Nanocrystals for Luminescent Solar Concentrators

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ABSTRACT: Luminescent solar concentrators (LSCs) harvest sunlight over large areas and concentrate this energy onto photovoltaics or for other uses by transporting photons through macroscopic waveguides. Although attractive for lowering solar energy costs, LSCs remain severely limited by luminophore reabsorption losses. Here, we report a quantitative comparison of four types of nanocrystal (NC) phosphors recently proposed to minimize reabsorption in large-scale LSCs: two nanocrystal heterostructures and two doped nanocrystals. Experimental and numerical analyses both show that even the small core absorption of the leading NC heterostructures causes major reabsorption losses at relatively short transport lengths. Doped NCs outperform the heterostructures substantially in this critical property. A new LSC phosphor is introduced, nanocrystalline Cd$_{1-x}$Cu$_x$Se, that outperforms all other leading NCs by a significant margin in both small- and large-scale LSCs under full-spectrum conditions.

KEYWORDS: Luminescent solar concentrator, phosphor, doped nanocrystal, nanocrystal heterostructure

Luminescent solar concentrators (LSCs) are antenna systems that harvest sunlight and concentrate photons through the processes of photon absorption, luminescence, and waveguiding. One attractive LSC device comprises a planar waveguide containing embedded luminophores with photovoltaics (PVs) mounted at the waveguide edges, as depicted in Figure 1A. In this device, the concentrated photons are converted to electricity by the PVs, allowing large-area solar harvesting while requiring only small-area PVs. Such LSCs can possibly lower the cost of solar energy.1–3 Specific LSC applications include solar collectors for integration into smart windows, electronic devices, or fiber optics,3,4 photon transport for passive daylighting,5,6 and active color filters (e.g., in tandem PV cells’ or greenhouse panels’). Regardless of their specific application, LSCs universally rely on photon transport over macroscopic distances, which makes them susceptible to a variety of loss mechanisms. For a waveguide as in Figure 1A made of glass or plastic (n ~ 1.5), approximately 75% of the emitted photons are successfully trapped in waveguide modes1 with the remainder lost to the “escape cone” defined by Snell’s law. Photons that are captured by total internal reflection can still be lost via scattering from the waveguide surface, internal defects, or even the luminophores themselves (such as with microcrystalline phosphors’9), or via reabsorption by the luminophores followed by nonradiative decay or emission into the escape cone. Reabsorption losses have historically limited practical implementation of large-scale LSCs.3,10,11

Recent advances in the synthesis of luminescent nanocrystals (NCs) with high photoluminescence (PL) quantum yields, tunable solar absorption, and good photostability have stimulated interest in nanocrystals for LSC technologies.12–14 Several reports have proposed that NCs can solve the reabsorption problem.15–19 One strategy for eliminating self-absorption involves the growth of NC heterostructures that integrate wider-gap semiconductors with small cores having a narrower bandgap (e.g., CdS on CdSe cores, Figure 1B–1G).15,18,19 In such NCs, the wider-gap material dominates the absorption spectrum, and red-shifted luminescence occurs either from the core or from spatially indirect transitions across the heterointerface. Large shell/core volume ratios imply small relative absorption from the luminescent excited state. Doped semiconductor NCs have also been demonstrated to show small LSC reabsorption losses.17 In Mn$^{2+}$-doped ZnSe NCs, for example, the NC efficiently sensitizes excitation of Mn$^{2+}$ impurity ions to their $^4T_1$ ligand-field excited state, which emits with high quantum yield and a very large effective Stokes shift that results in little or no reabsorption losses in the corresponding LSCs.17

The vastly different device configurations used in previous studies of nanocrystal LSCs make direct comparison of nanocrystal performance difficult. For example, device thicknesses ranged from a few hundred microns16,17 to over 1 cm15,18 and transverse optical densities at the NCs’ first absorption features (OD$_1$) ranged from 0.1 to 0.6. Both of these parameters affect reabsorption, which is proportional to the concentration of luminophore and hence determined by the ratio of OD$_1$ to waveguide thickness ($t$) according to Beer’s law.
For practical applications, both OD and \( t \) will undoubtedly require careful optimization in planar 2D LSCs based on physical and economic criteria, and developments in microcell LSCs or other configurations may even lead to entirely new structural paradigms. In parallel, the physical properties of NCs can be optimized independently to yield a portfolio of luminophores that will excel in many different LSC device configurations.

Here, we report the quantitative assessment of four types of nanocrystals as potential LSC luminophores: the CdSe/CdS core/shell and dot-in-rod heterostructures of Figure 1B-i,ii, and two new doped-nanocrystal LSC phosphors. In one, we have modified our previously reported motif of Mn\(^{2+}\)-doped ZnSe NCs by incorporating Cd\(^{2+}\) to increase solar absorption (Figure 1B-iii). For capture of an even broader portion of the solar spectrum, we have also used narrower-gap CdSe NCs to sensitize Cu\(^{+}\) luminescence (Figure 1B-iv).

