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Efficient Emission from Core/(Doped) Shell Nanoparticles: Applications for Chemical Sensing

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ABSTRACT

We have studied manganese doping of zinc selenide core/zinc sulfide shell nanocrystals (NCs) where the impurity phosphor resides primarily in the shell. We have found that a simple two-step synthesis can be used to create these nontoxic materials that display efficient energy transfer from the core to the Mn doped shell. These core/shell NCs retain ample quantum efficiency (∼25%) when solubilized in water, which opens the possibility of using these materials as bioimaging agents. As recent work has shown that nanocrystals can be functionalized with organic dyes to operate as ratiometric chemical sensing agents, we have conjugated the doped NCs with an organic dye to showcase efficient Förster resonant energy transfer from the shell-doped phosphor to the surface-bound dye. This result indicates that doped NCs can be used to develop nontoxic ratiometric sensing/biological imaging agents.

Direct band gap semiconductor nanocrystals (NCs) are inorganic lumophores that have high quantum efficiencies, tunable and narrow emission spectra, and excellent chemical stability.[1−3] These properties have created many applications of NCs for LEDs, lasers, barcoding, and biological and chemical sensing.[4−10] However, the band gap of most emissive semiconductors is either too high or too low to easily make visible emitting NCs, cadmium chalcogenide systems generally being the exception.[11] Unfortunately, the toxicity of cadmium is a concern that will limit the use of these visible emitting NCs, especially for applications directly related to human health. However, recent reports have demonstrated visible phosphorescence from doped NC systems,[12−18] which is especially interesting when observed in nontoxic doped NCs as this may circumvent the issues with cadmium toxicity.

Doping with atomic impurities is an efficient way to manipulate the emission spectra of semiconductor NCs. In this vein, many research groups have developed procedures for doping of high band gap materials such as zinc selenide with manganese (ZnSe:Mn NCs), which results in visible phosphorescence from the Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ transition centered at ∼580 nm. These materials may be then solubilized in water for use as nontoxic biological imaging agents.[19] Given the recent interest in water soluble NC−organic fluorescent dye conjugates for chemical and biological sensing, we examined whether doped NCs may also be utilized within a nontoxic sensing motif as well. To this end, we have developed a doping scheme for zinc selenide/zinc sulfide NCs with manganese impregnated primarily within the shell. We have shown that the chemical conjugation of an energy accepting organic fluorescent chromophore results in efficient energy transfer from core → shell → dye. This observation creates inroads toward the development of nontoxic ratiometric NC chemical sensors as discussed below.

In our early investigation, we found that doping core NCs, even semiconductors such as zinc selenide and cadmium sulfide, was difficult and often resulted in weakly phosphorescent materials. Given several recent findings on the doping of semiconductor NCs,[13−15] we adopted a core/shell scheme to impart phosphorescence to ZnSe NCs. First, core zinc selenide NCs were synthesized by a modification of a previously reported procedure.[21] Next, a trioctylphosphine (TOP) solution of zinc sulfide shell precursors with a small (∼10% vs Zn) level of manganese stearate was slowly dripped into the flask using an addition funnel at a reduced temperature.[22,23] While we were able to observe phosphorescence from the manganese dopants at this time, the emission was weak and was almost entirely quenched upon dilution into hexane, most likely due to the loss of organic caps off the NC surface. We then precipitated the NCs with a nonsolvent and then disbursed the material into a solution of distilled trioctylphosphine oxide (TOPO) and *n*-hexylphosphonic acid (HPA). At this point, the phosphorescence from the dopants greatly increased and further brightened as we slowly added more zinc and sulfur precursors to create

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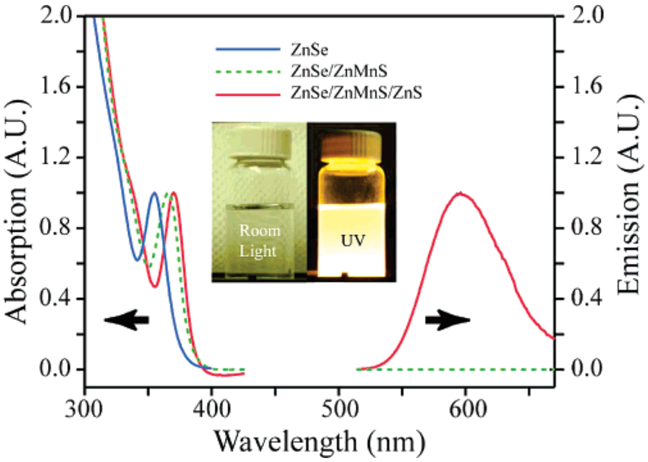

