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Multiple Exciton Generation and Dynamics in InP/CdS Colloidal Quantum Dots


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ABSTRACT

We report measurements of multiple exciton generation and recombination in InP/CdS (core/shell) colloidal quantum dots. Ultrafast transient absorption spectroscopy was used to measure the sub-nanosecond charge dynamics for a range of pump fluences and for different pump photon energies. Analysis of the resulting transients was used to determine the quantum yield of multiple exciton generation, which was found to be $1.22 \pm 0.01$ for a pump photon energy equivalent to three times the band gap.
INTRODUCTION

Colloidal quantum dots (CQDs) are nanometer-scale semiconductor crystals that can be produced by facile solution-phase chemistry. The size-tunable band gap, $E_g$, of CQDs coupled with the low-cost methods by which they can be fabricated and processed makes them attractive for a number of different applications. These include acting as the luminophores in efficient light sources, and as the photo-absorbing species in image processing devices and third-generation solar cells. CQDs have the potential to increase the efficiency of solar cells by the process of multiple exciton generation (MEG), also known as carrier multiplication. As first described by Shockley and Queisser, the efficiency of a conventional single-junction solar cell under un-concentrated sunlight is limited to ~33%, largely by the cooling to the band edge of carriers generated by the absorption of a photon with energy in excess of $E_g$. However, for CQDs the process of MEG can become competitive with carrier cooling, so that some or all of the initial carrier kinetic energy is used to generate additional electron-hole pairs rather than being lost as heat. Including MEG in the Shockley and Queisser analysis shows that this effect has the potential to increase the maximum solar cell efficiency to 44%.

MEG in CQDs was first proposed in 2001 and first experimentally demonstrated in 2005 for PbSe CQDs. Since then MEG has been demonstrated in CQDs composed of a range of single materials, including PbS, HgTe, CdHgTe and CuInSe$_2$, as well as in other forms of colloidal nanostructures such as PbSe nanorods and PbS nanosheets. One of the most useful aspects of the solution-phase synthesis of CQDs is that it allows a core-shell structure to be readily produced by the growth of a shell or shells of different material(s) around the original CQD. A spherical heterostructure is thus produced allowing control of the wave function of photo-generated carriers, and thus of their interactions and dynamics, and this can be used to
engineer the properties of CQDs for MEG-enhanced solar cells. These heterostructures can be in several forms depending on the relative $E_g$ and band offsets of the core and shell materials, including: Type I, in which both band edge carriers are confined to the core; Type II, where one carrier is confined to the core and the other to the shell; and quasi-Type II, where one or other of carriers is confined to the core or shell, and the other is delocalised over the whole CQD. A Type I CQD design can be used to reduce the trapping of hot carriers by the surface states that compete with MEG. A study of dispersions of InP/ZnS/ZnO (core/shell/shell) Type I CQDs reported an efficiency of 0.3,\textsuperscript{15} defined as the rate of increase with photon energy (in units of $E_g$) of the number of excitons produced per absorbed photon. However, a later study of CQD-sensitized solar cells\textsuperscript{16} showed that the addition of such wide band gap outer shell to CQDs can result in significantly reduced photovoltaic efficiency, an effect attributed to the outer shell acting as a barrier to charge extraction from the CQDs. In contrast, the shell is not a barrier to extraction for one or both of the photo-generated charges in a Type II or quasi-Type II CQD design; moreover, this design can also enhance the efficiency of the MEG process itself. An upper limit to MEG efficiency of 0.5 was estimated for Type II CdTe/CdSe CQDs dispersions\textsuperscript{17} and this high efficiency was attributed to a reduction in the wave function overlap between carriers resulting in a decreased rate of Auger cooling, another process that competes with MEG. A quasi-Type II PbSe/CdSe CQD design was used to achieve an MEG efficiency of 0.3, by suppressing the hole cooling which competes with MEG in this system.\textsuperscript{13}