Figure 1D shows representative TEM images of the CdSe/CdS core/shell NCs, CdSe/CdS dot-in-rod NCs, Zn\(_{0.87}\)Cd\(_{0.11}\)Mn\(_{0.02}\)Se/ZnS NCs, and Cd\(_{0.999}\)Cu\(_{0.001}\)Se NCs. The core/shell NCs of Figure 1D-i and the dot-in-rod NCs of Figure 1D-ii were grown using the same \( d = 2.7 \text{ nm} \) wurtzite CdSe cores. The CdSe/CdS core/shell NCs appear to be octahedrally faceted with an average side length of \( 13.5 \text{ nm} \), implying a CdS/CdSe volume ratio of 114:1. The CdSe/CdS dot-in-rod NCs have an average overall dimension of \( 6.1 \times 32.2 \text{ nm} \), and a CdS/CdSe volume ratio of 110:1. The Zn\(_{0.87}\)Cd\(_{0.11}\)Mn\(_{0.02}\)Se cores showed an average diameter of \( 3.2 \text{ nm} \) and a similar distribution of shapes. The Cd\(_{0.999}\)Cu\(_{0.001}\)Se NCs shown in Figure 1D-iv appear roughly spherical with an average diameter of \( 5.7 \text{ nm} \).

Using a one-dimensional liquid waveguide with translatable excitation (Figure 1C) as a standard device geometry, we have quantified the reabsorption losses of these four types of nanocrystals by measuring their luminescence spectra as a function of photon transport distance, \( L \), up to 1.2 m, encompassing the length scales considered relevant for practical solar windows, panels, or daylighting, for example. These measurements agree well with the reabsorption probabilities predicted from NC absorption and PL spectra. The results show that reabsorption losses remain a major problem for the two leading heterostructured NC phosphors but are more effectively eliminated in both types of doped semiconductor NCs. In particular, the copper-doped NCs are found to be the “best-in-class” phosphors for full-spectrum applications, outperforming the other nanocrystals in total solar concentration at both short and long LSC lengths. In addition to highlighting doped NCs as a promising new class of LSC luminophores, this work provides a benchmark for quantitative evaluation of new LSC luminophores developed in the future.

Figure 2A plots absorption and PL spectra of solutions of the same NCs, all with concentrations adjusted to reach OD \( \sim 1 \) at the first intense absorption feature in a 1 mm path length cuvette. The wavelengths of these first absorption features (\( \lambda_{\text{abs,max}} \)) are listed in Table 1. These data confirm previously reported spectra of similar samples. From these spectra, all samples appear to have minimal overlap between absorption and luminescence, as desired for LSC applications. It is...
important to recognize, however, that the critical transport direction in LSCs is lateral, not normal to the surface, and that lateral device dimensions are typically orders of magnitude larger than the pathlengths used to collect these and other published NC absorption spectra. To illustrate, Figure 2B plots absorption spectra of the same NC solutions measured using a 1 cm path length cuvette and magnified 10-fold for an effective 100× magnification. Absorption features from the CdSe cores of the CdSe/CdS heterostructures are now clearly visible, but the Zn0.87Cd0.11Mn0.02Se/ZnS and Cd0.999Cu0.001Se NCs still show only weak, broad absorption in the vicinity of their PL. On the basis of Mn2+-doped ZnS thin films,24 the extinction coefficient associated with the luminescent A1 → T1 transition is on the order of 1 M−1 cm−1, corresponding to an OD of less than 7 × 10−5 in Figure 2B. We thus attribute the small tail in the Zn0.87Cd0.11Mn0.02Se/ZnS absorption spectrum to NC surface states, or possibly trace impurities in solution, but not to the luminescent center itself. Indeed, some of this absorption tail could be removed by addition of tributyl phosphine (TBP, see Supporting Information Figure S1), which suggests it may arise from NC surface oxidation. Overall, this feature has an absorbance of 0.01 at 600 nm over 1 cm, and the TBP also contributes small vibrational overtone absorption peaks at 850 and 925 nm. The Cd0.999Cu0.001Se NCs have a small amount of strongly reabsorbed excitonic PL from a subset of undoped NCs, which accounts for roughly 3% of the overall PL. The magnified absorption spectrum of these NCs shows a broad absorption tail that overlaps the blue edge of the red-shifted PL feature (700–850 nm). We attribute this absorption to the MLCT transition that is responsible for the PL.25 Much of

Figure 2. (A) Absorption spectra (solid lines with shading) over a 1 mm path length and dilute photoluminescence spectra of Cd0.999Cu0.001Se (maroon, d = 5.7 nm), CdSe/CdS core/shell NCs (red, core d = 2.7 nm), CdSe/CdS dot-in-rod NCs (green, core d = 2.7 nm), and Zn0.87Cd0.11Mn0.02Se/ZnS (blue, core d = 3.2 nm). (B) Absorption spectra of the same samples measured in a 1 cm path length cuvette illustrating the overlap between absorption and PL. Note the 10x magnified y-axis. (C) Reabsorption probability, R(l), calculated from the spectra in panel B according to eq 1 and plotted versus l. The dashed line indicates R0.5, which for a given sample represents the value of l corresponding to 50% probability of reabsorption.

