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High-temperature growth of thick-shell CdSe/CdS core/shell nanoplatelets

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To optimize the optical properties of semiconductor nanoplatelets, simple routes to add high-quality shells are needed. We demonstrate uniform growth of CdS shells on CdSe nanoplatelets at 300 °C, overcoming limitations of previous low-temperature syntheses. We obtain core/shell nanoplatelets with spectrally narrow (20 nm) and efficient emission for shells up to 4 nm thick.

Colloidal semiconductor nanoplatelets (NPLs) are quasi-two-dimensional nanocrystals with atomically precise thicknesses. Due to their well-controlled size in one dimension, CdSe NPLs can exhibit narrower spectral linewidths in absorption and emission as well as larger absorption cross-sections compared to spherical CdSe quantum dots. Consequently, they are potentially useful as optical and optoelectronic materials.

However, in many applications, high input power densities are required. Under such conditions, NPLs often suffer from photo- and/or chemical instability. A general strategy to improve their performance is to add a shell of a larger band gap semiconductor, thereby separating the photoexcited excitons from the NPL surface. This can reduce interactions of excitons with surface charges and/or dangling bonds. It can also help avoid non-radiative Auger recombination. Thus, shells can reduce fluorescence quenching and intermittency (i.e., photoluminescence “blinking”). Indeed, suppressed blinking has been recently reported for core/shell NPLs.

In the specific case of CdSe/CdS core/shell NPLs, the hole is confined to the core while the electron penetrates into the shell. This leads to a significant red-shift and lengthening of the emission lifetime. Due to these properties and the enhanced absorption from the CdS shell, such core/shell NPLs can provide efficient red emitters for use in displays, LEDs, and lasers. Further, they can potentially impact luminescent solar concentrators, for which spherical quantum dots have already shown advantages.

To produce core/shell NPLs, one could adapt an approach recently developed for spherical CdSe-based quantum dots. There, shells are added through high-temperature reactions (300 °C) with low-reactivity precursors. Under such conditions, the shell grows uniformly and interfacial strains from the lattice mismatch between the core and shell are minimized by atomic reorganization. Nearly monodisperse particles with narrow emission linewidths, high photoluminescence quantum yields (QYs), and suppressed blinking can be obtained. A similar approach can also be applied to coat anisotropic shapes such as nanorods.

However, to date, this strategy has not been extended to NPLs because of their low thermal stability compared to quantum dots. Several routes have been reported for growing CdS or Cd,Zn,S shells on CdSe NPLs at room or moderate (~150 °C) temperatures. Unfortunately, due to the low reaction temperatures, such protocols have provided NPLs with low QYs or inhomogeneous shells. Especially for CdS, uniform shells and high QY have proven difficult to obtain. Hence, improved synthetic methods are needed to produce core/shell NPLs for optical applications.

Herein, we present a method for obtaining CdSe/CdS core/shell NPLs in which the shell is added at higher temperatures (~300 °C). This enables the growth of uniform and thick CdS shells, which is not possible with existing continuous-growth protocols. To develop our approach, conditions that avoid etching of the core NPLs during shell growth were first identified. We were then able to synthesize high-quality monodisperse CdSe/CdS core/shell NPLs with narrow emission linewidths, high QYs, uniform shell thicknesses, and suppressed blinking. Such samples exhibit significant spectral shifts in emission, e.g., from 515 nm for CdSe core NPLs to 670 nm for CdSe/CdS core/shell NPLs.

To prevent etching and dissolution of the NPL cores prior to shell growth, we investigated different reaction conditions. For CdSe quantum dots, shell growth involves first heating the CdSe...
cores in a mixture of 1-octadecene (ODE) and oleylamine (OAm). Then, Cd(oleate)$_2$ and 1-octanethiol, both dissolved in ODE, are slowly injected simultaneously at 310 °C. However, heating CdSe NPLs in such an ODE-OAm mixture leads to significant etching even before reaching 150 °C. This explains the disappearance of NPL absorption features in Fig. 1a. Continued heating dissolved the NPLs completely, consistent with prior studies on the etching of CdSe NPLs in the presence of OAm.$^{8,22}$ We observed that the omission of OAm resulted in reduced etching of the NPL cores (Fig. 1b). A further increase in the stability of the CdSe NPLs occurred when Cd(oleate)$_2$ was added to the mixture of ODE and NPLs (Fig. 1c). We hypothesize that the presence of excess carboxylates improves the NPL passivation (as shown recently$^{23}$), and the additional Cd$^{2+}$ ions in solution slow the dissolution of the NPLs. Unfortunately, the removal of OAm also had negative consequences. Colloidal stability and QY were reduced without OAm, presumably due to poor stabilization and passivation of neutral surface facets.$^{24}$ Thus, to maintain high QY and colloidal stability of the core/shell NPLs, we added OAm after elevated temperatures were reached. This minimized the contact time between bare NPLs and OAm. From these studies, we designed a shell synthesis where the CdSe core NPLs were first dispersed in ODE and Cd(oleate)$_2$ and degassed. Separately degassed OAm was then added before initiating the injection of 1-octanethiol. A detailed description of the synthesis protocol is provided in the ESI†.

