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Optimal quantum dot size for photovoltaics with fusion†

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Light fusion increases the efficiency of solar cells by converting photons with lower energy than the bandgap into higher energy photons. The solar cell converts the product photons to current. We use Monte Carlo simulation to predict that lead sulfide (PbS) quantum dot sensitizers will enable fusion with a figure of merit on the mA cm^{-2} scale, exceeding current records, while enabling silicon cell compatibility. Performance is highly sensitive to quantum dot size, on the order of $\text{mA cm}^{-2} \text{nm}^{-1}$.

1. Introduction

Solar cells recently became the cheapest source of electricity.¹ Increasing solar cell efficiency will decrease energy costs.² For wider bandgap solar cells, the main inefficiency is transparency.^{3,4} Here, we simulate the use of absorptive and tunable lead sulfide quantum dots to capture and convert the wasted light.

Triplet fusion,⁵ also known as triplet-triplet annihilation upconversion, photochemical upconversion,^{6,7} or Auger annihilation, utilizes light that passes through a solar cell. Triplet fusion uses two chemical species: a sensitizer and an emitter, as illustrated in Fig. 1. In a well-designed system, the sensitizer captures solar spectral irradiance which passes through the solar cell; *i.e.* the photons which lie below the cell bandgap. For sensitizers comprising semiconducting nanoparticles, the resulting excitons are transferred to the emitter triplet state. The emitter fuses the triplet excitons, producing higher energy singlet excitons. The fusion system fluoresces, releasing upconverted photons with an energy above the cell bandgap. The net effect is that photons spontaneously increase in energy, enabling higher solar cell efficiency.³

Alternate approaches to the utilization of sub-bandgap photons include multijunction^{8,9} and intermediate band devices.¹⁰

Fusion requires the annihilation of excitons, which only happens when the excitons are close together. To achieve a high density of excitons, it is essential to capture as much light as possible in a small volume.¹¹ This can be achieved by use of a sensitizer with a high molar absorption coefficient and excitation rate. Determining the excitation rate from the absorption spectrum of the sensitizer and spectral irradiance

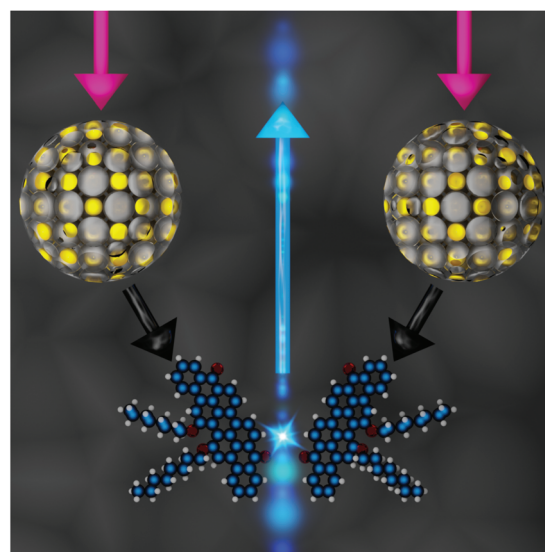


Fig. 1 Schematic illustration of the device architecture. Sunlight illuminates the device from the top (red arrows). A solar cell (not shown), which is transparent below its bandgap, filters the sunlight. Beneath the solar cell, a quantum dot sensitizer (halite structured spheres) captures the light. Quanta of energy are transferred (black arrows) to a hypothetical light fusion emitter (molecular model) which converts light from below the solar cell bandgap to above the solar cell bandgap. The upconverted light travels up to the solar cell (blue arrow). The sensitizer and emitter are uniformly distributed.

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of the sun is typically complicated, motivating our Monte Carlo simulations as a method of sensitizer selection.

Several groups have recently shown experimentally that quantum dots are superior to traditional organic sensitizers.^{12–25} The very large absorption coefficient of quantum dots outweighs their tendency to reabsorb converted light.²⁶ The absorption coefficient is not large enough to capture substantial light with one layer of particles. Quantum dots have the additional advantages that they are highly photo-stable, have an absorption cross-section which is tunable across a wide range of energies and, in some cases, are already used in the electronics industry.