Table 1. Characterization Metrics for Nanocrystalline LSC Phosphors

<table>
<thead>
<tr>
<th>NC Sample</th>
<th>λthresh (nm)</th>
<th>R0.5a</th>
<th>L1/2 (cm)b</th>
<th>ηPLc</th>
<th>abs. solar flux (Asol,NC) × 1020</th>
<th>projected FG 120 cm × 120 cm 2-D LSC (G = 300)</th>
<th>projected FGmax for 2-D LSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn0.87Cd0.11Mn0.02Se/ZnS</td>
<td>429</td>
<td>470</td>
<td>118</td>
<td>0.88d</td>
<td>1.5</td>
<td>8.6</td>
<td>32.9</td>
</tr>
<tr>
<td>Cd0.999Cu0.001Se</td>
<td>624</td>
<td>320</td>
<td>42</td>
<td>0.27d (0.40)d</td>
<td>8.9</td>
<td>10.1 (16.0)</td>
<td>15.6 (26.2)</td>
</tr>
<tr>
<td>CdSe/CdS core/shell</td>
<td>480</td>
<td>92</td>
<td>12</td>
<td>0.68d (0.86)d</td>
<td>3.3</td>
<td>5.7 (9.0)</td>
<td>7.2 (12.3)</td>
</tr>
<tr>
<td>CdSe/CdS dot-in-rod</td>
<td>476</td>
<td>24</td>
<td>4</td>
<td>0.86d</td>
<td>2.9</td>
<td>4.2</td>
<td>5.4</td>
</tr>
</tbody>
</table>

a Calculated using eq 1. b For comparison, measurements with the benchmark organic dye perylene yield L1/2 = 4 cm (Supporting Information, Figure S2). cWhere different from those measured for the samples in Figure 2, the best-reported luminescence quantum yields are given in parentheses. dFrom this work, measured using 385 nm excitation. e From ref 19. f In units of photons/(m² s). For reference, the total solar flux absorbed by bulk Si is 24.8 × 10²⁰ photons/(m² s) and for bulk CdSe is 11.6 × 10²⁰ photons/(m² s). gCalculated using the best-reported luminescence quantum yield.
the Cd$_{0.999}$Cu$_{0.001}$Se PL is shifted to even longer wavelengths (>850 nm), where the absorption spectrum shows only a very small tail that is again likely due to NC surface states.

To assess LSC applicability, the absorption and PL spectra in Figure 2 can be used to estimate the probability of reabsorption of emitted photons by these NCs. One way to do so is to quantify the parameter $S$ introduced in ref 10, which represents the ratio of extinction coefficients at the absorption and emission maxima. $S$ does not take into account the absorption or PL lineshapes, however, and it is difficult to interpret for some NCs that lack a well-defined absorption maximum. Instead, we analyze the probability that an emitted photon will be reabsorbed over a reduced path length $l$, as given by eq 1.26

$$R(l) = \int _{\lambda = \lambda_{\text{cut-off}}} ^{\lambda_{\text{em}}} PL_{\text{norm}}(\lambda) \left(1 - 10^{-A_{\text{norm}}(\lambda)}\right) d\lambda$$

$$l = \frac{L - \text{OD} t}{t}$$

Here, $PL_{\text{norm}}(\lambda)$ and $A_{\text{norm}}(\lambda)$ represent the luminescence and absorption spectra, normalized by area and at $\lambda_{\text{threshold}}$, respectively. The reduced path length $l$ is defined in eq 1b and accounts for device geometry trade-offs between luminophore concentration and waveguide thickness ($t$) governed by Beer's law. For example, the device structure from ref 18 ($t = 5$ mm, OD$_t = 0.2$, $L = 21.5$ cm) has a maximum $l$ of $\sim 8.6$, which corresponds to $L = 1.4$ cm in the liquid waveguide of Figure 1C ($t = 1.65$ mm, OD$_t = 1$). Other recent NC LSC devices have had maximum $l$ values of $\sim 5.5$, 17 $\sim 0.6$, 15 and $\sim 3$, 17 although exact determination of these values is difficult due to the varying shapes and configurations of these devices. Using eq 1a, $R(l)$ was calculated from each set of spectra in Figure 2 for values of $l$ up to 730 (Figure 2C). $R(l)$ increases most rapidly with increasing $l$ for the two NC heterostructures and less rapidly for the two doped NCs, illustrating smaller reabsorption losses in the latter. Because $R(l)$ is a complex function of $l$, it cannot be summarized using any single parameter, but we find that the reduced path length at which there is a 50% probability of reabsorption ($R_{0.5}$) provides a useful device-independent luminophore figure of merit calculable from only absorption and PL spectra. Values of $R_{0.5}$ for the nanocrystals of Figure 2 are compiled in Table 1. As anticipated from the spectra of Figure 2B, $R_{0.5}$ is significantly larger for the doped NCs than for the heterostructure NCs, which suggests that LSCs made from the doped NCs should suffer less from reabsorption losses. Although $R(l)$ and $R_{0.5}$ provide useful metrics for estimating reabsorption probabilities, any quantitative prediction of LSC device performance must take into account numerous other factors including device geometry, PL quantum yields, solar absorption, waveguide modes and losses, and scattering losses. It is thus challenging to compare phosphors for large-scale LSC applications with confidence without further experimental input. Motivated by this challenge, we therefore performed a direct empirical comparison of these NCs in the large-scale LSC configuration depicted in Figure 1C.

