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Analysis of Optical Losses in High-Efficiency CuInS₂-Based Nanocrystal Luminescent Solar Concentrators: Balancing Absorption versus Scattering

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Supporting Information

ABSTRACT: Luminescent solar concentrators (LSCs) use down-converting luminophores embedded in a waveguide to absorb sunlight and deliver high irradiance, narrowband output light for driving photovoltaic and other solar energy conversion devices. Achieving a technologically useful level of optical gain requires bright, broadly absorbing, large-Stokes-shift luminophores incorporated into low-loss waveguides, a combination that has long posed a challenge to the development of practical LSCs. The recent introduction of giant effective Stokes shift semiconductor nanocrystal (NC) phosphors for LSC applications has led to significant performance improvements by increasing solar absorption while reducing escape cone and nonradiative losses compounded by reabsorption, placing increased emphasis on the importance of minimizing parasitic waveguide losses caused by scattering from NC aggregates and optical imperfections. Here, we report a detailed analysis of optical losses in polymer–NC composite waveguide LSCs based on CuInS₂/CdS NC phosphors, which have been shown to provide best-in-class performance in large-area, semitransparent concentrators. A comprehensive analytical optical model is introduced enabling quantification of parasitic waveguide, scattering, escape cone, and nonradiative relaxation losses on the basis of distance-dependent edge-emission measurements. By examining the effect of NC loading, we show that NC clustering in polymer composite waveguides leads to light scattering losses that ultimately limit efficiency at large geometric gain. By optimizing NC concentration, optical power efficiencies up to 5.7% under AM1.5 illumination are demonstrated for devices having a geometric gain $G = 6.7 \times 10^3$, with limiting achievable efficiencies predicted to exceed 10%.

INTRODUCTION

Solar collectors capable of simultaneous spatial and spectral optical concentration can open new avenues for improving solar conversion efficiency, scalability, and cost by providing high brightness, narrow-bandwidth light optimized for photovoltaic (PV) or photochemical conversion. Luminescent solar concentrators (LSCs), which concentrate light in an inexpensive dielectric waveguide by active frequency shifting, have emerged as one of the most promising approaches for practical solar concentration (Figure 1A).1−3 LSCs employ downshifting luminophores to increase the spectral power of photons trapped in a waveguide by total internal reflection, theoretically enabling conversion efficiencies superior to other concentrator designs.4−6 PV cells or other converters coupled to the concentrator edges receive intense, bandgap-matched light, while excess energy from above-bandgap light is dissipated over the full area of the LSC. LSCs can concentrate diffuse light as well as direct sunlight, are tolerant to partial shading, and can be semitransparent, making them particularly useful for building-integrated PV applications such as energy-harvesting window layers.

Because some energy is sacrificed in the absorption, downshifting, and transport of sunlight by an LSC, achieving the required high levels of efficiency has long been an obstacle for practical concentrators. The theoretical performance limits of an LSC are established thermodynamically by the optical properties of the luminophores. The upper energy efficiency obeys the single-bandgap Shockley–Queisser limit,7 and the limiting energy concentration ratio (CRlim) depends on the Stokes shift. For visible to near-IR luminophores, thermodynamically limited theoretical energy concentrations of CRlim > 10⁴ are predicted at room temperature for a Stokes shift of ~500 meV, corresponding to >10³ W m⁻² of narrowband output.⁴−⁶ In practice, however, the performance of LSCs falls far below these thermodynamic limits,⁹ mainly because of four
dominating loss factors: (1) only a fraction of incident sunlight is absorbed, determined by the luminophore absorption spectrum, device thickness, and concentration; (2) only a fraction of absorbed sunlight is re-emitted, depending on luminophore photoluminescence (PL) quantum yield ($\Phi$); (3) only a fraction of this emitted light is captured in guided modes (e.g., $\sim$75% in a planar waveguide with refractive index $n \sim 1.5$), with the remainder lost to escape cones defined by Snell’s law; and (4) a fraction of guided light is lost during transport to the concentrator edges by parasitic waveguide losses.

For most LSC luminophores, mechanisms 2 and 3 account for the greatest losses because they occur repetitively, since only a fraction of this emitted light is captured in guided modes (e.g., $\sim$75% in a planar waveguide with refractive index $n \sim 1.5$), with the remainder lost to escape cones defined by Snell’s law; and (4) a fraction of guided light is lost during transport to the concentrator edges by parasitic waveguide losses.

Figure 1. In an LSC, broadband sunlight is absorbed by luminophores and emitted into a waveguide, traveling to the edge of the collector to provide concentrated narrowband light for driving conversion processes. With each emission, a fraction of light is lost to nonunity PL quantum yield or out the escape cone. Subsequent reabsorption of guided photons by other luminophores compounds these losses, causing efficiency to fall with concentrator size. Further optical losses result from parasitic waveguide attenuation.

EXPERIMENTAL METHODS

Nanocrystal Synthesis and Characterization. CuInS$_2$/CdS NCs were synthesized following the procedure outlined in ref 26 with small modifications. Briefly, CuInS$_2$ cores were prepared by adding indium acetate (0.292 g, 1 mmol), copper iodide (0.190 g, 1 mmol), and dodecanethiol (5 mL) to a 50 mL three-neck round-bottom flask. The solution was degassed three times at room temperature by evacuating the flask and refilling with nitrogen. After degassing, the reaction was heated to 110 °C under nitrogen for 10 min until the solution turned optically clear pale yellow. The reaction was then elevated to 230 °C for 10 min, during which time the solution turned from yellow to dark red. After 10 min, the reaction was quickly cooled to room temperature. A portion of the crude reaction solution (1.0 mL) was added to 1-octadecene (4.0 mL) in a clean 50 mL three-neck round-bottom flask. The cores were degassed with three pump–purge cycles using nitrogen at room temperature and were then heated to 210 °C. A shelling solution was prepared by heating and sonating cadmium myristate (0.272 g), sulfur (0.013 g), 1-octadecene (4 mL), and n-trioctylphosphine (0.4 mL) under a nitrogen atmosphere to form a uniform white dispersion. The shelling solution was injected into the reaction at 0.2 mL/min. After all of the shelling solution was added, the reaction was cooled gradually to 60 °C. Oleic acid (1 mL) and toluene (1 mL) were added, and the mixture was stirred for 10 min. The resulting CuInS$_2$/CdS core/shell nanocrystals were purified with several cycles of precipitation upon addition of ethanol by resuspension in toluene. Typical NCs prepared by this method were pseudospherical with diameters of $d \sim 3$–4 nm (Figure 2B). X-ray diffraction data (Figure 2C) are consistent with CuInS$_2$/CdS NCs in the chalcopyrite phase, with diffraction angles shifted slightly due to the thin CdS shell layers. NCs from several similar syntheses were then used to prepare LSCs. For most data reported here, the original colloidal NCs had $\Phi \sim$ 75% in toluene.

