(1\text{Se}-1\text{S}_{3/2}\)h absorbing transition. (b). The change in the absorption and emission profiles of OA-capped CdSe induced resulting from the SILA growth of \(2(\text{CdSe})_1\) monolayers. A distinct decline in the spectral width of the CdSe band gap emission and absorption profiles (red curves) upon the addition of a c-ALD saturated CdSe “shell” confirms the reduction in the nanoparticle size dispersion.
The quality of layer stacking in CdS NCs grown by SILA process was estimated from the rate of charge trapping on defects of the CdS shell associated with surface and interstitial dangling bonds. To this end, the fluorescence yield of a core/shell system comprising a 2-monolayer thick CdS shell grown onto 3-nm CdSe seeds using c-ALD technique was compared to that of bare CdSe NCs. The saturation of cation and anion half-monolayers during the CdS shell growth was attested by corresponding changes in the trap state emission (see Fig. 3.9b). The comparison reveals an 8-fold increase in the band gap emission of CdSe core NCs as a result of the CdS shell deposition (Fig. 3.9a). The increased emission yield points towards a negligible rate of charge trapping on either surface or lattice defects of the c-ALD CdS phase. Notably, the FL quantum yield of CdSe/CdS NCs (QY = 34%) is comparable to that of thin-shell CdSe/CdS$_{2\text{ML}}$ grown via hot-injection routes, which is consistent with a good quality of the ALD CdS phase. This conclusion is further verified by the emission lifetime measurements of core/shell NCs in Fig. 3.9c, showing a 6-fold increase in the trap-limited decay of SILA-grown core/shell NPs ($\tau_{\text{CdSe}} = 5$ ns, $\tau_{\text{CdSe/CdS}} = 32$ ns).
Figure 3.9. (a). Changes in the emission quantum yield of CdSe NCs resulting from the deposition of 2·(CdS)$_1$ monolayers via c-ALD. The 8-fold enhancement manifests the formation of a high-quality CdS crystalline phase. FL quantum yield was determined relative to a
Rhodamine B dye (see the experimental section for details). (b). Changes in the trap state emission of CdSe/CdS NCs upon sequential deposition of S^{2-} and Cd^{2+} half-monolayers. (c). Fluorescence intensity decay of CdSe NCs (green curve) and CdSe/CdS NCs (brown curve). The enhanced emission lifetime in core/shell nanoparticles reflects a reduction in the rate of charge trapping on defects.

In conclusion, a general strategy was demonstrated for the synthesis of monodisperse semiconductor nanocrystals exhibiting the standard size deviation below 5%. The present approach is based on the sequential deposition of fully saturated cationic and anionic monolayers onto semiconductor nanoclusters, which leads to focusing of the nanocrystal size with increasing particle diameter. The consecutive growth of ionic layers is performed through a room-temperature colloidal ALD process which keeps precursors and nanocrystals separated in the two non-miscible phases. As a result, unreacted precursors can be fully extracted after each half-monolayer deposition, which allows avoiding the secondary nucleation. In addition to a narrow size distribution, the demonstrated methodology offers an excellent batch-to-batch reproducibility and an improved control over the nanocrystal surface composition. The present synthesis is amenable to other types of semiconductor nanocrystals and can potentially offer a viable alternative to traditional hot-injection strategies of the nanoparticle growth.

3.4 EXPERIMENTAL SECTION

3.4.1 Chemicals. Oleylamine (OLAM, tech., 70%, Aldrich), sulfur (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), 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), formamide (FA 99.6%, Acros), sodium sulfide nonahydrate (Na2S, 98%, Aldrich), cadmium acetate dihydrate (Cd(OAc)2, 98%, Acros), selenium powder (Se, 200 mesh, Acros), chloroform (anhydrous, 95%, Aldrich), methanol (anhydrous, 99.8%, Aldrich), ethanol (anhydrous, 95%, Aldrich), and toluene (anhydrous, 99.8%, Aldrich) were used as purchased. All reactions were performed under argon atmosphere using the standard air free Schlenk technique unless otherwise stated.