Solutions of the four NC phosphors described above with OD$_t = 1$ (over 1 mm) were loaded into the liquid-waveguide device of Figure 1C. Figure 3A–D show their luminescence spectra collected at different values of $L$, where $L$ is the distance between the excitation source and the end of the waveguide (see Experimental Methods). The three-dimensional plots show PL intensity as a function of wavelength and $L$. Figure 3A shows that much of the CdSe/CdS dot-in-rod NC PL is lost within the first few centimeters, and only some of the lowest-energy PL is detectable beyond $\sim 20$ cm. The observed PL redshift is due to greater reabsorption losses on the higher energy side of the PL spectrum, as anticipated from Figure 2B and illustrated schematically in Figure 3E. The CdSe/CdS
core/shell NC data in Figure 3B also show a rapid loss of PL intensity accompanied by a PL red shift with increasing \( L \). In contrast with the NC heterostructures, the two doped NCs show little or no PL redshift with increasing \( L \). Figure 3C plots PL spectra of the Zn\(_{0.87}\)Cd\(_{0.11}\)Mn\(_{0.02}\)Se/ZnS NCs, which decrease gradually in intensity with increasing \( L \), accompanied by only minor spectral changes. These data are consistent with the absorption spectrum in Figure 2B, which shows nearly uniform, weak absorption across the PL energy range. At \( L \approx 50 \) cm, small dips become evident in the Mn\(^{2+}\) PL spectra arising from absorption by C–H stretching harmonics of the surface ligands and solvent. Similar data are obtained for the Cd\(_{0.999}\)Cu\(_{0.001}\)Se NCs (Figure 3D). As expected from Figure 2, the excitonic emission and the blue edge of the Cd\(_{0.999}\)Cu\(_{0.001}\)Se ML\(_{<10}\)CT PL band are lost to reabsorption, but the red edge decreases only gradually with increasing \( L \). The feature at \( \approx 930 \) nm arises from fiber transmission-loss effects.

Figure 4A summarizes the results of Figure 3 by plotting integrated PL intensities versus \( L \) for all four NC phosphors, normalized at \( L = 0 \). These traces were corrected for waveguide losses, obtained by measuring similar data from 100-fold diluted samples of Zn\(_{0.87}\)Cd\(_{0.11}\)Mn\(_{0.02}\)Se/ZnS and Cd\(_{0.999}\)Cu\(_{0.001}\)Se NCs, but the uncorrected data are qualitatively very similar (see Supporting Information), confirming that the actual device performance is primarily determined by the phosphor performance. Importantly, because these data were all collected under identical conditions, they allow a quantitative model-independent comparison of the four NCs for potential large-scale LSC applications. The dot-in-rod and core/shell NCs show distinctly nonexponential PL decay with \( L \), whereas the PL from the two doped NCs appears to drop more exponentially with \( L \). The nonexponential decay with \( L \) stems from the existence of nonuniform absorption across the PL spectrum in the two heterostructure NCs. This curvature is predicted remarkably well by eq 1, as shown in Figure 2C, confirming that the actual device performance is primarily determined by the phosphor performance. The trend in \( R_{\text{NL}} \) values is nearly an order of magnitude larger than the NC heterostructures (Table 1). The \( R_{\text{NL}} \) trend in nonuniform absorption across the PL spectrum.
FG = \frac{G_{\text{Sol}}/\eta_{\text{PL}}}{A_{\text{Sol,NC}}/\eta_{\text{PV}} + A_{\text{Sol,PV}}/\eta_{\text{PV}}} \int_0^L I_{\text{PL}}(L) dL \tag{2}