Several defect-based PL mechanisms have been proposed to explain the PL of CuInS$_2$ and related NCs. Recent results are consistent with rapid trapping of photogenerated holes at lattice Cu$^+$ ions, followed by “free-to-bound” recombination of conduction-band electrons with these trapped holes. Localized to a distance of $\sim 3$–4 nm (Figure 2B). X-ray diffraction data (Figure 2C) are consistent with CuInS$_2$/CdS NCs in the chalcopyrite phase, with diffraction angles shifted slightly due to the thin CdS shell layers. NCs from several similar syntheses were then used to prepare LSCs. For most data reported here, the original colloidal NCs had $\Phi \sim$ 75% in toluene.
slightly greater than in some other active NCs, it is far smaller than in organic dyes, and this feature combined with its high quantum yield relative to that measured in toluene ($\Phi \sim 75\%$). Other possible origins may involve surface polarization upon reduction in the NC surface ligand density or the effect of changing the dielectric of the surrounding material.

### RESULTS AND ANALYSIS

#### Experimental Characterization of CuInS$_2$ LSCs

Absorbance and edge-emitted PL spectra for a representative CuInS$_2$ LSC are presented in Figure 3. The first absorption feature is a broad band centered at $\sim 2.1$ eV, with an absorption tail that weakly overlaps the PL band centered at $\sim 1.6$ eV, measured here under 475 nm excitation. Emission spectra were measured...
by illuminating 5 mm diameter areas of the device located at various distances \(d\) from the waveguide edge and collecting edge-emitted light through a 7 mm aperture into an integrating sphere (inset, Figure 5). Three replicate measurements were performed on two orthogonal edges, and the results were averaged. Outside the collection aperture, all remaining waveguide perimeter was blackened to eliminate edge reflections. As shown in Figure 3B, the small overlap between absorption and PL bands results in the gradual loss of guided photons on the high-energy side of the PL peak with increasing optical path length.

We find that in devices prepared using a high NC loading scattering begins to make a contribution to total extinction. This observation is illustrated in Figure 4, which shows the measured extinction for an LSC containing 2.6 wt % CuInS<sub>2</sub>/PLMA, having a total extinction of 0.36 mm<sup>−1</sup> at \(\lambda = 575\) nm, corresponding to the first absorption feature. Below we show this scattering arises mostly from NC aggregation occurring at high NC concentrations. To determine the contributions from NC absorption and scattering individually, we make use of the fact that the absorption spectra were virtually unchanged going from toluene to PLMA (Figure S2), and we fit the measured spectra using the function, \(\varepsilon_{\text{total}}(\lambda) = A_{\text{toluene}}^{\text{NC}}(\lambda) + B/\lambda^4 + C\). Here \(\varepsilon_{\text{toluene}}\) is the normalized absorption spectrum measured in toluene, and \(A, B,\) and \(C\) are fitting constants. The first term accounts for NC absorption, the second for scattering, and the third for Fresnel reflections at the glass/air and glass/polymer interfaces. At low concentrations scattering losses are well-described by \(\lambda^{-4}\) wavelength dependence, consistent with a Rayleigh scattering mechanism (see below). In the following, for devices exhibiting measurable scattering, reported optical densities are based on the best-fit value of \(A_{\text{toluene}}^{\text{NC}}(\lambda)\).

Integrating the areas under the absorption and emission spectra in Figure 3B gives the fraction of photons absorbed by the LSC that reach the collection aperture as a function of excitation distance, or optical quantum efficiency, \(QOE_{\text{ap}}(d)\) (Figure 5, solid points). \(QOE_{\text{ap}}\) decreases with \(d\) due to both a geometric effect (the collection angle subtended by the edge aperture decreases as \(\tan^{-1}(1/d)\)) and compounding escapecone, nonradiative relaxation, and waveguide attenuation losses. The latter can be expressed as an optical path-length-dependent loss such that \(P = Pe^{-\alpha d/4.34}\), where \(P/P_0\) is the fraction of power remaining after a propagation distance \(\xi, \alpha \) (dB cm<sup>−1</sup>) is an attenuation coefficient, and the factor 4.34 arises from converting dB cm<sup>−1</sup> to Naperian units (cm<sup>−1</sup>). For reference, an attenuation coefficient of \(\alpha = 0.1\) dB cm<sup>−1</sup> results in a loss of \(\sim 2\%\) of guided photons per centimeter path length. The attenuation coefficient accounts for absorbance and scattering by the polymer as well as scattering from NCs, polymer/glass, and glass/air interfaces. We treat \(\alpha\) as wavelength-independent over the emission band of the phosphor.

In the following sections we show how device absorption and emission spectra, along with edge emission measurements performed at a series of illumination spot positions like the example in Figure 5, enable complete quantification of LSC optical properties. Such measurements were performed on eight devices, based on CuInS<sub>2</sub> NCs possessing very similar absorption and emission spectra, but different NC loadings, varying from 0.4 to 6.1 wt %. From these data the optical power efficiency (OPE), flux gain, edge-emission irradiance, and other characteristics are found for each experimental device and can be projected for any device configuration having a specified geometry, size, and NC loading. OPE is defined as

\[
\text{OPE} = \frac{\text{edge output irradiance} \times \text{LSC edge area}}{\text{solar irradiance} \times \text{LSC major area}}
\]

Figure 5. LSC characterization and projected performance. Solid points give the optical quantum efficiency measured at the small edge aperture. Line is a fit to eq 2. Inset: geometry used for LSC characterization.