We determined that the optimal reaction temperature was at 300 °C. Below 280 °C anisotropic shell growth occurred (Fig. S1a, ESI†), consistent with previous temperature-dependent studies on surface and absorption energies.$^{25}$ At temperatures higher than 300 °C, the NPLs increasingly morphed into spherical particles (Fig. S1b, ESI†). To minimize etching, the injection of 1-octanethiol was started at 180 °C, during the temperature rise to the reaction temperature. We observed increased emission broadening when the injection of 1-octanethiol occurred at higher temperatures (Fig. S2, ESI†) and increased formation of CdS nanocrystals as side products at lower temperatures. However, such side products can be removed by selective precipitation after the synthesis.

Following these guidelines, monodisperse CdSe/CdS core/shell NPLs with a uniform shell thickness of up to 4 nm (~14 monolayers) could be achieved (Fig. S3, ESI†). The particles emit at 660-670 nm with narrow linewidths [full-width at half-maximum (fwhm) between 60 and 70 meV]. The corresponding QYs were measured to be 50-60%. We also observed an increase in the photoluminescence lifetime compared to our CdSe NPL cores (Fig. S4, ESI†). Photoluminescence excitation spectra revealed that the emission remains efficient even with ultraviolet excitation (Fig. S5, ESI†). Our particles exhibited clear suppression of blinking (Fig. S6, ESI†).

Figure 2a shows the evolution of the absorption and emission spectra for our best synthesis, which produced core/shell NPLs emitting at 667 nm with a linewidth (fwhm) of 20 nm (~56 meV). The excitonic features continuously shift towards lower energies with increasing shell thickness due to the delocalization of the electron wave function into the shell. As is typical for our protocol, the features initially broaden and then become narrow as the synthesis proceeds. We attribute this effect to inhomogeneous shells in the early stages of growth (Fig. S7, ESI†). The shell deposits first on the edges and side facets which leads to slight thickness variations. These variations are then minimized as the growth proceeds at high temperature.

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**Fig. 1** Influence of OAm and Cd(oleate), on the etching rate of CdSe nanoplatelets. Shown is the temporal evolution of the NPL absorption features during heating of the CdSe NPLs dispersed in (a) ODE + OAm, (b) ODE, and (c) ODE + Cd(oleate)$_2$. The first data points, denoted as “RT”, are taken after degassing at room temperature.
However, we note that even for core/shell NPLs having a broader ensemble linewidth of ~70 meV, the corresponding single-NPL linewidths showed comparable values (Fig. S8, ESI†), implying minimal heterogeneous broadening. We attribute this increased linewidth to phonon coupling, perhaps due to enhanced electric fields within the particles from strain at the interface or uneven shell thickness.26 The extent of these thickness variations depends on the exact synthesis conditions.

Figures 2b and 2c show the transformation of the initial square CdSe NPL cores into rounded CdSe/CdS core/shell particles. The cubic crystal lattice of the CdSe NPL cores is preserved in the shell, as seen from close inspection of high-resolution transmission electron microscopy (HRTEM) images (Fig. 2c) as well as X-ray diffraction (XRD) measurements (Fig. S9, ESI†). Due to the slow shell growth at high temperature, the shell deposits with minimal interfacial defects. We hypothesize that defects are reduced by atomic diffusion and reorganization at these high temperatures. Previously, high-temperature annealing was shown to reduce defects in core/shell NPLs synthesized at room temperature.19

To evaluate the uniformity of the shell growth we performed scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) measurements (Fig. 3). Figure 3a shows a high-angle annular dark-field (HAADF) STEM image of an ensemble of core/shell NPLs. Particles in both top and side views are visible. Due to the higher atomic mass of Se versus S, contrast between the core and shell can be observed in the edge-on view of the NPLs. For such NPLs we measured a total thickness of ~8 nm which corresponds to a shell thickness of 3.5 nm (~12 monolayers). Furthermore, it can be seen that the shell was grown uniformly around the CdSe core. This is supported by the corresponding EDS data (Figs. 3b-d). Se and S are found in the core and shell, respectively. Figures 3e-h show EDS data of a single core/shell NPL from another synthesis. While the shell retained the original square shape of the NPL core, the core itself clearly shows a circular shape. We attribute this change in lateral extension of the CdSe core to etching of the CdSe and subsequent reorganization of the edges upon shell growth.27

In conclusion, we have presented a route to prepare CdSe/CdS core/shell colloidal nanoplatelets. By minimizing the etching of the CdSe core nanoplatelets, we were able to add CdS shells at high reaction temperatures. Thereby, we obtained uniform and bright core/shell nanoplatelets while retaining narrow emission. This synthesis protocol can result in significant improvements for a wide range of applications in optics and optoelectronics relying on efficient and narrow red emitters.

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Notes and references
§ The authors declare no competing financial interests.


