Nanoparticles

DOI: 10.1002/anie.201107452

Highly Luminescent Nanocrystals From Removal of Impurity Atoms Residual From Ion-Exchange Synthesis**

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Ion exchange of nanocrystals has the potential to emerge as an alternative to conventional routes for synthesis of ionic nanocrystals.[1–9] The facile ability to replace all cations of a nanocrystal with another cation, while preserving size and shape, allows us to employ nanocrystals as templates for the fabrication of other nanocrystals of interest.[6] Such a templated synthesis strategy is especially useful when the chemistry or crystallographic phase of the target nanocrystals is difficult to access via hot-injection methods. For instance, we recently showed[10] that $\mathrm{Cu^I}$ sulfide quantum dots prepared by hot injection mostly result in the highly Cu-deficient djurleite phase.[11,12] The stoichiometric chalcocite phase is achievable, however, by room-temperature cation exchange of template CdS quantum dots with $\mathrm{Cu^+}$ ions.

Cation exchange holds particular promise for the fabrication of multicomponent heterostructured nanocrystals,[6,9] which allow independent tunability of electron and hole wavefunctions, but present potential synthetic challenges due to their greater structural complexity. Here, it is advantageous that the anionic framework of the heterostructure is maintained during cation exchange, allowing structural preservation of interfaces and junctions that define the electronic band alignment within the heterostructure. This has made possible the design and templated fabrication of novel semiconductor heterostructures that can range[13,14] from type-I, with high quantum yield emission useful for imaging and light-emitting diodes,[15,16] to type-II, which allow charge separation for photovoltaic and photocatalytic applications.[9,17]

However, the ion exchange technique has been found to present a severe drawback: it results in nanocrystals with poor optoelectronic properties.[1] This is clear from a quantitative comparison of the optical properties of nanocrystals obtained from cation exchange with those prepared by standard hot injection for the model CdSe/CdS dot/rod heterostructure.[13–16] In this work, we trace the cause of the poor optical properties of cation-exchange-obtained nanocrystals to chemical impurities on the few atom per nanocrystal level. We have also found a method to purify the nanocrystals of these detrimental impurities post exchange and achieve optical properties comparable to those of hot-injection synthesized nanocrystals.

Hot-injection synthesis of CdSe/CdS dot/rods with a 3.9 nm dot yields highly photoluminescent nanorods with a quantum yield (QY) of over 55 %, enabled by the type-I band alignment. On the other hand, CdSe/CdS dot/rods obtained from room-temperature exchange of $\mathrm{Cu_2Se/Cu_2S}$ dot/rods with $\mathrm{Cd^{2+}}$ (see the Supporting Information) show relatively negligible emission, that is, a quantum yield (QY) of 0.07 %, almost three orders of magnitude smaller. This is despite the fact that the nanorods prepared by the two methods possess similar heterostructure morphologies, especially seed sizes, and consequently identical excitonic structures, as evidenced by the similarity of their absorption and photoluminescence spectra (Figure 1). The QY of emission is a useful optical probe of sample quality.[18] The insubstantial photoluminescence yield of the cation-exchanged samples is likely due to their poor crystallographic quality: cation exchange yields nanocrystals with a relatively high density of defect sites for nonradiative carrier recombination.

Optical and structural characterization of the cation-exchanged nanocrystals elucidated the presence of a variety of crystallographic defects, some or all of which may be responsible for the high rate of nonradiative carrier recombination. High-resolution transmission electron microscopy (HRTEM) of the cation-exchanged rods shows the presence of zinc-blende regions and associated stacking faults, as well as grain boundaries, absent in the hot-injection-synthesized

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[**] This work was supported by the physical chemistry of semiconductor nanocrystals program, KC3105 of the Director, Office of Science, Office of Basic Energy Sciences, of the United States Department of Energy under grant number DE-AC02-05CH11231. Work on cation exchange and defect purification by P.K.J. was supported by a Miller Fellowship from UC Berkeley. Work on defect purification by B.J.B. was supported by a fellowship from the Department of Energy Office of Science Graduate Fellowship Program (DOE SCGF), made possible in part by the American Recovery and Reinvestment Act of 2009, administered by ORISE-ORAU under grant number DE-AC05-06OR23100. M.J.P. was supported by a National Science Graduate Research Fellowship and by a National Science Foundation Integrative Graduate Education and Research Traineeship Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107452.