One can synthesize quantum dots from several semiconductor materials. Group IV quantum dots tend to have energy levels that are too high for our purposes. III–V quantum dots tend to be difficult to synthesize on a large scale. II–VI quantum dots are highly tunable across the visible spectrum, but cannot easily be tuned to absorb light below the bandgap of silicon, the most common solar cell absorber. Perovskite quantum dots have a similar limitation, but are tuned with a different mechanism. Cu–III–VI₂ chalcopyrite and IV–VI quantum dots do not have these problems. In chalcopyrites, the valence band maximum is at the Γ point,²⁷ while in IV–VI systems it is at the degenerate L point of the Brillouin zone.²⁸ The additional degeneracy and smaller unit cell of IV–VI valence electrons implies they will always have a higher molar absorption coefficient. This probably cannot be overcome with differences in quantum dot density. From the IV–VI family, we select elementally abundant and commonly synthesized PbS to investigate. PbSe is very similar.^{29,30}

Quantum confinement dictates the electronic structure of quantum dots. Synthesis parameters control the size of the nanoparticles and therefore the energy levels of the quantum dot. One can synthesize PbS nanoparticles with a wide range of molar absorption coefficients (or absorption peak locations), as illustrated in Fig. 2. The molar absorption coefficient and peak locations cannot be controlled independently; both arise from chemical structure. However, it is laborious to test the sensitization performance of a large number of quantum dot radii to find the ideal sensitizer.

While the overall efficiency of fusion systems involves an interplay between the properties of the sensitizer,³¹ emitter,³² and environment,^{33,34} here we focus on light capture by the sensitizer. Previous work shows that light capture is essential.¹¹ We quantitatively relate light capture to performance.

Here, we simulate fusion sensitized by lead sulfide quantum dots. We determine the optimal quantum dot size under the assumption that a hypothetical emitter with reasonable properties is used. We consider how the performance of the fusion system depends on the density of the quantum dots and the bandgap of the solar cell. We quantify device performance using the figure of merit,³⁵ which is the photocurrent added by upconversion to a solar cell with perfect external quantum efficiency. At solar irradiance, fusion is considered to be “device relevant”²⁶ and economically beneficial² at a figure of merit of 0.1 mA cm^{−2}. The best experimental fusion figure

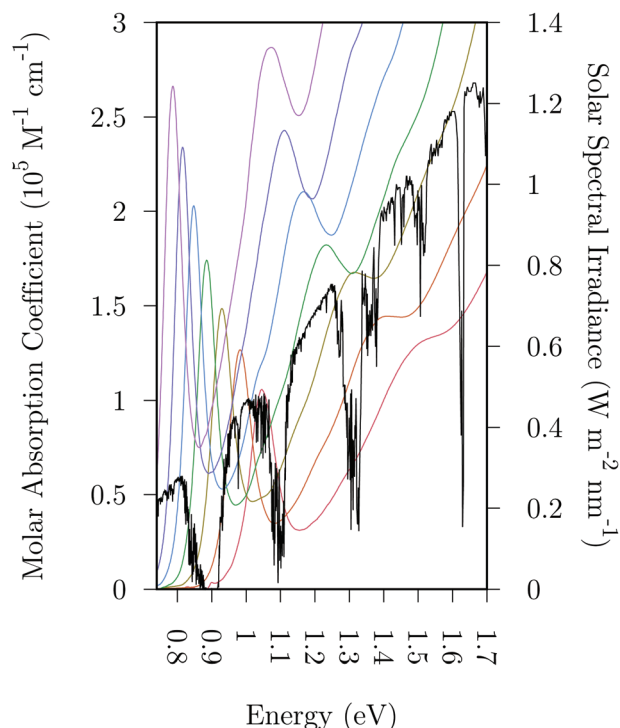


Fig. 2 Molar absorption coefficient of quantum dots with different radii²⁸ (colors) and the AM1.5G solar spectral irradiance (black). Bandgaps of interest for light fusion range from 1 eV to 1.5 eV.³ The major absorption lines displayed in the solar spectral irradiance are the overtones and combination bands of vibrational modes of water. The bandgap of silicon is 1.1 eV.

of merit we are aware of is 0.158 mA cm^{−2},⁶ just above this lower limit. Thus far, the best devices used organic sensitizers incompatible with silicon cells. They are incompatible because they do not absorb in the infrared beyond 1100 nm. Our calculations predict that devices incorporating PbS sensitizers will be able to achieve a new record for the figure of merit, while simultaneously meeting the requirements for silicon cell compatibility.