The best performing device is measured to have OPE = 5.7% at a geometric gain \(G = 6.7\), with a narrowband edge output irradiance of 385 W m<sup>−2</sup> centered at 760 nm, among the highest performance yet reported in a large-G LSC. Achieving this level of performance requires minimizing waveguide attenuation losses while maximizing solar absorption, which as described in the following trend in opposite directions with NC loading. Below, we provide a detailed analysis of the principal optical loss mechanisms and use the results to project the performance of fully optimized LSCs.

**Analytical Model of LSC Performance.** To determine attenuation and other losses individually, we introduce a new analytical optical model taking as inputs only the measured absorption and emission spectra, fitting \(QOE_{\text{ap}}(d)\) to determine the best \((\alpha, \Phi)\). Once these parameters are known, it becomes possible to compute for any \(G\) the impact of each loss mechanism as well as the optical power efficiency and edge output irradiance. Details of the model are given in the Supporting Information and are summarized here briefly as follows: For a photon absorbed at a location \((x, y)\) to reach the integrating sphere, it must be emitted into a guided mode whose path of propagation meets the aperture. During propagation the photon might be reabsorbed, with probability
determined by the photon’s wavelength and the NC absorption spectrum, and it may be attenuated, with probability determined by $\alpha$. For this situation, all photons that are reabsorbed even once can be treated as lost, even if potentially they could have been re-emitted in a direction allowing them to reach the edge aperture; in the Supporting Information we show that the probability of such photons being measured at the integrating sphere is very small and does not affect the estimation of $\Phi$ and $\alpha$.

Let $D$ be an illumination window within which solar absorption occurs and $|D|$ denote the area of this window. Let $\Theta(x, y)$ be the part of the unit sphere corresponding to guided modes intersecting the aperture. Let $l(x, y, \theta, \phi)$ be the path length of propagation within the full LSC from $(x, y)$ to the measurement aperture in the direction $(\theta, \phi)$, given in spherical coordinates. Along this path, attenuation is possible from scattering, absorbance by the polymer matrix, and other parasitic loss mechanisms. Since only the central composite layer of the LSC contains NCs, and the glass cladding is relatively lossless (see below), attenuation is considered in the composite layer only and the distance traveled subject to attenuation is less than $l$. Let $\xi(x, y, \theta, \phi)$ be this distance. If $\text{Abs}(\lambda) = A\varepsilon(x, y, \theta, \phi)$ and $\text{Em}(\lambda)$ denote the absorption and emission spectra of the NCs, then

$$\text{OQE}_{ap} = \frac{\Phi}{|D|} \int \int \frac{1}{4\pi} \int \Theta(x, y) e^{-\alpha(x, y, \theta, \phi)} \times \int \text{Em}(\lambda)e^{-\text{Abs}(\lambda)(\xi(x, y, \theta, \phi))} \sin \theta d\theta d\phi dA(x, y)$$

(2)

In fact, we also take into account the angle-dependent Fresnel reflection coefficient at the measurement aperture, where the refractive index changes at the LSC/air interface, but omit it here for brevity. We assume that scattering losses from the polymer–glass and glass–air interfaces are negligible, consistent with previously reported measurements on poly(methyl methacrylate)–glass waveguide LSCs.\(^{37}\) To determine NC PL quantum yield and the waveguide attenuation rate, measurements of $\text{OQE}_{ap}(d)$ are fit using eq 2 with a least-squares procedure. The solid line in Figure 5 gives the result of this fitting process for a representative device. For the example shown, $\Phi = 75\%$ and $\alpha = 0.46 \text{ dB cm}^{-1}$.

Having estimated the $\Phi$ and $\alpha$, we proceed to compute the expected OQE for LSCs of other dimensions when illuminated uniformly over the whole LSC, now considering photons that reach any point on the concentrator perimeter. From this, we can then compute the optical power efficiency and the edge output irradiance. For these computations, the model presented above is no longer appropriate because reabsorbed photons have a non-negligible probability of reaching an edge, possibly even after more than one reabsorption/re-emission event. Given initial absorption that is uniformly distributed over the full LSC, we assume that first-time reabsorbed photons are again uniformly distributed over the LSC, an assumption that is borne out in ballistic Monte Carlo simulations. In the Supporting Information, we present a complete derivation of the proportion of incident solar irradiance absorbed by the LSC, and the output edge irradiance, we integrate the AM1.5 spectral irradiance against the LSC absorbance. From these, of all initially absorbed photons, we obtain the total proportions: lost out the escape cone, $\mathcal{E} = (1 - \Phi)\mathcal{A}$, lost to attenuation, $\Phi\mathcal{F} = (1 - \Phi)\Phi\mathcal{A}$, lost due to subunit luminescence quantum yield, $\Phi(1 - \Phi)\Phi\mathcal{A}$, and reaching an edge, $\Phi(1 - \Phi)\Phi\mathcal{A}$.

In Figure 6, we apply this treatment to project how performance varies with $G$ for the device in Figure 5. The circled points correspond to the measured LSC. OPE decreases with increasing $G$ as reabsorption and waveguide attenuation losses grow with concentrator size; simultaneously, the collection area increases, increasing the solar irradiance absorption rate. The output irradiance approaches a limiting value of $\sim 770 \text{ W m}^{-2}$ at $G \approx 100$, corresponding to a square LSC with an edge length $\geq 2.8 \text{ m}$. Under full area illumination the efficiency of the best performing device was OPE = 5.7% ($G = 6.7\times$). The same parameters project OPE = 4.8% at $G = 10\times$. The latter represents a 50% relative efficiency improvement over the next-best performing nanophosphor in this category, also based on CuInN$_2$E$_2$ (E = S, Se) NCs,\(^{16}\) for a device of the same geometric gain.