3.4.2 Synthesis of CdS clusters and nanocrystals. CdS clusters and nanocrystals for seeding the ALD growth of the CdS shell were synthesized according to the procedure adapted from Ref. 59. Briefly, ODE (15 ml), OA (1.4 - 4.0 ml) and CdO (0.24g) were combined in a 50mL flask and heated to ca. 250°C until CdO fully reacted. At this point all of the sulfur precursor, prepared by dissolving 0.03 g of S in 5 ml of ODE through heating to 150 ºC under argon and cooling to the room temperature was injected into the Cd flask (at 250 ºC). The amount of OA in the flask was used to control the ultimate size of CdS NCs. Typically, small amount of OA (~ 1.4 ml) promoted a slow growth of CdS crystallites with 318 nm clusters forming 1 min after the injection (evident by a sharp exciton feature). Conversely, larger amount of OA (4.0 ml) promoted a faster growth, optimal for achieving size-focusing of structures with exciton features in the λ = 390-420 nm range. After the synthesis, nanocrystals were precipitated with methanol and redispersed in toluene. Typically, to isolate the 318-nm clusters, an additional size-selective precipitation procedure was used. To this end, the product, typically containing a mixture of CdS_{318} and CdS_{360} clusters, was precipitated with a mixture of chloroform and ethanol (1:2 ratio) to get rid of heavy nanocrystals followed by the addition of excess ethanol to precipitate the secondary “318-nm cluster” fraction, which ultimately was redispersed in the minimal amount of toluene.
3.4.3 Stepwise growth of CdS nanocrystals through the Saturated Ionic Layer Adsorption. At the beginning of the synthesis, a two-phase growth solution (toluene/formamide) was loaded into a 15-ml contribute tube. To this end, 6 mL of Na₂S solution in FA was prepared first. The concentration of Na₂S was determined based on the amount of nanocrystals in the toluene layer (Fig. 3.SF2). Subsequently, a toluene layer containing CdS clusters (or nanocrystals) and 0.01-0.2 mL of OLAM were added to the reaction test tube. The concentration of OLAM was determined based on the amount of CdS NCs using Figs. 3.3 and 3.SF2. To initiate the reaction, the test tube was placed under UV light (for monitoring the emission) and agitated on a vortex shaker for approximately 30 sec. If the concentration of Na₂S was insufficient for a full layer saturation, additional Na₂S dissolved in a minimal amount of FA was added into a formamide phase of the reaction mixture. When the S²⁻ layer is fully grown, the reaction mixture was centrifuged at 5000 rpm for 1-2 min to ensure a toluene/FA phase separation. At this point, most of unreacted Na₂S is found in the formamide phase with toluene solution showing very little trace of S²⁻ ions. Any residual S²⁻ in the toluene layer was subsequently removed from the (CdS)S²⁻ product via the toluene/formamide extraction. Washing cycles were repeated until the used up formamide solution contained no residual S²⁻ as was confirmed by injecting an excess of Cd(OAc)₂ to phase-separated formamide after cleaning. Upon washing, the (CdS)S²⁻ product was isolated from the polar phase and centrifuged to remove any precipitated dots.

To deposit a cadmium layer, sulfur-saturated (CdS)S²⁻ NCs were re-dispersed in 3ml of toluene and loaded into a test tube containing a 3-ml FA solution of Cd(OAc)₂ (C=0.029 M) (0.09 mol in 3ml that was prepared: 0.046 g Cd(OAc)₂ in 6ml FA). The toluene phase was also infused with a small amount of OLAM (typically not exceeding 0.05 ml). The reaction of Cd²⁺ ions with nanocrystal surfaces was carried out by inverting the test-tube several times under UV
light until the trap state emission reached its maximum. If the amount of Cd\(^{2+}\) precursor was not sufficient for the saturation of the emission intensity, additional Cd(OAc)\(_2\) dissolved in a minimal amount of FA was added into the formamide phase of the reaction mixture. As in the case of the sulfur deposition step, the two-solvent combination was reacted by shaking. Upon completion of the Cd layer growth, the toluene/formamide mixture was phase separated by centrifuging the contents for 1-2 min at 5000 rpm and the top layer containing CdS was transferred to a clean test tube. Unreacted Cd(OAc)\(_2\) was discarded through several formamide/toluene extractions which were performed until the used-up formamide solution contained no noticeable traces of cadmium (as verified by inducing the reaction with Na\(_2\)S). Following the cleaning step, the nanoparticle layer was centrifuged to remove any aggregates.