In this work, we study MEG in dispersions of quasi-Type II CQDs formed by the growth of a CdS shell around a InP core; in this CQD structure, the electron is delocalised over the core and shell whilst the hole is confined to the InP core,\textsuperscript{18} as illustrated in Figure 1. InP CQDs form with a cubic crystal structure (lattice constant 5.87 Å)\textsuperscript{19} but the thermodynamically stable phase
of CdS is hexagonal\textsuperscript{18}. However, CdS can also exist in a cubic phase (lattice constant 5.83 Å)\textsuperscript{19} which, as we show below, can form when thin shells of CdS grow on to an InP core. Thus, InP/CdS CQDs can be produced with a common crystal structure and a lattice mismatch of only 0.7%; in contrast, to grow a CdS/InP CQD with a similar common crystal structure would be more problematic since it would require the initial synthesis of CdS cores in the thermodynamically unstable cubic phase. There are several reasons why InP/CdS CQDs are of particular interest for MEG-enhanced solar cells. As mentioned above, Type I CQDs based on InP cores exhibit good MEG efficiency.\textsuperscript{15} The addition of a CdS shell can redshift the absorption edge significantly,\textsuperscript{18} so that it closer to the ideal value for optimal exploitation of the solar spectrum.\textsuperscript{5} A CdS shell has also been shown to be an effective means of passivating surface traps, as evidenced by the increase in photoluminescence (PL) and reduction in PL intermittency (also known as ‘blinking’) resulting from the addition of such a shell.\textsuperscript{18} Moreover, this surface passivation does not come at the cost of extraction efficiency from the CQD. Wu et al.\textsuperscript{20} showed that the characteristic electron transfer time from an InP CQD to a methylviologen acceptor molecule was just 11 ps, and was little changed after the addition of a CdS shell at 15 ps. Importantly, both of these values are much less than the biexciton lifetime in InP/CdS CQDs, which can be as long as 7 ns,\textsuperscript{18} indicating that the additional excitons produced by MEG can be extracted with high efficiency from the CQD rather than being lost to recombination. The single exciton recombination lifetime is also extended to several hundred nanoseconds in InP/CdS CQDs, for both isolated CQDs\textsuperscript{18} and CQD-acceptor complexes;\textsuperscript{18} calculations for similar CdSe/CdTe CQDs indicate that the increase in recombination lifetime produced by a quasi-Type II structure can significantly increase solar cell efficiency.\textsuperscript{21} However, it is still unclear how MEG efficiency itself will be affected by the addition of a CdS shell to an InP CQD, which will
depend on the interplay of several competing processes, each of which is affected by the change in structure. The reduced wave function overlap between carriers produced by the quasi-Type II structure may simultaneously reduce the rate of MEG and of the Auger relaxation with which it competes, but by different amounts. The reduced confinement resulting from the addition of the CdS will reduce the separation of energy levels for the electron, which may increase the rate of phonon-mediated cooling.

The efficiency of MEG in InP/CdS CQDs is reported for the first time in this work. The characterisation of these CQDs by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and absorption and photoluminescence (PL) spectroscopies is described initially. The sub-nanosecond charge dynamics are then studied using ultrafast transient absorption spectroscopy. The absorption transients are obtained for a range of pump fluences, and for pump photon energies both below and above the MEG threshold, and analysed to obtain the MEG quantum yield, QY. We thus show that the MEG QY for quasi-Type II InP/CdS CQDs is similar to that already reported for Type I InP CQDs. This establishes that changing the CQD heterostructure in such a way does not adversely affect the MEG efficiency, enabling the advantages of a quasi-Type II design for a CQD-based solar cell, such as increased excitonic lifetimes and reduced band gap, to be exploited without reducing the potential benefit to photo-voltaic efficiency produced by MEG.
Figure 1. Schematic representation of the InP/CdS (core/shell) CQD structure and the resulting quasi-Type II band alignment. Also shown is the lowest electron energy level in the conduction band and the hole energy levels corresponding to the B1 and B2 transitions, with indicative energies corresponding to the samples studied.

RESULTS AND DISCUSSION

CHARACTERISATION

Steady-state absorption and PL spectra for the InP/CdS CQDs are shown in Figure 2. The absorption spectrum of the InP cores before the addition of the CdS shell is also shown for comparison. The InP cores have an absorption edge at 550 nm, which corresponds to an average CQD diameter of 3.9 nm. The average diameter of 20 InP/CdS CQDs measured from the TEM image shown in Figure 3 was found to be 5.2 ± 0.1 nm, with a standard deviation of 0.6 nm, indicating the shell thickness is approximately 0.7 nm. On the addition of the CdS shell, the absorption edge is red-shifted to 600 nm and weakens; the corresponding transition is shown in Figure 1, labelled as B2. Both observations are consistent with the formation of a quasi-Type II CQD, and are attributable to a decreased confinement of the electron as its wave function spreads into the shell, resulting in reduced wave function overlap between the carriers, which reduces the absorption strength of the band edge transition. The absorbance of the InP/CdS CQDs increases...
sharply for wavelengths less than ~500 nm; this corresponds to transitions now involving de-localised hole as well as de-localised electron states with consequently increased wave function overlap and thus absorption strength. The lowest energy transition of this type is to the conduction band minimum from a valence band state somewhat below the maximum, and is labelled as B1 in Figure 1, (this labelling corresponds to bleach peaks observed in previous transient absorption studies\textsuperscript{20}).