Here, \(A_{\text{Sol,NC}}\) and \(A_{\text{Sol,PV}}\) are the solar fluxes absorbed by the NCs and the Si PV, respectively, \(G_{\text{Sol}}\) is the geometric gain of the device, \(\eta_{\text{PL}}\) is the NC PL quantum yield, \(\eta_{\text{PV}}\) is the escape cone loss factor, \(\eta_{\text{NC}}\) is the efficiency of the Si PV either at the PL wavelength or under AM 1.5 irradiation as indicated, and \(I_{\text{PL}}(L)\) is the experimental distance-dependent waveguided PL intensity reported in Figure 4A. The absorbed solar flux (\(A_{\text{Sol}}\)) is calculated using eq 3, where \(A(\lambda)\) represents the absorption spectrum of the PV or LSC, and \(S(\lambda)\) represents the solar spectrum in units of photons/(nm m^2 s).

\[A_{\text{Sol}} = \int S(\lambda)(1 - 10^{-A(\lambda)}) d\lambda\] \tag{3}

In the case of the square quartz liquid waveguide used here (Figure 1C), \(\eta_{\text{PL}} \sim 0.5\) because there are two escape cones (vertical and horizontal), whereas a planar LSC would have \(\eta_{\text{PL}} \sim 0.75\). The ratio \(\eta_{\text{PL}}/\eta_{\text{PL}0.51}\) was taken as 1 based on the Panasonic 25.6% efficiency crystalline Si solar cell reported in ref 28, which shows \sim 100% EQE from 500 to 1000 nm. These calculations were performed using two sets of \(\eta_{\text{PL}}\) values, those measured experimentally for the samples of Figure 4A, and the largest reported values (see Table 1). Additionally, to highlight the effects of reabsorption, the FG values presented in Figure 4B were calculated using the PL intensities corrected for waveguide losses, but FGs calculated from raw PL intensities are very similar (Supporting Information, Figure S3), again confirming that the actual device performance is primarily determined by the phosphor performance. Importantly, the FG analysis using eq 2 is validated by experimental measurement of the solar FG for the \(Zn_{0.87}Cd_{0.11}Mn_{0.02}Se/ZnS\) NCs using the full-length device of Figure 1C, which yielded a value of \(FG = 3.7\) that is in reasonable agreement with the value predicted for this sample in Figure 4B (\(FG = 4.1\)).

For short LSCs (magnified in the inset of Figure 4B), reabsorption losses are not yet dominant and all four NCs show nearly linear increases in FG with \(L\). The slope in this region is determined by the product \(A_{\text{Sol,NC}} \times \eta_{\text{PL}}\). Even though the highest observed \(\eta_{\text{PL}}\) of \(Cd_{1-x}Cu_{x}Se\) NCs is only 0.4, \(A_{\text{Sol,NC}}\) for these NCs is over twice that of the other NCs (Figure 2A, Table 1). The \(Cd_{0.999}Cu_{0.001}\) Se NCs are thus the top performer in short LSCs, followed by the \(CdSe/CdS\) core/shell NCs. The \(Cd_{0.999}Cu_{0.001}\) Se NCs continue to excel as the LSC length increases because of their combination of large \(A_{\text{Sol,NC}}\) and small reabsorption losses and thus remain the clear top performer at all 1D LSC lengths examined here. \(Cd_{0.999}Cu_{0.001}\) Se NCs therefore outperform all other nanocrystal LSC phosphors reported to date by a significant margin. We note that the highest value of \(\eta_{\text{PL}} = 0.4\) measured here is the highest yet reported for \(Cd_{1-x}Cu_{x}Se\) NCs, but passivation of surface states (e.g., via shell growth) may allow this value to be increased further, as reported for other copper-doped NCs.59 We have also noticed variations in \(L_{1/2}\) due to differences in the non-specific absorption attributed to surface traps or impurities discussed above (see Supporting Information), for example, we measured \(L_{1/2} = 51\) cm for a different \(Cd_{0.999}Cu_{0.001}\) Se NC sample.

It is instructive to compare the \(CdSe/CdS\) heterostructures and \(Zn_{0.87}Cd_{0.11}Mn_{0.02}Se/ZnS\) NCs in Figure 4B. \(A_{\text{Sol,NC}}\) is almost twice as large for both of the heterostructure NCs as for the \(Zn_{0.87}Cd_{0.11}Mn_{0.02}Se/ZnS\) NCs, and all have comparable \(\eta_{\text{PL}}\) so the heterostructures perform much better in small LSCs (Figure 4B, inset). As the LSC length increases, however, the heterostructure NCs suffer from major reabsorption losses and their FGs plateau. In contrast, the \(Zn_{0.87}Cd_{0.11}Mn_{0.02}Se/ZnS\) NCs show only minor losses with increasing LSC length. They surpass the dot-in-rod NCs at \(L \sim 7\) cm, and surpass the core/shell NCs at \(L \sim 37\) cm. The lack of a FG plateau up to \(L \sim 120\) cm with both of the doped NCs highlights the substantially smaller reabsorption in these NCs than in the heterostructure NCs. For large-scale LSC applications, the \(Zn_{0.87}Cd_{0.11}Mn_{0.02}Se/ZnS\) NCs are thus superior to the heterostructure NCs despite absorbing less of the solar spectrum. LSCs made with luminophores that do not absorb very much visible light, such as \(Zn_{0.5}Cd_{0.5}Mn_{0.02}Se/ZnS\) or related Mn^{2+}-doped NCs, are particularly attractive when transparency is desired, for example, in smart-window applications.