Figure 1. Absorption and emission of core ZnSe, core/shell ZnSe/ZnMnS, and ZnSe/ZnMnS/ZnS NCs. The formation of the final layer improves the manganese emission by a factor of several hundred fold. Inset: ZnSe:Mn^{2+} NCs solubilized in water under room light and UV irradiation.

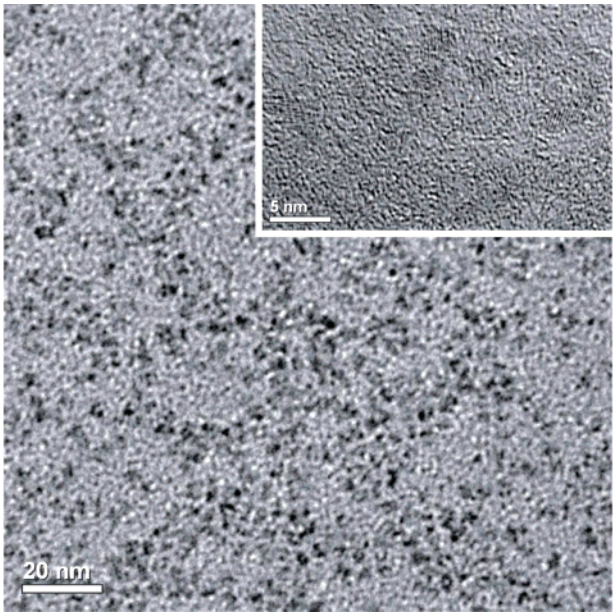

Figure 2. TEM micrograph of the ZnSe/ZnMnS/ZnS NCs. Inset reveals the crystallinity of the core/doped shell NCs.

a thicker ZnS shell. Shown in Figure 1 is the absorption and emission spectra of the ZnSe cores, ZnSe/ZnMnS doped shell materials, and ZnSe/ZnMnS/ZnS NCs. As can be seen, the absorption red-shifts with every added layer, which is indicative of shell formation. Further, Mn^{2+} centered emission at ~580 nm is increased dramatically from surface passivation as seen in the ZnSe/ZnMnS to ZnSe/ZnMnS/ZnS spectra. Shown in Figure 2 are TEM micrographs of our multilayered doped NCs, which are larger (3-4 nm) than the ZnSe cores (~2.5 nm)[24] and appear to have a slightly elongated structure.

Our development of efficient phosphorescent NC materials from core/doped shell NCs relied on several previous observations. First, small semiconductor clusters are more resistant to impurity doping than larger NCs.[13] Further, it is known that the binding, and thus residence time, of guest impurities on a growing NC surface has a large effect on the ability to envelop that impurity within a host NC framework.[13,14] As it has been predicted from theoretical modeling that the manganese has a greater interaction with a zinc sulfide surface versus zinc selenide, doping a ZnS shell should result in better incorporation of Mn^{2+} into the NC system.[13,14] Impurity emitters are also known to be more efficient and less prone to self-quenching if they are diluted within the outer edges of a NC (or located in shell of a core/shell material).[15] Our method combines all of these effects in the approach to impregnate impurity phosphors within the outer shell of a strongly binding material. In the course of this work, we discovered that shell-doped NCs are also very sensitive to the organic passivating layer on their surface through the observation of phosphorescence quenching upon dilution of ZnSe/ZnMnS NCs and their subsequent brightening in TOPO solution. This fact led us to grow a thicker shell of ZnS in TOPO/HPA solution, which results in enhanced stability toward dilution or aqueous micelle encapsulation as discussed below. The quantum yield of these ZnSe/ZnMnS/ZnS samples was on average 25%, with 35% representing our best sample and 10% our worst. We also determined whether phosphorescence was occurring from the few dopants that become embedded directly in the core during the first ZnMnS passivation by addition of the manganese precursor in TOP solution without the zinc sulfide shell-forming compounds. We then precipitated the materials and overcoated the core Mn^{2+} doped ZnSe NCs with a shell of ZnS in TOPO/HPA solution. While we do observe phosphorescence from Mn^{2+} impurities that must be bound within the core, the emission is overall 10× weaker than observed in core/doped shell NCs. At the suggestion of a reviewer, we also examined the hyperfine coupling of the Mn ions from EPR experimentation. The hyperfine coupling was found to be $63.5 \pm 1.4 \times 10^{-4}$ cm^{-1}, which is more similar to Mn^{2+} ions bound in a ZnS NC matrix (64.5×10^{-4} cm^{-1})[25] compared to ions within ZnSe NCs (60.4×10^{-4} cm^{-1}).[26]