No significant PL was obtained from the InP cores, but after the addition of the shell emission increased and the photoluminescence quantum yield was measured to be 10 ± 2 %; this can be attributed to the CdS acting as a barrier that reduces the interaction of holes with the CQD surface, which has been shown to mediate non-radiative recombination.\textsuperscript{24,25} The PL spectrum has a peak at 700 nm and a half-width at half-maximum on the short wavelength side of 50 nm.\textsuperscript{26} These optical properties are consistent with previous results both for InP/CdS CQDs\textsuperscript{18,20} and other quasi-Type II CQDs.\textsuperscript{27}

![Figure 2. Absorbance (black) and photoluminescence (red) spectra for the InP (dashed lines) and InP/CdS (solid lines) CQD samples. Inset: an expanded view of the absorption edge region. The labelled absorption features, B1 and B2, correspond to the transitions illustrated by Figure 1.](image-url)
Also shown in Figure 3 are the X-ray diffraction patterns for the InP and InP/CdS CQDs, with reference peaks corresponding to the cubic phases of both InP and CdS also shown for comparison. The diffraction peaks observed for the InP CQDs agree well with the expected peak positions and relative intensities. Dennis et al.\textsuperscript{18} reported that for ‘giant’ InP/CdS CQDs, with shells that were up to 4 nm thick, the CdS forms in its more thermodynamically stable hexagonal phase. However, here the diffraction peaks are little changed on the addition of the shell, and are consistent with the formation of CdS in its cubic phase (zinc blende/Hawleyite). This indicates that for thin shells the cubic template provided by the InP is a more important factor than thermodynamic stability in determining the lattice structure of the shell.

Figure 3. (Left) TEM image of the InP/CdS CQDs. (Right) X-ray diffraction patterns for the InP (red) and InP/CdS (black) CQDs. Reference peaks for InP (red) and cubic phase (zinc blende/Hawleyite) CdS (black) are also shown (Powder Diffraction Files 01-073-1983 and 00-042-1411, respectively).

X-ray photoelectron spectroscopy (XPS) was used to investigate the composition of the InP and InP/CdS CQDs. As described in the experimental section, the ligands on the as-synthesised CQDs were exchanged for 3-mercaptopropionic acid (3-MPA) in order to prevent charging during exposure to the X-ray beam. The normalised In 3d, P 2p, Cd 3d, S 2p, C 1s and O 1s core peaks are presented in Figure 4 for both the InP core and the InP/CdS core/shell CQDs. The
cores showed a P:In ratio of 0.4 ± 0.1. This ratio was not significantly different after the addition of the CdS at 0.5 ± 0.1, indicating that the core composition is not appreciably changed by the shelling process. The low value of the P:In ratio determined by XPS measurements has been reported previously\textsuperscript{28,29} for InP QCDs synthesised by the same method and was attributed to the effect of an In rich surface. In Figure 4(b) the lower binding energy (BE) P 2p doublet (P 2p\textsubscript{3/2} at 128.9 eV) is characteristic of InP. The second, higher BE doublet (P 2p\textsubscript{3/2} at 133.3 eV) is attributed to InPO\textsubscript{x}. The same degree of oxidation of the core can be seen both before and after the addition of the shell, implying that no further oxidation of the core occurs during the shelling procedure. Similar observations have been reported previously for InP QCDs and were explained as arising due to a ketonization reaction during synthesis producing an oxidative environment which results in conversion of the top layer of the InP QCDs into InPO\textsubscript{x} (where x=3,4, but predominantly 4).\textsuperscript{29} However, the authors noted further oxidation on the addition of a ZnS shell, which is not observed here for the case of a CdS shell.\textsuperscript{28,29}