Photoconverters such as PVs or photodetectors that are optically coupled to LSCs receive high irradiance, narrowband light, producing an enhanced photocurrent density $J = I_{AM1.5G}\varepsilon(\text{OQE})\varepsilon(\text{OPC})(\lambda_{em}/h\nu_c)$, where $I_{AM1.5G}$ is the solar irradiance, $\text{OQE}$ is the photocurrent external quantum efficiency at the NC peak emission wavelength $\lambda_{em}$, and $\nu_c$ is Planck’s constant, $h$ is the speed of light, and $\nu_c$ is the number of electrons per Coulomb. For $\text{EQE} = 1$, the projected limiting photocurrent density $J_0 = 24 \text{ mA cm}^{-2}$ for the LSC in Figure 6 at $G = 5.7\times$ neglecting coupling losses, increasing to a maximum of $J_0 \approx 47 \text{ mA cm}^{-2}$ for $G \geq 100$. The latter represents a nearly 2-fold increase in current density for an ideal single-junction photoconverter based on a bandgap matching $\lambda_{em}$. For LSC-coupled PVs, the corresponding flux gain $F$, defined as the ratio of the power produced by edge-attached PVs to the power produced by the same PVs under AM1.5 illumination, is proportional to the ratio of the short-circuit currents: $F = (\text{EQE})J_0/J_{AM1.5G}$, where $J_{AM1.5G}$ is the photocurrent under direct AM1.5G exposure. Taking high-performance a-Si PVs as an example,\(^{38}\) the right-hand axis in
Figure 7 shows the projected flux gain increases from ~1.3× at G = 6.7× to ~2.6× in the large-G limit.

**Examination of Loss Processes.** The impacts of nonradiative relaxation, parasitic attenuation, and escape-cone losses and their dependence on geometric gain are shown in Figure 7, again computed for the device in Figure 5 as an example. The dominant loss mechanism is found to depend on concentrator size. For small devices (G ≤ 10), nonradiative relaxation presents the largest loss, followed by escape cone loss. This conclusion is consistent with the measured PL quantum yield, which gives a 1 − Φ = 25% nonradiative loss each time a photon is absorbed. Since emission is directionally isotropic, escape-cone losses are Φ(1 − 1 − n_eff^2/n_sc^2)^2/3 17% each time a photon is absorbed, where n is the refractive index. For larger devices, however, attenuation losses become limiting. This surprising finding is a direct result of the high LQY and large effective Stokes shift of the CuInS_2/CdS phosphors employed in these LSCs and emphasizes the importance of waveguide transparency for large area, high performance concentrators. In the majority of LSCs studied to date, such losses have typically been either neglected (as being relatively small compared to nonradiative and escape cone losses) or not separately analyzed and determined. It is noteworthy that the LSCs reported here appear almost entirely loss. This conclusion is consistent with the measured attenuation rate α = 0.16 dB cm^{-1} and negligible single-particle scattering losses (β = 0.02 dB cm^{-1} wt %). The latter is consistent with an estimate of the Rayleigh scattering cross section, which indicates that scattering from individual NCs is 1−2 orders of magnitude too small to account for the observed attenuation, and also with the observations of Knowles et al., who found no significant scattering for similar CulnS_2 NCs in toluene at even greater volume fractions and over a path length of 1.2 m. At low NC loadings, α is dominated by intrinsic waveguide losses. The intrinsic attenuation of optical-grade methacrylate polymers in this wavelength range is ~1 × 10^(-3) dB cm^{-1}, and that of the glass cladding is even lower (1.8 × 10^(-4) dB cm^{-1}), suggesting it should be possible to reduce α further through improved purification or fabrication methods. At high NC concentrations g_0 ≥ ~2 wt %, the analysis indicates that scattering losses from NC aggregates begin to dominate, as evidenced by the signature cubic scaling of attenuation rate with NC concentration. This result can be understood by the fact that although aggregation reduces the number density of scattering objects by a factor n^{-1/3} (where n is the number of NCs per aggregate), the scattering cross section of such aggregates scales as n^{-2}.

![Figure 8. Dependence of waveguide attenuation on NC loading. The points represent experimental attenuation coefficients measured for individual LSCs. The line results from fitting eq 3.](image)

Since both scattering losses and solar flux absorbed by the LSC increase with increasing NC concentration, there exists for a given G an optimal NC concentration that maximizes the OPE. The opposing effects of increasing absorption and attenuation are illustrated in Figure 9A and the consequence for OPE in Figure 9B. To compare devices prepared using NC samples having different values of Φ, OQE and OPE are normalized by setting Φ = 1, but otherwise using identical properties to the experimentally measured devices (α, absorption, and emission spectra). The maximum OPE is predicted to occur at an optical density at λ = 575 nm equal to ~0.3 mm^{-1}, corresponding closely to the LSC analyzed in Figures 5 and 6, which was in fact the best performing device studied here.

![Figure 7. Optical loss mechanisms. The statistical fate of absorbed solar photons depends on geometric gain, with losses dominated by nonradiative relaxation at small G, and waveguide attenuation at large G. Results are computed for the device in Figure 5.](image)
thickness, computed for a 1 m² LSC, which is representative of the size of a typical window in a commercial building. NC concentration is expressed in terms of the optical density at the first absorbance feature (575 nm), where OD = 1.0 mm⁻¹ equates to 7.2 wt % NC loading. The attenuation coefficient is calculated using eq 3, and all other properties (Φ, absorbance, and emission spectra) correspond to the device in Figure 5. The results in Figure 10 show that for a 1 m² LSC a polymer layer thickness of 1.7 mm produces the largest flux gain, using 1.2 wt % NC loading. This concentrator achieves a projected output irradiance of nearly 1000 W m⁻² with a thin waveguide geometry minimizing photoconverter area and weight, satisfying important requirements for practical solar energy harvesting window layers.

Comparison of Best-Performing and Idealized NC LSCs. Finally, we apply these results to examine the performance of CuInS₂ NC LSCs if further improvements can be made to α and Φ. As noted, the NC PL quantum yield falls by up to 30% upon polymer incorporation, and the observed parasitic attenuation loss rate is 10–100 times greater than the intrinsic attenuation limits imposed by the PLMA waveguide, polymer, or single-NC scattering. Since these factors limit performance in small and large devices, significant further improvements should be possible. The host CuInS₂ bandgap can also be reduced via anion alloying or growth of larger diameter NC cores, improving solar spectrum matching. Figure 11 projects the impacts on performance from improve-
loading result in substantially improved efficiency in the present LSCs.