We have additionally extrapolated the performance of these NCs to large-area 2D LSCs. FG was calculated as a function of side length for square LSC devices with \(t = 1\) mm, \(OD_t = 1\), and Si PVs attached to all four edges using the NC absorption and luminescence spectra from Figure 2B along with the \(\eta_{\text{PL}}\) values reported in Table 1 (see Supporting Information). Figure 4C plots the calculated FG values versus 2D LSC side length. The trends with increasing LSC size are similar to those found for the 1D device (Figure 4B). In particular, the \(Cd_{0.999}Cu_{0.001}\) Se NCs are again the top performer in both small- and reasonably large-area LSCs, despite their relatively low \(\eta_{\text{PL}}\). As anticipated from the 1D measurements and calculations, the \(Zn_{1-x}Cd_{x}Mn_{0.02}Se/ZnS\) NCs excel at extremely large dimensions, surpassing first the \(CdSe/CdS\) core/shell NCs (at an LSC size of \(\sim 1.3\) m \(\times 1.3\) m) and then even the \(Cd_{0.999}Cu_{0.001}\) Se NCs (at \(\sim 10\) m \(\times\) 10 m, see Supporting Information). Table 1 summarizes the calculated FG values for a device area of \(1.2\) m \(\times 1.2\) m (the square equivalent of our laboratory 1D liquid waveguide), as well as the projected maximum FG values. Overall, these calculations reaffirm the "best-in-class" performance of the new LSC phosphor, \(Cd_{0.999}Cu_{0.001}\) Se NCs, on many length scales and validate the use of the 1D waveguide for experimentally assessing the performance of luminophores in large-scale 2D LSCs. The similarity of the size-dependent FG curves for the \(Cd_{0.999}Cu_{0.001}\) Se and \(CdSe/CdS\) core/shell NCs demonstrates that high PL quantum yields not only improve FG in small LSCs but also mitigate reabsorption losses in large LSCs through increased photon recycling. This principle is also evident from comparison of the curves calculated for the same sample using as-measured and best-reported \(\eta_{\text{PL}}\) values (Figure 4).

In summary, semiconductor NCs have recently been proposed as attractive spectral conversion phosphors for next-generation LSCs, but to date a quantitative assessment of these materials for this purpose has been lacking. In this study, we have performed a variety of spectroscopic and one-dimensional waveguide measurements aimed at comparing the leading NC candidates for potential large-scale LSC applications. The experimental results demonstrate that even seemingly small absorption features in the region of luminescence are detrimental to LSC performance on large length scales. \(CdSe/CdS\) heterostructure NCs perform well on small length scales but on large length scales they suffer from major losses due to reabsorption of emitted photons. For the two doped NCs, whose luminescent transitions are subject to very little
reabsorption, the performance at large length scales is in fact limited only by parasitic absorption from vibrational harmonics of the matrix, matrix impurities, surfactants, or NC surface states. These limitations are not intrinsic to the phosphor and can be circumvented. Among the four types of NCs examined here, the “best-in-class” phosphors for full-spectrum concentration by a substantial margin are the Cd$_{1-x}$Cu$_x$Se NCs, which absorb the greatest fraction of the solar spectrum and display relatively small reabsorption losses. LSC applications of copper-doped NCs have not been demonstrated previously. The Zn$_{0.87}$Cd$_{0.11}$Mn$_{0.02}$Se/ZnS NCs excel at very large dimensions while retaining visible transparency and are thus attractive for smart-window applications.

In addition to experimental measurements of luminescence in large-scale waveguides, this study presents, and validates with experimental data, a standardized methodology that allows facile prediction of the performance of new luminophores in LSCs from their absorption and PL spectra. The calculation of $R(l)$ using eq 1 allows evaluation of reabsorption for any luminophore without the need for elaborate device fabrication, and it yields easily interpretable results. The predicted reabsorption losses with LSC length agree with experimental results remarkably well, lending credence to flux gains projected from these same experimental parameters for large-scale 2D LSCs. Because the properties of high-performance LSC luminophores are largely independent of any specific LSC device configuration, such independent performance quantification is useful for assessing luminophore potential in a broad suite of LSC technologies.