Additional monolayers of CdS were deposited through a copious procedure. At the beginning of each cycle, CdS nanoparticles were reacted with Na\(_2\)S until the surface saturation with sulfur was reached. This process was monitored by measuring the kinetics of both the absorption and the emission profiles (Fig. 3.6a-c). The product was then washed with formamide until the residue solution became chemically pure. The used-up formamide solution was analyzed for the residue of unreacted Na\(_2\)S by inducing a reaction with Cd(OAc)\(_2\). Subsequently, Cd layer was deposited until the saturation of trap state emission was reached. Unreacted precursors were removed through several toluene/formamide extractions while aggregated nanoparticles were discarded by centrifuging. Due to changes in the total surface area of growing nanoparticles at each step, the saturation of each layer had to be verified after each half cycle.

3.4.4 Characterization. UV-vis absorption and photoluminescence spectra were recorded using a CARY 50 scan spectrophotometer and a Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy measurements were
carried out using JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanoparticle solution in organic solvent onto a carbon-coated copper grid and allowing it 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), and an id50 avalanche photodiode (Quantique).

3.4.5 Fluorescence quantum yield measurements. The FL quantum yield of both colloidal and solid NC samples was determined relative to organic dyes with known emission efficiencies using the following equation:

\[
QY_{NC} = QY_{dye} \frac{I_{NC}}{I_{dye}} \left( \frac{n_{NC}}{n_{dye}} \right) \frac{1 - 10^{-A_{dye}}}{1 - 10^{-A_{NC}}}
\]

where I is the spectrally integrated fluorescence, n is the refractive index of the sample (which for solid samples was measured using a Cauchy model at 632 nm and extrapolated down to the excitation wavelength of 532 nm), and A is the optical absorbance of the sample at the excitation wavelength. The NC samples were exited using a 532-nm monochromatic laser (GS3230-20). Rhodamine B dye in ethanol with the emission at \( \lambda = 610 \) nm was used as a reference for QY measurements. The FL was detected using a home-built system comprising Shamrock spectrograph and Andor Newton EMCCD camera.
Figure 3.SF1. A schematic illustration of the key differences between SILAR and c-ALD techniques for the nanocrystal shell growth. (a). The SILAR synthesis is performed in a single-phase reaction mixture, which results in the accumulation of unreacted precursors causing the secondary nucleation (at high precursor concentrations) or sub-monolayer growth (at low precursor concentrations). (b). The c-ALD employs a two-phase growth mixture, which is designed to separate precursors from nanoparticles. As a result, unreacted precursors can be removed after the half-monolayer (cationic or anionic) is grown.
**Figure 3.SF2.** The relationship between the minimal concentration of the Na$_2$S precursor in the formamide layer (needed for a saturated half-monolayer growth) and the concentration of CdS seeds in the toluene phase. The minimal concentration of OLAM (for stabilizing nanocrystals in the non-polar phase) is indicated for each measurement.
Figure 3. FTIR spectra of the OLAM-capped (CdS)S$_2^-$ NCs (black curve) and pure OLAM (red curve). The absence of the NH$_2$ stretch modes tells us that OLAM attaches to the surface of nanoparticles by forming a complex with the sulfur ion.
Figure 3.SF4. Evolution of the CdS$_{318\text{nm}}$ cluster absorption profile upon reacting with increasing amount of Cd(OAc)$_2$ ions in solution. The position of the exciton peak does not red-shift indicating that the surface of the CdS$_{318}$ cluster is likely to be saturated with Cd.
Figure 3.SF5. Additional TEM images of CdS NCs grown by SILA technique. (a).

CdS\textsubscript{390nm}+4(CdS\textsubscript{1}) NCs grown to a full layer saturation (b). CdS\textsubscript{390nm}+10(CdS\textsubscript{1}) NCs grown \textit{without} full layer saturation.
Figure 3 SF6. $^1$H NMR spectra of (a). OA-capped CdS and (b). OLAM-capped (CdS)S$^{2-}$ NCs after the deposition of a sulfur layer.
3.6 REFERENCES


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