**CONCLUSION**

In summary, we report NC–polymer composite waveguide LSCs based on CuInS$_2$/CdS NC phosphors demonstrating record high performance in large geometric gain, semi-transparent concentrators, with optical power efficiencies up to 5.7% under AM1.5 illumination for $G = 6.7\times$. A new analytical framework is introduced enabling quantitative analysis of each principal loss mechanism on the basis of straightforward luminophore concentration- and excitation distance-dependent measurements without the need for ray-tracing or Monte Carlo simulation. Application of this model shows that waveguide losses grow in proportion to NC loading, leading to an optimal concentration corresponding to an optical density of $\sim 0.3 \text{ mm}^{-1}$ at the first absorption maximum, equivalent to $\sim 2 \text{ wt \%}$ NC content. An analysis of optical losses shows that nonradiative relaxation losses dominate at small geometric gain, but scattering losses from NC aggregates become limiting in larger devices. These results demonstrate the importance of understanding and balancing each optical loss mechanism in order to maximize performance in LSCs based on large Stokes shift NC phosphors.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b12379.

Experimental details of NC synthesis and device fabrication; derivation of the optical model; thermogravimetric analysis of NC loading; Fourier transform infrared spectroscopy measurements of the degree of polymerization; derivation of the light scattering model (PDF)

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**Notes**

The authors declare no competing financial interest.

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Supporting Information:

Analysis of Optical Losses in High-Efficiency CuInS$_2$-Based Nanocrystal Luminescent Solar Concentrators: Balancing Absorption vs Scattering

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1. LSC Fabrication. Empty shells were prepared by bonding two 0.90 mm-thick B270 glass sheets (Howard Glass Inc.) with a transparent acrylic adhesive gasket (VHB tape, 3M Inc.), forming a sealed cavity. The inner surfaces of this glass shell were coated by a layer of 3-(trimethoxysilyl)propylmethacrylate (Aldrich Inc.), used as an adhesion promoter to inhibit delamination. Empty shells were purged with N$_2$ and filled through a hypodermic needle with a 3:1 wt:wt mixture of lauryl methacrylate (Scientific Polymer Products Inc., SPP) and PLMA (molecular weight = 250,000, SPP Inc.), with the latter included to reduce shrinkage upon polymerization. The mixture included 2 wt% ethyleneglycol dimethacrylate as a crosslinker (Aldrich), 0.5 wt% Irgacure 651 photoinitiator (Ciba Inc.), and NCs. Polymer solutions were thoroughly degassed in vacuum and stirred for at least 12 hours prior to filling. After filling, cells were immediately photopolymerized under uniform UV exposure for 1 hr. The final fabrication step was to apply a layer of transparent UV curing optical epoxy ($n = 1.56$, Norland 63, Norland Products Inc.) around the perimeter to give LSCs smooth, optically clear edges. Completed LSCs measured 75 mm × 75 mm × 2.8 mm (Fig. S1). Absorption extends across nearly the entire visible spectrum, giving devices a brown/red appearance (Fig. 1B and S1).
Upon incorporation into the polymer, NC PL spectra undergo a ~80 meV bathochromic shift and a slight narrowing (Fig. S2). This effect was observed even in samples having low optical density, with excitation near the edge to minimize the optical pathlength. Hence the shift is not a

**Fig. S2.** Absorbance and normalized PL spectra of CuInS$_2$ NCs in dilute solutions of toluene (solid lines) and PLMA (dashed lines). Absorbance spectra are nearly indistinguishable. The bathochromic shift and narrowing of the PL spectrum in PLMA is not caused by self-absorption. The PL spectrum in PLMA was acquired from an LSC with low NC loading with the excitation source located <5 mm from the edge and corrected for self-absorption as described at the end of section S3.

2. LSC Characterization. Upon incorporation into the polymer, NC PL spectra undergo a ~80 meV bathochromic shift and a slight narrowing (Fig. S2). This effect was observed even in samples having low optical density, with excitation near the edge to minimize the optical pathlength. Hence the shift is not a
result of self-absorption losses such as those shown in Fig. 3B. Possible origins of this shift may include: a size-dependent change in the PL QY, surface polarization due to reduction in the NC surface ligand density, the change in the dielectric of the surrounding material (solvent to polymer), or a combination of these. Absorbance measurements were performed with a Jasco UV-VIS spectrophotometer. Edge emission measurements were performed using a Horiba Fluorolog model FL3-21 fluorometer connected via liquid light guide to an integrating sphere. The fluorometer emission response function in the wavelength range 500 – 900 nm was calibrated using the reference dye 4-dimethylamino-4’-nitrostilbene in o-dichlorobenzene.¹

After spectroscopic characterization several samples were disassembled and the polymer/NC composite analyzed by Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). TGA was performed in the temperature range 25 - 1000 °C using a TA Instruments thermogravimeter. Samples were heated at 20 °C min⁻¹ under flowing N₂ to a temperature of 500 °C, and above that, under air. As shown in Fig. S3(a), degradation began at ~375 °C and was complete by 450 °C. The residual mass remaining at 540 °C arises from NCs. The relationship between wt% NCs and optical density determined from measurements on three samples with different NC loadings is wt% = 7.2x(OD mm⁻¹ @ 575) (%).

A comparison of FTIR spectra of NC/polymer composites from LSCs and unpolymerized laurymethacrylate shows the disappearance of alkene peaks at 1640, 1295, 814, and 650 cm⁻¹, indicating undetectable levels of residual monomer (Fig. S3(b)) after device fabrication.
Determination of emission spectra, and estimation of attenuation coefficient and quantum yield, from aperture measurements of OQE.

To begin with, assume that the emission spectra is known. We will return to the question of determining this spectra after describing how to estimate the attenuation coefficient and the quantum yield.