2. Methods

To determine optimal sensitizer parameters, we generated spectra for arbitrary quantum dot sizes. PbS absorption spectra from ref. 36 were transformed to reduce the apparent size dependence. The energy scale was transformed to place the E_1 and E_4 peaks³⁶ at the same locations and the absorption scale was transformed so all E_1 peaks were the same amplitude. Cubic radial basis function interpolation³⁷ was used as a function of radius. The generated spectra were transformed into molar absorption spectra using the energy level and extinction formulas in ref. 36, restoring the size dependence. Examples are shown in Fig. 2. The exact meaning of quantum dot radius is stoichiometry-dependent.²⁹ We use the definition in ref. 36.

The device figure of merit was computed using the previously reported algorithm.³⁸ In brief, we used 10^9 Monte Carlo samples of the AM1.5G 1 kW m^{-2} solar spectrum (other values are used in ESI Fig. 4†) with a sharp cutoff of 1100 nm as a transparency model for a thick silicon solar cell. The spatial distribution of absorption and self-absorption of quantum dots was computed at 10^5 locations. No energy loss caused by the presence of trap states was included. A reflector was included at the optimal location.²⁶

Since this paper focusses on sensitization, we modeled hypothetical properties that a sensible emitter molecule would possess. We assumed the emitter molecule would have no self-absorption; large sensitizer self-absorption makes emitter absorption negligible. The emitter molecule emission was assumed to be evenly spread between 10 and 60 nm above the solar cell bandgap to approximate the observed insensitivity to absorption spectrum details. We assumed the emitter first order decay rate was 10^3 s^{-1} and the second order decay rate was $4.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (ref. 26) in imitation of diphenylanthracene.^{32,39} The results are generalized by calculating the performance of devices using a wide range of emitter first and second order decay rates. This is displayed in ESI Figs. 2 and 3.† Energy transfer to the uniformly distributed emitter was assumed to be exothermic and in dynamic equilibrium.

The yield for production of fluorescence from triplet annihilation was assumed to be one. While these properties have each been demonstrated in different emitters, they have not all been demonstrated in the same molecule. Thermal and concentration quenching effects were omitted for lack of information. The intensity of upconversion fluorescence was simulated according to the established rate equations.¹¹

We assumed the concentration of quantum dots was limited by the Kepler theorem for close packed spheres. To leave room for passivating ligands, the radius associated with each particle was optimistically assumed to be 0.5 nm larger than the quantum dot radius. Close packing leaves 26% of the volume available for exciton transport and emitter materials.

3. Results and discussion

As shown in Fig. 3, we find that for silicon solar cells, the locally optimal PbS quantum dot radius is around 2.2 nm, and the diameter is about seven lattice parameters. Precision synthesis has been demonstrated on the scale of 0.01 eV.³⁶ Quantum dots with a lower energy absorption peak (0.95 eV to 0.85 eV, ESI Fig. 6†) are less effective because of the lack of solar spectral irradiance at 0.9 eV and increased self-absorp-