Observation of the Cd 3d and S 2p signals, shown in Figures 4 (c) and (d), revealed that Cd and S are present in broadly equal amounts with Cd:In and S(CdS):In ratios of 2.6 ± 0.3 and 3.2 ± 0.5 respectively, consistent with the addition of a CdS shell to the InP core. Two S 2p doublets were observed in the InP/CdS sample, one characteristic of CdS at 161.7 eV BE,\textsuperscript{30} and a second at 162.9 eV BE attributed to the 3-MPA ligand bound to the CQD surface. The latter was also observed in the InP sample, which was also capped with 3-MPA. No S 2p doublets were observed at higher binding energies (centered around 168 eV BE), where sulfur oxidation products such as SO\textsubscript{4}\textsuperscript{2−} and SO\textsubscript{3}\textsuperscript{2−} would be present,\textsuperscript{31} indicating that the shell did not oxidize. The Cd 3d\textsubscript{5/2} peak was observed at 405.2 eV BE, consistent with other reports for CdS.\textsuperscript{32} A
binding energy shift was observed in the In 3d peaks between the InP/CdS and InP CQDs (see Figure 4(a)), with In 3d$_{5/2}$ was found at 445.0 eV BE and 445.3 eV BE respectively.

The C 1s spectra, (see Figure 4(e)) contain a dominant peak associated with hydrocarbon chains, at 284.8 eV, and two higher binding energy peaks at 286.2 eV and 288.5 eV, associated with C-S and O-C=O respectively, originating from the 3-MPA ligands. The O 1s spectra (see Figure 4(f)) contain two components in both samples. The lower binding energy component at 531.4 eV is attributed to hydroxide species (InOOH or In(OH)$_3$), and the higher component at 532.5 is attributed to both InPO$_x$ and O-C=O.$^{29}$
Figure 4. Comparison of (a) In 3d, (b) P 2p, (c) Cd 3d, (d) S 2p, (e) C 1s, and (f) O 1s X-ray photoelectron spectra for an InP (bottom, red) and InP/CdS (top, black) CQDs. The spectra are normalised to the In 3d signal for each sample.

The Cd 3d:In 3d XPS ratio was used to calculate the shell thickness of the CdS Shell with an analytical model developed by Shard. This method also requires the core size, determined as 3.9 nm from the absorption spectrum, and the inelastic mean free paths of electrons in the core...
and shell material, calculated with the TPP-2M formula. This calculation revealed a thickness of 0.7 ± 0.1 nm, approximately equal to three monolayers of CdS, and thus gave total diameter of 5.2 ± 0.2 nm, consistent with the size extracted from TEM imaging of the core/shell CQD.

ULTRAFAST CHARGE DYNAMICS

Figure 5 shows the fractional transmittance change spectrum for the InP/CdS CQDs acquired at a pump probe time delay of 3 ps, corresponding to the time of maximum bleach signal. Two distinct bleach peaks are evident, corresponding to the B1 and B2 transitions, and are both attributed to state-filling at the conduction band edge. The inset to Figure 5 compares the decay dynamics of both features, which were found to occur with identical rates, as has been observed previously for InP/CdS CQDs and in other quasi-Type II CQDs, confirming this attribution. Both these bleach features thus allow the transient population of photogenerated band-edge electrons to be monitored; for this study the B1 bleach was used primarily, due to its larger response and thus better signal-to-noise ratio.

The evolution of the B1 bleach for a range pump fluences, $J$, is shown in Figure 6 for pump wavelengths of 420 nm and 232 nm, corresponding to excitation photon energies of 2.96 eV and 5.35 eV, respectively. Taking the peak of the PL as a measure of $E_g$, these photon energies are equivalent to 1.7$E_g$ and 3.0$E_g$ and thus correspond to pumping below and above the threshold for MEG, respectively. Each transient exhibits a very rapid initial rise of a few ps duration followed by a decay to a plateau. This behavior is typical for CQDs, with the rise corresponding to increasing state-filling as photo-generated electrons cool to the band edge, and the decay corresponding to the recombination of biexcitons, formed either by MEG or by the absorption of more than one photon per CQD per excitation pulse, which depopulates the band.
edge by an efficient Auger process; the plateau is associated with state-filling by single excitons which recombine with a lifetime that is long compared to the duration of the experiment. Charges can become trapped on the surface of some CQD types for a time longer than the duration between pump pulses. This can result in the formation of a trion when an exciton created by the absorption of a subsequent pump photon combines with the geminate partner of the trapped charge. These trions decay on a similar time-scale to biexcitons, and their presence can lead to an over-estimation of the MEG QY if they are mis-identified.\(^{39}\) However, it has also been shown\(^ {40,41}\) that sufficient stirring or flowing of the sample can prevent trion formation by refreshing the pumped sample volume. Transients obtained when the sample was static and when it was stirred are compared in Figure S1 of the Supporting Information. There is no significant difference between these transients, indicating that trion formation is not an important process for the InP/CdS CQD samples under the experimental conditions used here.