We choose coordinates so that the LSC is situated in $[-\frac{W}{2}, \frac{W}{2}] \times [0, L]$ with the measurement aperture at $-\frac{A}{2} < x < \frac{A}{2}, y = 0$. The LSC is illuminated within disks $D_i$ of radius $r_{ilt}$ at centers $(0, y_i), i = 1, ..., n$. Of all photons absorbed within $D_i$, a proportion are re-emitted and of

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**Fig. S3.** Representative results from characterization of NC/polymer composites from dissassembled LSCs. (A) Thermogravimetic analysis to determine NC mass loading. (B) FTIR spectra comparing the polymerized composite to laurylmethacrylate monomer. Several alkene peaks, present in the monomer but absent in the polymer, are indicated.

3. Determination of emission spectra, and estimation of attenuation coefficient and quantum yield, from aperture measurements of OQE. To begin with, assume that the emission spectra is known. We will return to the question of determining this spectra after describing how to estimate the attenuation coefficient and the quantum yield. We choose coordinates so that the LSC is situated in $[-\frac{W}{2}, \frac{W}{2}] \times [0, L]$ with the measurement aperture at $-\frac{A}{2} < x < \frac{A}{2}, y = 0$. The LSC is illuminated within disks $D_i$ of radius $r_{ilt}$ at centers $(0, y_i), i = 1, ..., n$. Of all photons absorbed within $D_i$, a proportion are re-emitted and of
these a proportion \(m_i\) are measured at the aperture. From knowledge of the absorption and emission spectra of the NCs, and from the measurements \(m_i\), we wish to estimate the attenuation coefficient \(\alpha\) and the quantum yield \(\Phi\). For this estimation we make the assumptions that any attenuated photon is lost and any absorbed photon is lost. The motivation for the second of these assumptions is the following: if a photon is absorbed by a NC somewhere within the LSC, there is a chance \(\Phi\) that it is re-emitted; of the re-emitted photons, there is a 75% chance that it is emitted outside of the escape-cone of the LSC; and of these photons emitted within the total internal reflection of the LSC, approximately 2.5% are in the direction of the aperture. Thus, for a NC with \(\Phi = 50\%\), at most \(100(0.5 \times 0.75 \times 0.025) = 0.9\%\) of the absorbed photons could be measured within the aperture. Such a small correction does not result in a change in \(\alpha\) or \(\Phi\) of any significance.

The probability that a photon emitted from position \((x, y)\) in the LSC reaches the aperture is calculated as follows. If a photon is emitted at wavelength \(\lambda\), then the probability that it will travel distance \(\xi\) within the doped layer, without being absorbed, is \(e^{-\text{Abs}(\lambda)\xi}\), where \(\text{Abs}(\lambda)\) is the absorption spectrum of the NC. Let \(Em(\lambda)\) be the probability distribution for emission at wavelength \(\lambda\) (normalized so that \(\int Em(\lambda)d\lambda = 1\)). Thus, the probability that an emitted photon (of any wavelength) travels distance \(\xi\) within the doped layer before being absorbed is

\[
\int Em(\lambda)e^{-\text{Abs}(\lambda)\xi}d\lambda.
\]

Taking into account total internal reflection, let \(l(x, y, \theta, \phi)\) be the total distance from \((x, y)\), in the direction \((\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)\), to the edge of the LSC, for \(\frac{\pi}{2} - \theta_{esc} < \theta < \frac{\pi}{2} + \theta_{esc}\). Since the LSC consists of three layers, two being un-doped glass layers of thickness \(\tau_{gl}\) and one being doped of thickness \(\tau_{QD}\), the proportion of propagation that occurs within the doped layer is \(\xi(x, y, \theta, \phi) = \frac{\tau_{QD}}{\tau_{QD} + 2\tau_{gl}}l(x, y, \theta, \phi)\). Not all directions from \((x, y)\) reach the aperture; define \(\Theta(x, y) \subset \mathbb{S}^2\) (\(\mathbb{S}^2\) is the unit sphere) to be the solid angle of directions which reach the aperture from \((x, y)\). If we now introduce a wavelength-independent attenuation coefficient \(\alpha\), then the probability that an emitted photon reaches the aperture is

\[
\frac{1}{4\pi} \int_{\Theta(x,y)} e^{-\alpha l(x,y,\theta,\phi)} \int Em(\lambda)e^{-\text{Abs}(\lambda)\xi(x,y,\theta,\phi)} d\lambda \sin \theta d\theta d\phi.
\]

Letting \(|D_i| = \pi r_{ill}^2\) be the area of the illumination disk, of the photons absorbed within \(D_i\), the proportion which reach the aperture is thus

\[
\frac{\Phi}{|D_i|} \int_{D_i} \frac{1}{4\pi} \int_{\Theta(x,y)} e^{-\alpha l(x,y,\theta,\phi)} \int Em(\lambda)e^{-\text{Abs}(\lambda)\xi(x,y,\theta,\phi)} d\lambda \sin \theta d\theta d\phi dA(x, y).
\]
The measurements made by the integrating sphere at the aperture are not index-matched to the LSC. As a result we must take into account the reflection coefficient at this interface. Letting this be $R(\theta, \phi)$, the proportion of all absorbed photons which are measured at the aperture is, finally,

$$P_i = \frac{\Phi}{|D_i|} \iint_{D_i} \frac{1}{4\pi} \int_{\theta(x,y)} (1 - R(\theta, \phi)) e^{-\alpha l(x,y,\theta,\phi)} \int E_{m}(\lambda) e^{-\text{Abs}(\lambda) \xi(x,y,\theta,\phi)} d\lambda \sin \theta \ d\theta \ d\phi \ dA(x,y).$$

Within this integral, the unknown quantities are $\alpha$ and $\Phi$. It is the lack of knowledge of $\alpha$ that restricts us from computing the integral. To get around this problem, we expand the exponential $e^{-\alpha l}$ in a power series based at 0 under the assumption that $\alpha l$ is small over the range of $l$ relevant to the computation. We find that this is indeed a reasonable assumption provided we approximate the infinite series by a finite series of sufficiently many terms. Replacing $e^{-\alpha l}$ by $\sum_{j=0}^{N} \frac{(\alpha l)^j}{j!}$, the above integral becomes $P_i = \Phi \sum_{j=0}^{N} \alpha^j I_{i,j}$ where

$$I_{i,j} = \frac{1}{j!} \frac{1}{|D_i|} \iint_{D_i} \frac{1}{4\pi} \int_{\theta(x,y)} \left(1 - R(\theta, \phi)\right) I(x,y,\theta,\phi)^j \int E_{m}(\lambda) e^{-\text{Abs}(\lambda) \xi(x,y,\theta,\phi)} d\lambda \sin \theta \ d\theta \ d\phi \ dA(x,y).$$

These are integrals which can be computed explicitly. We can now find the $\alpha$ and $QY$ that minimize the least-squares error between the measured $m_i$ and the computed $P_i$:

$$\sum_{i=1}^{n} \left(m_i - \Phi \sum_{j=0}^{N} \alpha^j I_{i,j}\right)^2.$$ 

How large $N$ need be can be determined by observing at what point the minimizing $\alpha$ and $QY$ no longer change with the addition of further terms in the series.