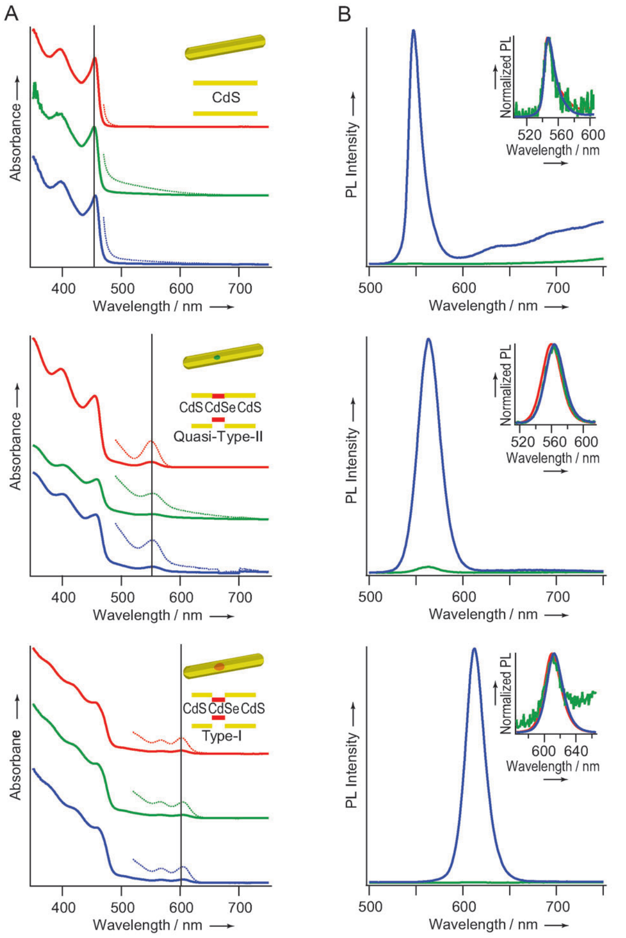

Figure 1. A) Absorbance and B) photoluminescence spectra of CdS nanorods (top), CdSe/CdS dot/rods with a 2.5 nm dot (middle), and CdSe/CdS dot/rods with a 3.9 nm dot (bottom) obtained from hot-injection (red), cation exchange (green), and post-exchange purification (blue). Dotted line shows the magnified (×5) absorption spectrum highlighting the absorption of the dot. The vertical black line in the left panel graphs indicates the peak position of the lowest exciton showing the similarity in excitonic structure for nanorod samples obtained from the three methods. Inset of A: Model of nanorod heterostructure and its band alignment. Inset of B: Normalized photoluminescence showing similarity in the photoluminescence peak positions between samples obtained from the three different methods. All photoluminescence spectra were corrected for absorbed intensity at the excitation wavelength and for self-absorption at the emission wavelength. Corrected photoluminescence spectra following integration show that the photoluminescence yield was enhanced 363-fold (top), 35-fold (middle), and 413-fold (bottom), respectively, upon purification.

nanorods, further supported by X-ray diffraction (XRD, see the Supporting Information) and previous evidence from Son et al.[1] It has also been suggested that cation-exchange results in poorly passivated nanocrystal surfaces, which may enhance the surface trapping of carriers.[1] However, for our model type-I heterojunction system, the detrimental effect of a poorly passivated surface on the photoluminescence is expected to be much smaller than that observed here due to the excitonic confinement within the CdSe dot. This implies that the surface is an unlikely contributor to the photoluminescent deterioration. However, the interface between the dot and rod may itself have a defective or strained epitaxy, serving as a strong channel for carrier dissipation. Yet another possibility is the presence of Cu impurities remnant from the cation exchange process, the likelihood of which is supported by the common occurrence of Cu doping in CdS and CdSe materials.[19–22]

Semiconductor nanocrystals synthesized by careful hot injection can be made in such a way as to have a negligible number of defects (structural or chemical impurities).[23,24] It has been suggested, although without conclusive experimental verification, that defects, if any, are “self-purified” during the nanocrystal growth process or even post synthesis (typically on the time-scale of minutes to hours), possibly due to the ease with which defects can migrate to the surface of the nanocrystal.[23–25] The anomalously high density of defects resulting from cation exchange may be a result of the fast kinetics (millisecond timescale[26]) of the process relative to thermal energy at room temperature, resulting in the defects being kinetically frozen.[27] One may therefore extrapolate that the defective nanocrystals made by exchange can undergo self-purification over time.