![Fractional transmittance change, $\Delta T/T$, spectrum for the InP/CdS CQD sample collected at a pump-probe delay of ~3 ps. The sample was pumped at a wavelength of 420 nm with a fluence of $1.1 \times 10^{14}$ photons cm$^{-2}$ per pulse. The large feature for wavelengths less than ~430 nm is due to scattered pump light.](image)

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Figure 6. Fractional transmittance change ($\Delta T/T$) transients for the peak of the B1 bleach for the InP/CdS CQD sample below and above the MEG threshold. The sample was pumped at a wavelength of (top panel) 420 nm with fluences of $(0.5 - 3) \times 10^{14}$ photons cm$^{-2}$ per pulse, and (bottom panel) 232 nm with fluences of $(0.4 - 4.8) \times 10^{14}$ photons cm$^{-2}$. Red lines are fits using Equation 2.

The ratio, $R$, between the bleach amplitude at its peak and at the plateau depends on the average number of excitons per photo-excited CQD, with $R > 1$ corresponding to the formation of multi-excitons in some fraction of the CQD population. At high pump fluences, multi-excitons can be created in a CQD by the absorption of more than one pump photon per pulse, as well as by MEG. However, for low pump fluences, the probability of absorbing more than one pump photon per pulse becomes negligible and in this case an observation of $R > 1$ indicates
that MEG is occurring. For core only and Type I core/shell CQDs, the MEG QY for a particular pump photon energy is typically determined from similar bleach transients by measuring $R$ for a range of fluences and extrapolating to the value corresponding to negligible fluence by fitting these data to the following equation:

$$R(J) = \delta QY \langle N \rangle [1 - \exp(-\langle N \rangle)]^{-1} \tag{1}$$

where $\langle N \rangle = \sigma J$ is the average number of photons absorbed per CQD, $\sigma$ is the absorption cross section at the pump wavelength, and $\delta$ is a factor which accounts for the decay of single excitons over the observed time window. However, Eqn. (1) is only valid for samples with an absorbance length, $l_A$, for the pump wavelength which is long compared to the beam path through the sample, $l_S$. Moreover, as discussed previously, for $l_A \ll l_S$ the value of $\Delta T/T$ observed will be reduced, since the volume of excited sample through which the probe beam passes is decreased as the pump beam is completely absorbed close to the front facet of the cuvette. A dilemma arises because the magnitude of $\Delta T/T$ is also proportional to the absorbance at the probe wavelength, $A$, i.e. reducing the sample concentration so that $l_A$ is long compared to $l_S$ results in a weak fractional change in transmittance.

The InP/CdS CQDs studied here is just such a case for which $l_A \ll l_S$; as shown in Figure 2, the pump absorbance, $A_p$, at the shortest wavelength of 232 nm is ~40 times greater than at the probe wavelength of 470 nm. Therefore, we analyse the effect of MEG on the fractional transmittance change transients, $\Delta T(t)/T$, and thereby determine its $QY$, by instead fitting them to the following expression (derived in the Supporting Information) which takes into account strong pump absorbance. For an average number of photons absorbed per CQD as the pump beam enters the sample, $\langle N \rangle_0$,
\[
\frac{\Delta T(t)}{T} = \frac{A}{A_p} \left[ D(t) \sum_{n=1}^{\infty} \frac{(-\langle N \rangle)^n}{n^n!} (e^{-nA_p} - 1) - E(t) \left( e^{-\langle N \rangle e^{-A_p}} - e^{-\langle N \rangle} \right) \right]
\]  

(2)

where

\[
D(t) = \frac{k_{xx} + k_x}{2k_{xx}} e^{-k_x t} - \frac{k_x - k_{xx}}{2k_{xx}} e^{-(k_{xx} + k_x)t}
\]  