Finally, we consider the potential for future improvement of NCs as LSC luminophores. The PL quantum yields and solar absorption of the CdSe/CdS heterostructure NCs are both near their theoretical limits, meaning that any improvements must come from reduced reabsorption. Although larger shell volumes would reduce reabsorption, previous studies have pointed out that larger shell thicknesses may lead to reduced or excitation-wavelength dependent quantum yields. Calculations also indicate that Rayleigh scattering from core/shell NCs becomes appreciable over meter-scale pathlengths for NCs with diameters $>10$ nm and that the optimum balance between reabsorption and scattering still involves appreciable losses (see Supporting Information). New heterostructures such as PbSe/CdSe NCs could increase $A_{\text{abs,NC}}$ and offset some of the major reabsorption and scattering losses in large-scale LSCs. For the doped NCs, tuning the bandgap (either by size or alloying) and increasing PL quantum yield could potentially increase performance by over a factor of 2. In Zn$_{1-x}$Cd$_x$Mn$_y$Se/ZnS NCs, tuning $A_{\text{abs,NC}}$ to $\sim480$ nm by changing size or alloy composition would more than double $A_{\text{abs,NC}}$ relative to the NCs reported here without introducing new reabsorption losses. Narrower energy gaps ($\Delta g_{\text{thr}} > 480$ nm) lead to recovery of excitonic emission via thermal repopulation and would not be beneficial. Similarly, adjusting the energy gap of Cd$_{1-x}$Cu$_x$Se NCs to the bulk limit would increase $A_{\text{abs,NC}}$ by over 35% relative to the NCs studied here. Even though the best Cd$_{1-x}$Cu$_x$Se PL quantum yield achieved here ($\eta_{\text{PL}}=0.4$) is the highest yet reported for Cd$_{1-x}$Cu$_x$Se NCs, it may be possible to further increase $\eta_{\text{PL}}$ by passivation of surface states, as reported for other copper-doped NCs which could improve performance of this “best-in-class” phosphor by more than a factor of 2 at all LSC length scales and even more for large-path length devices due to greater photon recycling efficiency (see Supporting Information). Switching from CdSe to other related copper-doped phosphors such as Cu$_x$:InP$^{33}$ or CuInS$_2$/ZnS$^{29}$ would yield similarly small PL reabsorption while eliminating Cd$^{2+}$. A challenge with all of the copper-doped NCs is their broad PL, which begins to extend past the absorption threshold of silicon when the energy gap becomes too narrow. And lastly, the observation that weak, nonspecific absorption attributed to direct excitation of surface traps can be moderated chemically points to the possibility of further improvements in this direction for all NC phosphors. Overall, even with their relatively low $A_{\text{fl}}$, the Cd$_{1-x}$Cu$_x$Se NCs reported here combine effective solar absorption with very low reabsorption to substantially outperform all other NCs tested here at all but the largest LSC lengths and areas, marking a significant advance in the development of nanocrystalline phosphors for LSC applications. More generally, these results highlight the attractiveness of doped nanocrystals as phosphors for LSCs.

**Experimental Methods.** *Synthesis.* All chemicals were used as supplied from Aldrich with the exception of tri-n-octyl phosphine (TOP), which was purchased from Strem. Zn$_{0.87}$Cd$_{0.11}$Mn$_{0.02}$Se NCs. Zn$_{1-x}$Cd$_x$Mn$_y$Se NCs were grown with slight modifications to previously reported synthetic methods$^{33}$ based on the thermal decomposition of the cluster (NMMe$_2$)$_2$Zn$_{1-x}$SePh$_{10}$. A flask containing 10.8 g of hexadecyl amine with 12 mg of MnCl$_2$·4H$_2$O and 15 mg of CdCl$_2$ was first degassed under vacuum at 130 °C for 1 h after which 400 mg of (NMMe)$_2$Zn$_{1-x}$SePh$_{10}$ and 20 mg of Se were added anaerobically. The resulting mixture was again degassed at 130 °C for 1 h before ramping the temperature to 270 °C, where it was held for 15 min before cooling slowly to 100 °C. The resulting NCs were twice crushed out with ethanol, separated by centrifuging, and resuspended in toluene.

Zn$_{0.87}$Cd$_{0.11}$Mn$_{0.02}$Se/ZnS NCs. ZnS shells were grown by transferring the toluene suspension of Zn$_{1-x}$Cd$_x$Mn$_y$Se NCs to a flask containing 3 g of oleylamine and 3 g of octadecane from which the toluene was removed and the resulting suspension degassed for 1 h at 130 °C. Zn(Oleate)$_2$ was prepared by reacting 440 mg of Zn(OAc)$_2$ with 4.4 g of oleic acid and 4.4 mL of octadecane under vacuum at 110 °C until all volatile components were removed. The flask was then put under a nitrogen atmosphere, 36 mg of S dissolved in 3.6 mL of TOP was injected, and the resulting mixture cooled to room temperature. The temperature of the flask containing the NCs was raised to 225 °C and the Zn(Oleate)$_2$-TOP-S mixture was injected via syringe pump at a rate of 0.5 mL/h. The resulting NCs were again purified by flocculation with ethanol followed by resuspension in toluene.