Indeed, CdSe/CdS dot/rods obtained from cation exchange recovered their QY up to several-fold over a period of few months at room temperature, likely because of slow purification of defects post exchange. Such purification or expulsion of defects is expected to be thermally activated. Consistently, by heating of colloidal solutions of the dot/rods (with a 3.9 nm dot) at 100 °C, we obtained a 400-fold enhancement in their photoluminescence yield within 30 h (Figure 1, bottom right). No significant change in the excitonic spectra or photoluminescence peak position was observed during the purification process, implying that no significant compositional or morphological changes accompanied the process. Control experiments with dot/rods made by hot injection showed no increase or rather a small decrease (possibly because of ligand loss) in the QY under identical heating conditions.

HRTEM images of the purified nanorods show no appreciable difference in the density of grain boundaries, zinc-blende regions, or stacking faults compared to nanorods immediately following exchange (see the Supporting Information). Thus, the photoluminescence recovery is not due to the annealing of these structural defects. Likewise, the XRD pattern stays relatively unchanged through the purification process (see the Supporting Information). Thus, the above-mentioned structural defects are not the primary cause of the poor QY and inferior optoelectronic properties of exchanged nanorods.

Attempts to passivate the surface of exchanged dot/rods by excess addition of ligands such as oleic acid did not provide any significant QY enhancement (see the Supporting Information), proving that loss of ligands is not a major cause of a poor QY. The poor QY cannot be attributed to a defective CdSe/CdS interface either: CdS nanorods without a CdSe dot show a similar purification effect. The QY of CdS nanorods obtained from exchange is enhanced 360-fold within 61 h upon heating at 65 °C (Figure 1, top right).

While structural defects appear to be relatively benign, Cu impurities remnant from cation exchange can serve as nonradiative deep electron traps or recombination centers.[28] We tested this possibility by intentionally doping CdSe/CdS dot/rods (with a 3.9 nm dot) made by hot injection with a small percentage of Cu impurities. Cu^+ impurities, being highly diffusive in a CdS lattice,[29,30] can be easily incorporated into the nanorod. There is an appreciable reduction in the photoluminescence yield even at the lowest doping of 0.02 % or 4×10^{18} cm^{-3}. The latter amounts to two impurities per nanorod on average, implying that the photoluminescence and possibly other optoelectronic properties of a nanocrystal could be sensitive to the presence of single impurity atoms. Doping with 0.4 % Cu is found to result in a 100-fold reduction in the photoluminescence QY (Figure 2, left), clearly showing the detrimental effect of Cu impurities. At such a low doping percentage, no change in excitonic absorption of the rods is observed (Figure 2, left inset), eliminating any morphological or compositional changes, especially the formation of Cu_2S domains.

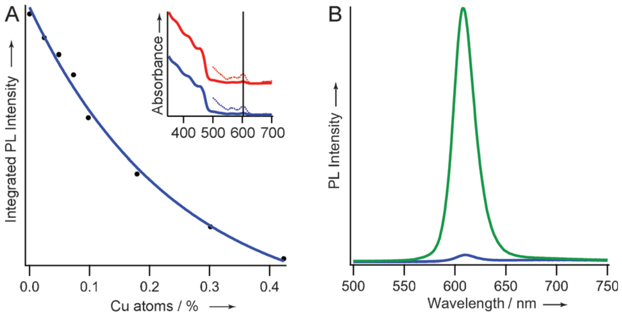

Figure 2. A) Integrated photoluminescence of hot-injection-synthesized CdSe/CdS dot/rods with a 3.9 nm dot with various percentages of Cu doping. The Cu doping percentage is an upper limit arrived at by assuming that the intentional doping method has a 100% yield. The inset shows the absorbance spectra of the dot/rods showing that the excitonic spectra are identical for as-synthesized rods (red) and those following 0.4% Cu doping, indicating that no compositional or morphological changes accompany the intentional doping at such a low doping percentage. B) Photoluminescence spectrum of CdSe/CdS dot/rods with a 3.9 nm dot from hot injection with 0.4% Cu doping (blue) and defect purified (green) by standing in solution in the presence of tributyl phosphine at room temperature for 24 h. The photoluminescence spectra were corrected as described in the caption of Figure 1. Corrected photoluminescence spectra following integration show that the photoluminescence yield was enhanced 38-fold upon purification.