(3)

\[
E(t) = (2 - QY) \left( \frac{k_x}{2k_{xx}} e^{-k_x t} - \frac{k_x - k_{xx}}{2k_{xx}} e^{-(k_{xx} + k_x)t} \right)
\]  

(4)

and where \(k_{xx}\) and \(k_x\) are the rate constants for decay of biexcitons and single excitons, respectively. A global fit of Eqn. (2) to the transients shown in Figure 6 was undertaken for both pump wavelengths simultaneously. The values of \(A_p\) and \(A\) determined from the steady-state absorbance spectrum, i.e. Figure 2, were used, whilst values of \(k_x\) and \(k_{xx}\) common to all the transients were determined by the fitting process. The value of \(QY\) was fixed to unity for those transients corresponding to pumping below the threshold for MEG; a \(QY\) value for pumping at a photon energy of \(3E_g\), common to the corresponding transients, was found from the fit.

This process yielded biexciton and single exciton lifetimes of \(\tau_{xx} = k_{xx}^{-1} = 50 \pm 2\) ps and \(\tau_x = k_x^{-1} = 3.05 \pm 0.06\) ns, respectively. This biexciton lifetime is consistent with the value of \(58 \pm 12\) ps for a similar InP/CdS CQDs reported previously for excitation below the MEG threshold.\(^{18}\) It is also somewhat larger than the \(41 \pm 3\) ps biexciton lifetime reported for an InP/ZnS/ZnO (core/shell/shell) Type I CQDs with a similar \(E_g\), consistent with the reduced wave function overlap in a quasi-Type II CQD. Moreover, at 50 ps this lifetime is significantly longer than the characteristic time for electron transfer to an acceptor molecule reported by Wu et al.\(^{20}\) suggesting that extraction of the additional charge carriers generated by MEG should be possible with good efficiency in this system. The single exciton lifetime measured is also consistent with
the observations of Wu et al.\textsuperscript{20} of \(~4\) ns, determined from measurement of PL decay transients. A similar measurement on the current sample yielded a decay that was well-described over a 10 ns time-window by a lifetime of \(4 \pm 1\) ns – see Figure S3 in Supporting Information.

The MEG \(QY\) for pumping at a photon energy equivalent to \(3E_g\) was determined to be \(1.22 \pm 0.01\) by the fitting process. For InP/ZnS/ZnO Type I CQDs with a similar \(E_g\) an MEG \(QY\) of \(1.18 \pm 0.03\) for a photon energy equivalent to \(2.6E_g\) has been previously reported.\textsuperscript{15} However, that work used the position of the absorption edge as a measure of \(E_g\), rather than the PL peak as in this study; using instead the PL peak, yields a photon energy equivalent to \(2.7E_g\). For its reported efficiency of 0.3, the Type I InP/ZnS/ZnO CQDs would thus be expected to have a MEG \(QY\) of \(1.27 \pm 0.04\) for a pump photon energy equal to \(3E_g\). The efficiency of the MEG process in CQDs with an InP core thus seems to be not greatly affected by the change from a Type I to a quasi-Type II core/shell heterostructure, with the difference in MEG \(QY\) at \(3.0E_g\) reported for the two types being similar to the experimental accuracy.

SUMMARY AND CONCLUSION

InP/CdS CQDs have been synthesised and characterised by absorbance and photoluminescence spectroscopy, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. These measurements show that quasi-Type II core/shell structures have been synthesized, with a zinc blende crystal phase. The core diameter was determined to be \(3.9 \pm 0.1\) nm from optical measurements and the thickness of the shell was \(0.7\) nm, as determined consistently by both TEM and XPS. An oxide layer was found to form on the surface of the In-rich InP core, but not on the surface of the CdS shell layer, which was broadly stoichiometric. The multi-exciton dynamics in these CQDs have been investigated on a sub-nanosecond time-
scale using ultrafast transient absorption spectroscopy. The bleach transients produced by biexciton recombination were analysed, taking into account the effect of strong pump absorbance, and were used to determine the quantum yield of multiple exciton generation in InP/CdS CQDs for these first time. This was found to be similar to that previously reported for Type I InP CQDs.