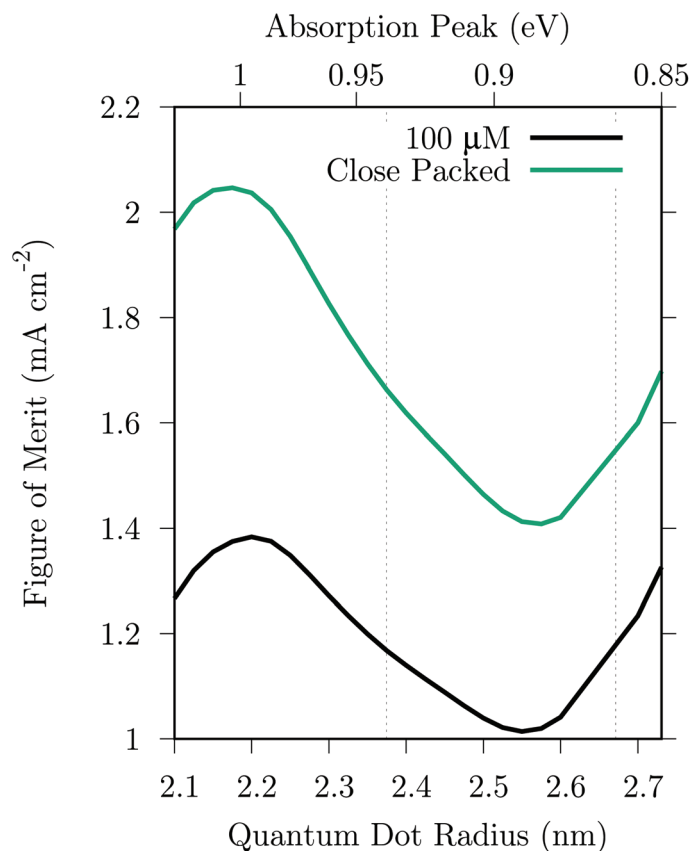


Fig. 3 Calculated fusion figure of merit of a PbS quantum dot sensitized silicon solar cell. The black curve assumes the sensitizer concentration is 100 μM . The green curve assumes the sensitizer is close packed. The anabathmophore thickness is optimized as previously reported²⁶ with range 1 μm to 270 μm . The dashed lines indicate a diameter change of one lattice parameter.

tion. Smaller quantum dots are ineffective because of the reduced solar spectral irradiance at 1.1 eV, which is just below the bandgap of silicon. If the sensitizer has no absorption below the bandgap of silicon, the figure of merit is zero.

A naive model of quantum dot performance would assume that a larger quantum dot with less quantum confinement implies a larger region of the solar spectrum will be captured. In addition, a larger quantum dot has a higher density of states and therefore absorbs more light at a given wavelength. Owing to the nonlinearity in the exciton fusion rate equation, the naive model concludes that larger quantum dots always produce a device with a higher energy efficiency. Our simulations show quantitatively that this naive model is conceptually correct, but omits four important details. The first three are addressed here; the fourth was covered in our previous paper.²⁶

First, as shown in Fig. 2, the near infrared spectrum of sunlight at the Earth's surface has a complicated structure, which is mostly influenced by Planck's law and the water in the atmosphere. When the absorption peaks of a quantum dot sensitizer are tuned through the spectral irradiance peaks, the device efficiency is modulated.

Second, excessively large quantum dots are disadvantageous owing to lower colloidal stability.^{40,41} They have more traps per particle,⁴² reducing fusion efficiency. Quantum dots must not overlap, indicating that concentration (number density) must eventually be sacrificed for large size.

Third, increased sunlight absorption by the sensitizer implies increased parasitic absorption of the upconverted light by the sensitizer. Unlike some molecular sensitizers, quantum dots are never transparent at energies above the first excited state.

Fourth, to achieve efficient fusion, energy must be exothermically transferred from the sensitizer to the emitter molecule. A larger quantum dot absorbs lower energy photons by having a lower exciton energy level. The exciton energy level limits the triplet energy level of the emitter molecule.²⁶ This level must be more than half the solar cell bandgap. Other possible practical constraints on the triplet energy level merit investigation.

In Fig. 3, we find that a wide range of quantum dot radii and concentrations will produce a figure of merit exceeding 1 mA cm^{-2} , which, if realized, would be an order of magnitude improvement on the state of the art,⁶ despite the additional challenge of silicon compatibility. The black curve is the results under the assumption that the quantum dot concentration is $100 \mu\text{M}$. This is a reasonable concentration for quantum dots in solution. In the absence of self-quenching,^{31,38} the figure of merit increases as a function of quantum dot concentration, as shown in ESI Fig. 5.†

The green curve (Fig. 3) indicates figure of merit at the number density limit corresponding to close-packed (Kepler) quantum dots. The number density decreases with quantum dot size. As a result, a small penalty is imposed on the performance of devices with larger quantum dots. This effect shifts the optimal diameter by about one tenth of the $5.9 \text{ \AA}$ lattice parameter. For a device with the maximum possible