While doped NCs are of fundamental interest and may be useful as nontoxic bioimaging agents, we examined these materials as candidates for ratiometric sensing using Förster resonant energy transfer (FRET). Recently, there has been a great effort to develop and study NC/dye-coupled complexes where the NC donates energy to the organic fluorophore.[27−33] By manipulating the transfer of energy within the NC/dye coupled constructs, several investigators utilized NCs to study dynamical biological processes, to monitor sugar levels in solution, to detect explosives, and to measure solution pH.[10,29−33] We sought to study energy transfer in doped NCs by attaching an organic dye with an absorption spectrum that overlaps the dopant emission, where the efficiency was measured by the quenching of dot fluorescence and by time-resolved emission. First, the ZnSe/ZnMnS/ZnS NCs were solubilized in water by mixing precipitated NCs with an octylamine-modified poly(acrylic acid)[34] in a chloroform cosolvent.[35] The solvent is removed in vacuo and the material is then solubilized in water, with the NCs residing within the hydrophobic core of the micelles formed by the am-

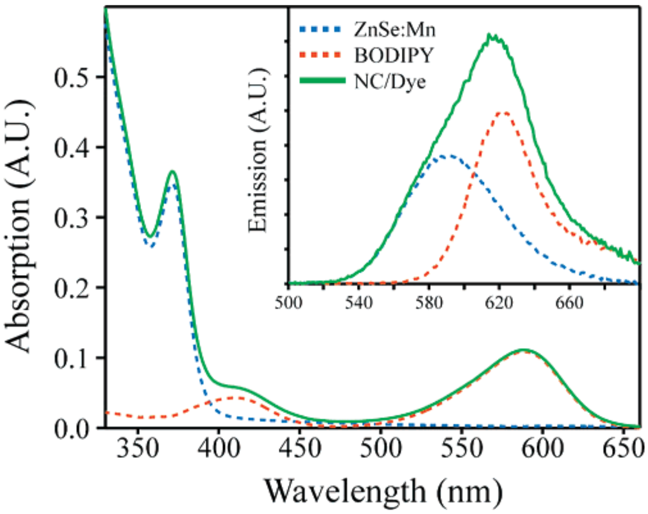

Figure 3. Absorption and emission of BODIPY 577/618 labeled ZnSe:Mn. The spectra are easily deconvolved using the NC and dye alone spectra (dotted lines). The quenching of the manganese emission suggests ~45% FRET efficiency as supported from time-resolved emission studies.

phiphilic polymer.[35] The quantum yield of these materials is still appreciable (25%) after water solubilization. After filtering and dialysis, the aqueous solution is charged with a small amount quantity of BODIPY 577/618 maleimide dissolved in dimethylformamide. The conjugation of the maleimide dye with the thiol group[34] of the modified poly-(acrylic acid) is performed overnight, with subsequent dialysis to remove any unreacted dye. While the coupling efficiency of the dye to the NC appears to have occurred with 100% yield, the BODIPY 577/618 dye is hydrophobic, so preferential solubilization of the dye into the hydrophobic interior of the NC containing micelles vs the chemical conjugation to thiol functionality is likely a factor in this observation.[36]