Thus, Cu impurities, even on the level of few atoms per nanocrystal, are enough to result in suppressed emission in the dot/rods made by cation exchange. Note that at such low impurity concentrations, analysis of the Cu impurity levels by inductively coupled plasma mass spectroscopy is bound to be unreliable because of a much higher background of Cu^+ ions in solution, remnant from the cation exchange step. The amount of Cu is too low to be even detected in elemental analyses of the nanorods through energy dispersive X-ray spectroscopy.[6]

The intentionally doped dot/rods, when allowed to stand in solution in the presence of tributyl phosphine (TBP), conditions similar to nanorod samples obtained from cation exchange, show an enhancement in QY nearly 40-fold over 24 h at room temperature (Figure 2, right). No significant change in excitonic absorption was seen. Phosphines, being soft bases, are common binding ligands for Cu^+, a soft acid,[31–34] providing an additional driving force for the expulsion of Cu impurities. Control experiments with undoped dot/rods from hot injection allowed to stand in the presence of TBP did not show any QY enhancement, rather a slight decrease by 13 %.

Purification of Cu impurities from cation-exchanged nanorods is thus aided by the driving force provided by selective binding of Cu^+ ions by phosphine and thermal activation of impurity diffusion by heating. It is possible that there is an equilibrium between Cu^+ impurities within the lattice and those bound to phosphine. Addition of excess TBP during cation exchange would favor Cu^+ expulsion, however, severe ligand exchange and nanorod etching limit high TBP concentrations.

Cation-exchanged nanorods following purification compare well with those made through conventional synthesis, in terms of their QY (see the Supporting Information). For instance, exchanged dot/rods (with a 3.9 nm dot) following purification show a QY of 30 % approaching the 55 % QY of dot/rods obtained from hot-injection synthesis. When the marginal reduction in photoluminescence because of heating-induced ligand loss is accounted for by a heating control, we found that the QYs of these dot/rods are similar for exchanged and hot-injection-synthesized samples. Similarly, exchange-obtained CdS nanorods (without a dot) following purification achieve a QY that is three-fifths that of nanorods obtained from hot injection, even without accounting for ligand loss. Impurity purification thus allows exchanged nanocrystals to achieve a QY approaching the inherent value in the absence of detrimental impurities.

Dot/rods with a smaller 2.5 nm dot (quasi type-II alignment[13]) show order-of-magnitude QY recovery, but lower compared to the above two cases: following purification we obtain a QY that is one quarter the QY of dot/rods from hot-injection. It is likely, due to entropic reasons that, even following purification, a small number of impurities remain behind, distributed over the ensemble of nanocrystals. Since the quasi type-II dot/rod is a charge-separated system with a more delocalized electronic wavefunction,[13,14,17] the efficiency of radiative e-h recombination would be more sensitive to these remnant impurities. On the other hand, in the type-I dot/rods and the CdS rods, where the e-h pair is relatively bound,[35,36] the effect of remnant impurities on radiative recombination would be lower. For CdS nanorods (Figure 1 B, top panel), in addition to excitonic emission, surface trap emission (at $\lambda > 600$ nm) is also enhanced upon purification, corroborating the role of Cu impurities as nonradiative traps or recombination centers. While it is difficult to ascertain the location of the Cu impurities, if the impurities were localized chiefly to the surface of the nanorod, the emission of the type-I dot/rods (where the exciton is shielded from the surface) would not be affected as drastically.

In summary, we have found that by providing appropriate thermal activation and driving force, nanocrystals obtained from ion exchange can be purified of residual impurities, resulting in materials of high optoelectronic grade. It is possible that the relative ease and speed of the purification process are unique to nanosized crystals, which have implications for models of doping and self-purification on the nanoscale.[18] The activated dopant purification method showed here may extend to other nanostructure fabrication methods that result in inherently impure samples.

Received: October 22, 2011
Revised: December 19, 2011

Keywords: copper · impurity removal · ion exchange · luminescence · nanoparticles

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