An MEG quantum yield not adversely affected by a change in CQD structure from Type I to quasi-Type II allows the advantages of a quasi-Type II design to be exploited in CQD-based solar cells without sacrificing the potential benefit of MEG. The extended biexciton and single exciton lifetimes confirmed in this study and resulting from the reduced wave-function overlap between charge carriers produced by the quasi-Type II structure, allow more time for charge extraction before recombination. In addition to forming a quasi-Type II structure, the CdS shell also effectively passivates the InP core surface, but without adding a barrier to electron extraction. Finally, the CdS shell also redshifts the band gap towards the optimum for exploitation of the solar spectrum. These advantages will be key to the effective exploitation of multiple exciton generation for enhanced solar cell performance.

METHODS

Synthesis

InP/CdS nanoparticles were synthesised according to literature procedures, with slight modifications.\(^{18,20}\) The amount of CdS precursor solution added was calculated based on the InP core size, itself calculated from the absorption spectrum, described in the literature.\(^{23}\)

Indium acetate (InAc\(_3\), 0.117 g, 0.4 mmol), myristic acid (MA, 0.274 g, 1.2 mmol) and 14 mL of dry 1-octadecene (ODE) were degassed and kept under vacuum for 30 minutes, followed by
heating to 120 °C under vacuum for a further 30 minutes. The mixture was then heated to 285 °C under argon, and tristrimethylsilyl phosphine (TMSP, 1 ml, 0.2 mmol) was injected and the temperature dropped to 270 °C for the growth period. The reaction was stopped after 4 minutes by removing the heat source and cooled to room temperature. The InP QDs were precipitated out of solution by the addition of ethanol. This was repeated several times and the washed QDs were re-dispersed in dry toluene for analysis.

Precursor solutions of cadmium oleate and sulfur were prepared for the shelling process. The cadmium solution (0.04 M) was prepared by dissolving CdO (0.077 g, 0.60 mmol l) in OA (1.2 mL) and 15 mL of dry ODE at 300 °C to obtain a colourless solution. The precursor solution was then maintained at above 100 °C. A sulfur injection solution (0.015 M) was prepared by dissolving sulfur (20 mg 0.62 mmol) in 20 mL of ODE at 100 °C. 5 mL of oleylamine and 3 mL of ODE were degassed. Washed cores in hexane (3.7 mL, ~44 μM) were added and the solvent subsequently removed under vacuum with the temperature gradually raised to 100°C. The flask was refilled with Ar and the temperature was raised to 150 °C for the first cation addition. (Note: the first addition of cadmium oleate and the initial annealing step were conducted at 150 °C due to an observed sensitivity of the InP core to etching at high temperatures under these reaction conditions, i.e. in presence of oleylamine and/or with these particular shell precursors). The cadmium precursor solution was added dropwise to the solution, followed by 10 minutes' annealing and the first injection of the sulfur solution. The temperature was then raised to 240 °C for all subsequent precursor additions. The first shell was annealed for 30 minutes at this elevated temperature. All subsequent additions were annealed at this temperature at for 45 minutes. Three layers of CdS shell were formed in the course of this reaction. After the shelling was complete, the reaction was cooled to room temperature and washed by precipitating with
ethanol. The washed samples were re-dispersed in dry hexane or toluene for the optical studies in this report, and diluted to an absorbance of approximately 0.1 at the band edge transition wavelength. Samples were kept under nitrogen after washing and for all the optical studies.

**X-ray diffraction**

X-ray diffraction measurements were made on a Bruker D8 Discover diffractometer, equipped with a LynxEYE detector and a Cu source (λ = 1.5406 Å) with generator settings of 30 mA and, 35 kV. Data were collected in continuous scan mode, over the 2θ range 10-75 °, with step size 0.1 and step time 411 s. The samples were prepared by repeated washing in ethanol and re-dissolution in dry hexane. The hexane solution was dropped onto a glass slide in multiple layers and dried before measurement.

**Transmission electron microscopy**

Bright field images were obtained using a Philips CM20 transmission electron microscope equipped with a LaB₆ electron source and operated at 200 kV. The samples were prepared by repeated washing with ethanol and re-dissolution in dry hexane. The dilute hexane solution was dropped onto holey carbon TEM grids, washed with dry hexane and dried under vacuum at room temperature before use.