Shown in Figure 3 is the absorption and emission spectrum of our doped NC/organic dye-coupled construct, which is easily deconvolved into ZnSe/ZnMnS/ZnS and dye-only properties. We found that the energy efficiency of donation from the NC to the fluorescent organic dye is 45% based on the NC emission quenching compared to a control sample of the same ZnSe/ZnMnS/ZnS composition. We also confirmed energy transfer through examination of the time-resolved emission using a Perkin-Elmer Victor ^{3}V multichannel plate reader. Shown in Figure 4 is the early time-resolved emission of Mn^{2+} from water-solubilized ZnSe/ZnMnS/ZnS and ZnSe/ZnMnS/ZnS:BODIPY conjugates. These data have multiple decay channels that were fit to a stretched exponential form $e^{-(t/\tau)^{\beta}}$, where t is time, τ is the characteristic lifetime, and β is the stretching parameter. The emission of the Mn^{2+} impurities decays at a faster 650 ± 80 μs rate when conjugated to the BODIPY dye acceptor compared to the unconjugated material (870 ± 70 μs). The stretching factor β also decreases from 0.67 in the fit to ZnSe/ZnMnS/ZnS down to 0.57 in the NC/dye couple, which implies that more emissive decay channels are operating in the coupled NC/dye as expected. While the FRET efficiency of 26 ± 11% is less than observed based on NC quenching in the coupled construct, the differences are likely due to our use of a stretched exponential fit, overlap of the NC, and dye emission and possibly dye photobleaching during the experiment.

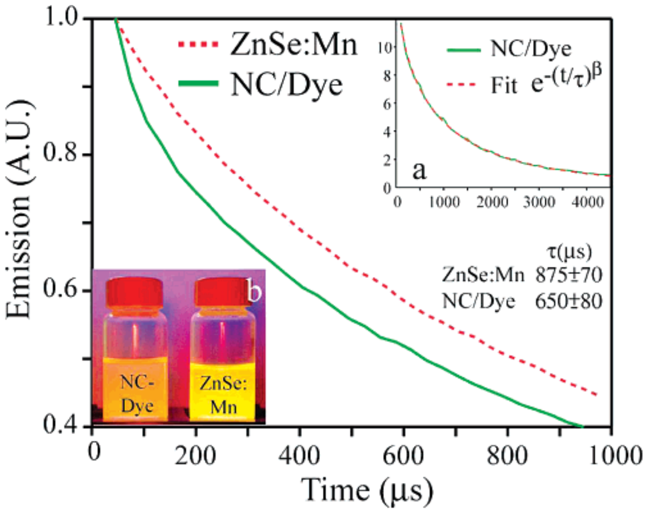

Figure 4. Early time-resolved 580 nm emission from ZnSe:Mn and dye-conjugated ZnSe:Mn:BODIPY. Inset: (a) The long time scale decay and subsequent stretched exponential fit for the NC/dye couple. (b) Photograph of water-soluble ZnSe:Mn NCs and the ZnSe:Mn:BODIPY dye coupled construct under UV excitation. The NC/dye is red-shifted with respect to the unconjugated material due to BODIPY 577/618 emission.

These data suggest that we may use doped NCs as phosphorescent donors in FRET sensing schemes. First, sensing as a function of donor lifetime is much easier when using phosphorescent materials and helps reduce problems with autofluorescence background from biological samples.[37] Further, the efficiency of energy transfer is likely facilitated though the coupling of the phosphors in the shell; this should have the effect of reducing the distance between the donor and acceptors, which if not controlled properly can result in poor FRET efficiency.[38] Most importantly, the nontoxic nature of ZnSe/ZnMnS/ZnS:dye sensing NCs will pave inroads for semiconductor nanotechnology in matters of direct concern for human health. In the future, we hope to use doped NCs to create two sensing motifs within the same construct where the emission of the core and a lightly doped shell undergo energy transfer to two different chemically sensitive dyes. Consequently, the use of doped NC materials as FRET chemical detectors has enormous possibilities for ratiometric, nontoxic multiplexed chemical sensing.

In conclusion, we have shown that doping the shell of NCs is an efficient way to synthesize bright, emissive ZnSe:Mn NCs. After secondary passivation with zinc sulfide, these materials are easily water solubilized and may be conjugated with organic energy accepting fluorescent dyes. We have found that this process is robust and insensitive toward variations in the reaction conditions as discussed in the Supporting Information. These nontoxic emissive NCs can thus be used within chemical/biological sensing motifs and will open inroads for the development of these materials in areas that directly impact human health.

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Supporting Information Available: All procedures, chemicals, and processing methods as well as characterization; also photoluminescence excitation (PLE), elemental analysis, and EPR data. This material is available free of charge via the Internet at http://pubs.acs.org

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