We return to the question of determining $E_{m}(\lambda)$. From illuminating a fixed, preferably closest to aperture, spot, we measure the intensity reaching the aperture, as a function of wavelength $\lambda$. If there was no absorption nor scattering occurring between the illumination window and the aperture, normalizing this data would provide $E_{m}(\lambda)$. If we neglect scattering, then, as above, the measurement $m(\lambda)$ at wavelength $\lambda$ is proportional to

$$E_{m}(\lambda) \int_{D} \int_{\theta(x,y)} e^{-\text{Abs}(\lambda) \xi(x,y,\theta,\phi)} \sin \theta \ d\theta \ d\phi \ dA(x,y).$$

If we denote the computed integral by $I(\lambda)$ then $E_{m}(\lambda) = m(\lambda)/I(\lambda)$. The resulting profile will be correct up to the effects of scattering over the distance between the illumination window and the aperture, which are likely to be small. An improved profile can be obtained by using this computation as a first estimate of $E_{m}(\lambda)$, estimating $\alpha$ as above, then repeating the fixed $\lambda$ computation with attenuation taken into account by the estimated $\alpha$. This can be repeated in a boot-strapping manner as necessary.
4. Computation of full-edge OQE and flux gain.

Having estimated the attenuation coefficient $\alpha$ and the quantum yield $\Phi$ using the method described above, we now use these quantities to compute the expected OQE for an LSC which has index-matched capture on all four edges. For this computation it is no longer appropriate to regard re-absorbed photons as lost. There is a non-negligible probability that an absorbed photon can be re-emitted and propagate to the edge.

Fix a wavelength $\lambda$ and let $\text{Abs} = \text{Abs}(\lambda)$ be the absorbance of the QDs at this wavelength. Because the proportion of the path from a point in the LSC to an edge which lies within the doped layer is $\tau = \frac{\tau_{QD}}{\tau_{QD} + 2\tau_{gl}}$, we scale the absorbance accordingly, replacing $\text{Abs}$ by $\tau \text{Abs}$.

Let $\delta r \ll 1$ be a small positive propagation distance. After propagating distance $\delta r$, of all photons emitted from a (fixed for now) point within the LSC, approximately $(1 - e^{-\alpha \delta r})$ have been lost to attenuation, $(1 - e^{-\tau \text{Abs} \delta r})$ have been absorbed, and so

$$1 - (1 - e^{-\alpha \delta r}) - (1 - e^{-\tau \text{Abs} \delta r}) = e^{-\alpha \delta r} + e^{-\tau \text{Abs} \delta r} - 1 = R,$$

remain un-absorbed. (This is an approximation in the sense that it becomes exact as $\delta r \to 0$, a limit we shall compute presently.) If we repeat this process, after a propagation distance of $2\delta r$,

$$1 - (1 - e^{-\alpha \delta r})(1 - e^{-\tau \text{Abs} \delta r})(1 + R),$$

have been lost to attenuation, similarly, $(1 - e^{-\tau \text{Abs} \delta r})(1 + R)$ have been lost to attenuation, and

$$1 - (1 - e^{-\alpha \delta r})(1 + R) - (1 - e^{-\tau \text{Abs} \delta r})(1 + R) = R^2$$

remain. Continuing, after propagation distance $N\delta r$, $(1 - e^{-\alpha \delta r})(1 + R)\sum_{n=0}^{N} R^n$ have been lost to attenuation, $(1 - e^{-\tau \text{Abs} \delta r})\sum_{n=0}^{N} R^n$ have been absorbed, and $R^N$ remain. From this we can derive the proportion of photons which, somewhere along the path of propagation, are lost to attenuation, are absorbed, or survive to travel distance $\xi$. We define $\delta r = \frac{\xi}{N}$, and consider the limit as $N \to \infty$:

$$\lim_{N\to\infty} \left(1 - e^{-\alpha \xi/N}\right)\sum_{n=0}^{N} R^n = \frac{\alpha}{\alpha + \tau \text{Abs}} (1 - e^{-(\alpha + \tau \text{Abs})\xi}),$$

and

$$\lim_{N\to\infty} \left(1 - e^{-\tau \text{Abs} \xi/N}\right)\sum_{n=0}^{N} R^n = \frac{\tau \text{Abs}}{\alpha + \tau \text{Abs}} (1 - e^{-(\alpha + \tau \text{Abs})\xi}).$$

These quantities are for a fixed wavelength, and for a fixed propagation distance. To compute the proportion of all emitted photons which are lost to attenuation before reaching an edge or being absorbed, we integrate against the probability of emission at each wavelength, over all directions outside of the escape cone, and over all emission locations $(x, y)$ in the LSC, which we take to be of dimensions $L \times W$:
\[
S = \frac{1}{LW} \iiint_{LSC} \frac{1}{4\pi} \int_{\Theta(x,y)} \frac{\alpha}{\alpha + \tau Abs(\lambda)} \left( 1 - e^{-(\alpha + \tau Abs(\lambda))l(x,y,\theta,\phi)} \right) d\lambda \sin(\theta) \, d\theta \, d\phi \, dA(x,y).
\]

Similarly, the proportion of emitted photons which are re-absorbed exactly once before reaching an edge, nor attenuating, is
\[
\mathcal{A} = \frac{1}{LW} \iiint_{LSC} \frac{1}{4\pi} \int_{\Theta(x,y)} \frac{\tau Abs(\lambda)}{\alpha + \tau Abs(\lambda)} \left( 1 - e^{-(\alpha + \tau Abs(\lambda))l(x,y,\theta,\phi)} \right) d\lambda \sin(\theta) \, d\theta \, d\phi \, dA(x,y).
\]

Define \( E = 1 - \sqrt{1 - \frac{1}{n^2}} \), the proportion of photons which are emitted in directions within the escape cone of the LSC. Then \( C = 1 - \mathcal{A} - S - E \) is the proportion of initially emitted photons which reach an edge without being absorbed nor attenuated. From these quantities we can now compute the expected OQE.