 CdSe (Core) NCs. CdSe cores were synthesized according to the standard hot-injection synthesis as reported in ref 16 wherein 60 mg of selenium dissolved in 360 mg of TOP is rapidly injected into a degassed solution of 60 mg of CdO, 280 mg of octadecylphosphonic acid, and 3 g of trietylphosphine oxide (TOPO) at 380 °C. The heating mantle was removed immediately after injection and the cooled solution of nanocrystals was purified by flocculation with ethanol followed by resuspension in toluene. These NCs had $d = 2.7$ nm.

 CdSe/CdS Core/Shell NCs. CdS shells were grown on the above cores according to ref 19, wherein 20 mL of a 0.08 M Cd(Oleate)$_2$ solution in octadecene (ODE) and 20 mL of 2 mM solution of octanethiol in ODE were separately injected at 2.5 mL/h to a degassed solution containing 100 nmol of CdSe cores in 3 mL of ODE and 3 mL of oleylamine at 310 °C. Two milliliters of oleic acid was injected 2 and 4 h after the
beginning of the injection. After injection was complete, the solution was allowed to stir at 310 °C for an additional 15 min before cooling and purification by flocculation with ethanol followed by resuspension in toluene.

CdSe/CdS Dot-in-Rod NCs. CdS rods were grown onto the above cores according to ref 16, wherein 2 nmol of the CdSe cores dissolved in 1.5 g of TOP with 120 mg of sulfur was injected rapidly into a degassed solution containing 60 mg of CdO, 80 mg of hexylphosphonic acid, 0.29 g of octadecylphosphonic acid, and 3 g of TOPO at 360 °C. After injection, the solution is stirred for 8 min with the temperature recovering to 360 °C, after which it was cooled and purified by flocculation with ethanol followed by resuspension in toluene.

Cd$_{1-x}$Cu$_x$Se NCs. Cd$_{1-x}$Cu$_x$Se NCs were synthesized by adapting the “heat-up” method for the synthesis of CdSe NCs first reported by Chen et al. Briefly, cadmium myristate (113 mg), selenium dioxide (22 mg), and copper(1) chloride (4 mg) were degassed under vacuum in octadecene (10 g) at room temperature for 30 min. Heating this mixture to 230 °C under nitrogen for 5 min produced a dark brown solution. After dropwise addition of 0.2 mL of oleic acid, the mixture was cooled to room temperature. Addition of 1 volume equivalent of anhydrous ethanol followed by centrifugation produced dark brown pellets that were resuspended in toluene, sonicated, and centrifuged again to remove insoluble impurities. Any adventitious CuSe formed during the reaction was reduced and removed by adding ~0.5 mL of TOP followed by flocculation with ethanol and resuspension in toluene or tetrachloroethylene. Quantum yields as high as 0.4 were obtained for Cd$_{1-x}$Cu$_x$Se NCs, but synthetic conditions were not optimized to reproduce this high quantum yield in batches large enough to fill the liquid waveguide. These quantum yields are higher than the previous best reported value for Cd$_{1-x}$Cu$_x$Se NCs of 0.25.

Spectroscopy and Characterization. Absorption measurements were taken using a Cary 500 spectrometer, and PL was measured using an Ocean Optics USB-2000+ spectrometer or a liquid-nitrogen-cooled CCD (Acton) coupled to a 0.5mm monochromator (for Cd$_{0.99}$Cu$_{0.01}$Se measurements), both corrected for spectral sensitivity. Quantum yields were measured using a Hamamatsu integrating sphere quantum yield measurement system with 385 nm excitation. TEM images were collected on an FEI Tecnai microscope, and NC compositions were determined by inductively coupled plasmaatomic emission spectrometry.

The liquid waveguide apparatus for measuring LSC reabsorption losses (Figure 1C) is based on a 120 cm long square quartz tube (supplied by Friederick and Dimmock Co.) with a 1 mm inner dimension (1.65 mm outer dimension) suspended over a black aluminum channel that was illuminated by a 1 mm spot from a 385 nm LED at variable distances from the end. Waveguided light was then collected through high numerical aperture (NA = 0.79) lenses through a diffuser to ensure equivalent collection of all waveguide modes, and measured using a fiber-coupled spectrometer. Because one end of the tube was sealed and flattened to avoid effects of a meniscus on detection, the tube was filled with toluene solutions of luminophore through a removable capillary. Because the Cd$_{0.99}$Cu$_{0.01}$Se NC PL overlaps with strong vibrational overtones of toluene (see Supporting Information, Figure S4), these NCs were measured in tetrachloroethylene. Before measurement, each sample was filtered through a 200 nm pore-size PTFE syringe filter. Photographs of this device are provided in Supporting Information, Figure S5.

ASSOCIATED CONTENT

5 Supporting Information

Additional experimental and calculated results (eight figures) and details pertaining to the calculation of 2D LSC flux gains. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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