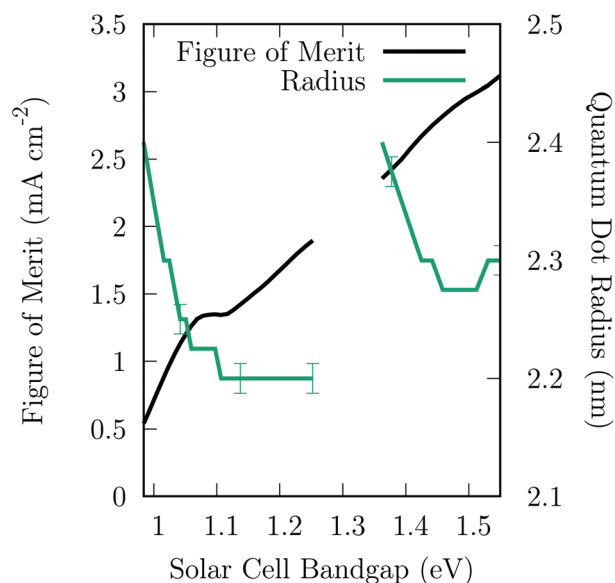


Fig. 4 Calculated optimal figure of merit and quantum dot size as a function of solar cell bandgap. The anabathmophore thickness is optimized as previously reported²⁶ with range $66 \mu\text{m}$ to $340 \mu\text{m}$. Selected numerical error estimates for the quantum dot radius are shown as vertical bars. No data is shown for solar cell bandgaps where larger quantum dots are always better.

number density, a quantum dot which is too large can decrease the figure of merit by 31%.

Fig. 4 shows the value of the optimal quantum dot radius and corresponding figure of merit as a function of solar cell bandgap. Many laboratory solar cells have wider bandgaps than silicon (1.1 eV). The Shockley–Queisser limit on solar cell efficiency is for an optimal bandgap of 1.33 eV, but the upconversion detailed balance limit is at a bandgap of 1.53 eV.³⁸ While a bandgap exceeding 1.53 eV will increase the figure of merit, it is unlikely to increase overall device performance.

The optimal quantum dot radius is discontinuous as a function of solar cell bandgap. For smaller bandgaps, the excitonic absorption is tuned to match the first region of high spectral irradiance beneath the bandgap. For larger bandgaps, multiple quantum dot absorption peaks are tuned to match multiple areas of high spectral irradiance. For bandgaps near 1.3 eV, the figure of merit increases monotonically as a function of quantum dot size. In this situation, the best quantum dot cannot be selected without detailed knowledge of the corresponding emitter molecule and quantum dot colloidal stability. The increase in figure of merit with bandgap found in Fig. 4 by definition does not include the benefit of the increase in cell voltage.

4. Conclusions

We conclude that PbS quantum dot sensitizers have the absorption properties required to create upconversion devices with a figure of merit that far exceeds the current record,⁶ even

if constrained to be silicon-compatible. While the total figure of merit will remain modest, PbS sensitization is compatible in principle with all photovoltaic devices that have a bandgap bigger than bulk PbS, which includes all plausible solar cell technologies. Since light fusion technology can be synthesized in the liquid phase, it has the potential to be cheap enough that small figures of merit may be cost effective. Under our assumptions, PbS sensitization will exceed the performance required for economic benefit, which is estimated to be 0.1 mA cm^{-2} .²

Our algorithm, which is distributed freely, can simulate scenarios with arbitrary illumination, absorption, and emission spectra.³⁸ In this work we have addressed bandgaps and rate constants over the ranges relevant to photovoltaics. Any quantum dot which possesses an absorption peak will sensitize most effectively when the absorption peak is at the same energy as an illumination peak.

To create a commercial device, it is necessary to create an emitter with suitable properties. These include statistically and kinetically efficient energy transfer from the quantum dot sensitizer to the emitter, stable energy storage, rapid exciton transport, efficient annihilation, and efficient fluorescence. All these properties have been demonstrated separately in experiments, but not simultaneously.

Conflicts of interest

There are no conflicts to declare.

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