Of all initially absorbed photons, \( \Phi \) are emitted, \( \mathcal{A} \Phi \) are re-absorbed (for the first time), \( S \Phi \) are lost to attenuation, \( E \Phi \) are lost out the escape cone, and \( C \Phi \) are captured at an edge. Next, of the \( \mathcal{A} \Phi \) re-absorbed photons, \( \mathcal{A} \Phi^2 \) are emitted, of which \( \mathcal{A}^2 \Phi^2 \) are re-absorbed for a second time, \( S \mathcal{A} \Phi^2 \) are lost to attenuation, \( E \mathcal{A} \Phi^2 \) are lost out the escape cone, and \( C \mathcal{A} \Phi^2 \) are captured at an edge. These processes repeat, recycling absorbed photons. Summing we obtain, of all initially absorbed photons, the proportion:

- absorbed at least once is \( \sum_{j=1}^{\infty} \mathcal{A} \Phi^j = \frac{\mathcal{A} \Phi}{1 - \mathcal{A} \Phi} \);
- lost to attenuation is \( S \Phi \sum_{j=0}^{\infty} \mathcal{A} \Phi^j = \frac{S \Phi}{1 - \mathcal{A} \Phi} \);
- lost out the escape cone is \( E \Phi \sum_{j=0}^{\infty} \mathcal{A} \Phi^j = \frac{E \Phi}{1 - \mathcal{A} \Phi} \);
- captured at an edge is \( C \Phi \sum_{j=0}^{\infty} \mathcal{A} \Phi^j = \frac{C \Phi}{1 - \mathcal{A} \Phi} \). This is the OQE.

To compute the proportion of the full solar flux of photons which can be captured at the edge, set \( F_{sol}(\lambda) \) to be the (normalized) probability distribution of the solar flux based on the ASTM G173-03 reference spectrum (fixed place receptor, 1000 W m\(^{-2}\)) and compute
\[
\frac{C \Phi}{1 - \mathcal{A} \Phi} \int F_{sol}(\lambda) \left( 1 - e^{Abs(\lambda)} \right) d\lambda.
\]


Assuming each scattering event results in the loss of the scattered photon and treating scattering in the Rayleigh regime: \( \alpha_s \approx 3\rho \sigma_1/4\pi r^3 \), where \( \rho \) and \( r \) are the NC volume fraction and radius, respectively, and the scattering cross-section is
\[
\sigma_1 = \frac{8\pi n^6}{3} \left( \frac{2\pi}{\lambda} \right)^4 \left| \frac{n_{np}^2-n_{poly}^2}{n_{np}^2+2n_{poly}^2} \right|^2.
\]
Here $\lambda = 760$ nm is the wavelength of scattered light, and $n_{np} \approx 2.8$ and $n_{poly} = 1.5$ are the nanoparticle and polymer refractive indices. Taking $r = 3$ nm gives $\alpha_s \approx 10^{-3}$ dB cm$^{-1}$ for a NC loading of 1 wt%. Thus compared to other loss mechanisms, scattering from single NCs is expected to be negligible.

At high enough concentrations NC aggregation may occur. In this case the scattering cross-section depends on the aggregate size distribution, and whether the clusters formed are compact or extended fractal objects. Here we introduce a simple model to describe optical attenuation by light scattering from these aggregates.

Aggregating particles typically produce mass fractals with a radius of gyration $R_g$ related to aggregate mass by $R_g \propto M^{1/D}$, where $M$ is the number of primary particles in the aggregate and $D$ is the fractal dimension. In the diffusion-limited aggregation regime, the aggregate concentration $C$ and average size are time-dependent and proportional to the initial primary particle concentration,

$$C \propto c_o$$

$$M \propto c_o$$

(though with different proportionality constants and time dependencies). Since the scattering properties of LSCs are stable over a period of weeks or longer, we assume that aggregation is essentially arrested upon polymerization, freezing the aggregate concentration and size distribution. For simplicity, we model the distribution as consisting of just two sizes, monomers and clusters of average size $M$. Then the attenuation coefficient can be written as

$$\alpha = \alpha_0 + c_0 (1 - \kappa)\sigma_1 + C_0 \sigma_M$$

(5.3)

where $0 \leq \kappa \leq 1$ is the proportion of monomers incorporated into aggregates. The first term accounts for propagation losses in the absence of NCs, and arises from absorption and scattering by the polymer, and at interfaces and imperfections. The second and third terms describe scattering from single particles and aggregates, respectively. In the Rayleigh regime, the light scattering cross-section of an individual fractal aggregate can be approximated as

$$\sigma_M = M^2 \sigma_1 \left(1 + \delta R_g^2\right)^{-D/2},$$

where $\delta$ is a wavelength-dependent constant. Using (5.2a), (5.3) can be re-written as

$$\alpha = \alpha_o + \beta c_o + \gamma c_o^3 \left(1 + \delta c_o^{2/D}\right)^{-D/2}$$

(5.4)

where $\beta$ and $\gamma$ are constants.

For $D \approx 2$, Equation 5.4 is insensitive to $D$, and equally good fits were obtained for any value in the range $D = 1.5 - 3.0$. We therefore fixed its value at $D = 1.8$, typical of aggregates formed by diffusion-limited cluster aggregation. In all cases, the best-fit value found for the single-particle scattering coefficient was $\beta \approx 0$, consistent with the calculation above that the contribution to scattering from single particles should be negligible.
References.