**X-ray photoelectron spectroscopy**

The CQDs (3ml) were precipitated with ethanol and re-dispersed in chloroform (3 mL) before being added to a solution of 3-mercaptopropionic acid (3ml, 0.03 mol) in H₂O (3 mL) with stirring under argon. The mixture was stirred for 2 hours, until the dots had moved into the aqueous layer. They were then washed alternately with toluene and ethanol (3 times with each).
The CQDs were re-dispersed in methanol then drop cast onto glass and XPS was performed with a Kratos Axis Ultra spectrometer, with excitation from focused monochromated Al Kα (1486.6 eV) X-rays and using an electron flood gun for charge neutralization. Peaks were recorded with a pass energy of 40 eV. All spectra were calibrated to C 1s hydrocarbon at 284.8 eV. Peaks were fitted with a nonlinear Shirley-type background, using 70% Gaussian 30% Lorentzian line shapes. Core level intensities were corrected for their photoionization cross sections\(^\text{43}\) and relative sampling depths.

**Optical studies**

The steady state absorption and the PL spectra were measured with the use of a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer and a Horiba Jobin Yvon Fluorolog model iHR(FL3-22) spectrofluorometer, respectively. The PL quantum yield measurements were made with the same spectrofluorometer, utilising its integrating sphere attachment and an excitation wavelength of 420 nm.

The sub-nanosecond charge dynamics were studied using a home-built ultrafast transient absorption spectrometer which has been reported previously.\(^{10,11,15,25}\) A Ti:Sapphire regenerative amplifier (Spectra-Physics Spitfire-Pro) seeded by a mode-locked Ti:Sapphire oscillator (Spectra-Physics Tsunami) produces pulses of 100 fs duration and ~1 mJ energy at a wavelength of ~800 nm and 1 kHz repetition rate. Using a beam splitter, 95% of this beam is passed to an optical parametric amplifier (OPA, Light Conversion Ltd. TOPAS-C) with harmonic generating crystals to produce the pump beam, tuneable from the infra-red to the ultra-violet with a minimum wavelength of 232 nm. The pump beam is passed through a mechanical chopper synchronised to half the pulse repetition rate and then focused onto the sample. A neutral density
filter is used to tune the time-averaged pump power at the sample. At 420 nm, with 1mW output and a beam diameter of 2.2 mm, the pump density was 26 mW cm\(^{-2}\), which is equivalent to a fluence of \(1.1 \times 10^{14}\) photons cm\(^{-2}\) per pulse. At 232 nm with a similar beam diameter, the maximum fluence was \(0.5 \times 10^{14}\) photons cm\(^{-2}\) per pulse. The remaining 5% of the beam from the amplifier is directed through a computer-controlled delay stage to vary the arrival time difference between pump and probe pulses at the sample. This beam is then passed through a sapphire plate to produce a white light continuum, which is split to form the probe and reference beams. The first was directed through the sample and then both through a spectrometer (Princeton Instruments Acton sp2500i) and detected by Si photodiodes. The changes of the probe beam were recorded using a digital lock-in amplifier (Stanford Research Systems SR830). Data shown here are averages of 5-10 scans. In order to prevent photo-charging of the CQDs the samples were stirred by a magnetic stirring system (Thermo Scientific Variomag Mini) at approximately 1000 rpm.

The photoluminescence lifetimes were measured using the time correlated single photon counting technique.\(^{44,45}\) A mode-locked Ti:sapphire laser (Mai Tai HP, Spectra-Physics) was used to produce \(\sim 100\) fs pulses at 80 MHz repetition rate and a wavelength of 840 nm. This rate was reduced to 2 MHz by an acousto-optic pulse picker (Pulse Select, APE) before the wavelength was converted to 420 nm via second harmonic generation (APE Harmonic Generator) for sample excitation. The resultant emission was passed through a monochromator (Spex 1870c) tuned to the PL peak before detection by a multi-channel plate (Hamamatsu R3809U-50). The time correlation of the detected photons was performed using a TCC900 PC card from Edinburgh Instruments.
SUPPORTING INFORMATION

Comparison of stirred and static fractional transmittance change data for InP/CdS CQD.

Derivation of equation 2. Photoluminescence decay curve for InP/CdS CQD.

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REFERENCES


(26) The spectral range of the detector used limited photoluminescence measurements to <800 nm.


TOC Graphic:
Intensity (counts) vs. 2 (degrees) for InP and InP/CdS. Peaks at (111), (200), (220), (311), (222), (331), and (400) are highlighted.