Multiple-exciton generation—a process in which multiple charge-carrier pairs are generated from a single optical excitation—is a promising way to improve the photocurrent in photovoltaic devices and offers the potential to break the Shockley–Queisser limit. One-dimensional nanostructures, for example nanorods, have been shown spectroscopically to display increased multiple exciton generation efficiencies compared with their zero-dimensional analogues. Here we present solar cells fabricated from PbSe nanorods of three different bandgaps. All three devices showed external quantum efficiencies exceeding 100% and we report a maximum external quantum efficiency of 122% for cells consisting of the smallest bandgap nanorods. We estimate internal quantum efficiencies to exceed 150% at relatively low energies compared with other multiple exciton generation systems, and this demonstrates the potential for substantial improvements in device performance due to multiple exciton generation.
Solar cells fabricated from conventional bulk semiconductors such as silicon or gallium arsenide are approaching the physical limit of solar power conversion efficiency. Thermalization of hot carriers is the predominant cause of this limitation. A promising strategy to overcome such phonon-related loss processes is to harvest multiple charge-carrier pairs generated from a single excitation. Recently, it has been demonstrated that these mechanisms are particularly efficient in colloidal quantum dots (QDs) where the process is termed multiple-exciton generation (MEG). MEG is enhanced in systems where the limited spatial extent of the excited states relaxes the requirements for conservation of crystal momentum that apply in typical bulk systems and increases the MEG yield. In an ideal system, bi-exciton states will be formed efficiently once the excitation energy exceeds twice the bandgap.

The multiple-exciton state formed by MEG in PbSe QDs has been shown in spectroscopic experiments to relax on a time scale of 20–200 ps (ref. 3) to a single-exciton state, by an Auger-like process that is the reverse of the MEG process. To harvest charge carriers from multiple-exciton states, it is necessary for charge separation to occur on much faster time scales than Auger decay, and this is not necessarily easy to achieve in a device structure. We note that it is important to achieve two rapid charge transfer events for each doubly excited nanoparticle, since the trion state formed after the first charge transfer event is known to decay rapidly.

Recent results have shown that the initial yield of multi-exciton states is enhanced in PbSe nanorods (NR) systems. It has been proposed that this may be due to enhanced MEG rates arising from larger Coulombic electron-hole binding in NRs. Furthermore, Auger relaxation is found to be slowed in these one-dimensional systems. It has been argued that this is due to a slower bimolecular Auger-type recombination in elongated nanostructures compared with a faster, three-particle Auger-type process in zero-dimensional QDs. NR films are therefore attractive for photovoltaics exploiting MEG; however, fabrication of working devices from NRs has so far proved very challenging.

Here we present the synthesis and characterization of PbSe NRs and their incorporation into working devices. We demonstrate that charges generated by MEG can be extracted from solar cells consisting purely of PbSe NRs with external quantum efficiencies (EQEs) exceeding 120%.

**Results**

**Nanorod synthesis.** PbSe NRs of three different bandgaps (1.05, 0.95 and 0.80 eV) were synthesized following a method modified from that reported by Koh et al. (see Fig. 1a). We employed an additional *in situ* CdCl₂ treatment at the end of the NR synthesis to provide additional surface passivation (see the Methods section for further details). It has been shown that this approach minimizes the occurrence of sub-bandgap tail states which improves solar cell performance significantly. The NR synthesis was optimized to minimize the diameter and length distributions and to reduce the formation of dots and hooks, to improve charge transport (see the Supplementary Note 1). Transmission electron microscopy (TEM) confirmed only negligible quantities (<5% by particle number) of non-NR structures, and diameter and length s.d. of ca. 8% and 13%, respectively (Fig. 1b–f).

**Photovoltaic device fabrication.** We fabricated solar cells by depositing a dense array of PbSe NRs on a ZnO film, which was produced using a sol–gel method. The NRs were deposited in a layer-by-layer approach using the ligand 1,2-ethanediol (EDT) for the first layers and hydrazine as the exchanging ligand for the final NR layer (see the Methods section for further experimental details). It has been shown recently that QDs treated with amine-functionalized ligands exhibit highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, which are closer to the vacuum level compared with analogous QD films employing thiol-functionalized ligands. A multi-layer QD film where the bottom layers are treated with EDT and the top layer with hydrazine is therefore likely to show an energy cascading structure that promotes charge extraction. The relevant energy levels were determined using a combination of ultraviolet photoelectron spectroscopy (UPS) and absorbance spectroscopy as described in previous work (Supplementary Fig. 4) and are presented in Fig. 2b. Current–voltage characteristics of the optimized solar cells made from three different bandgap NRs are shown in Fig. 2c and the standard photovoltaic device parameters are listed in Table 1.

**Device quantum efficiencies.** Figure 3 displays the short-circuit EQE spectrum for NR devices. Interestingly, we observe maximum EQEs of 109 ± 3%, 113 ± 4% and 122 ± 3% for devices with NR bandgaps of 1.05, 0.95 and 0.80 eV, respectively, at high-photon energies (ca. 3.3 eV). We note that no antireflective coating was employed to reduce reflectance losses at the glass/air interface. Reassuringly, we can reconstruct the measured short-circuit current within ca. 1% measurement error by integrating the EQE over the AM1.5G solar spectrum (Supplementary Table 1). Furthermore, measuring the EQE under different white light biases produced identical spectra, suggesting a current collection that is independent of the charge-carrier density (Supplementary Fig. 7). For the lowest photon energies, we recognize a clearly visible first excitonic peak in all three test devices and explain the steep drop in quantum efficiency for photon energies exceeding 3.5 eV by the onset of absorption of the ZnO layer (Supplementary Fig. 8).

To allow for incomplete absorption of incident photons, we next determined the internal quantum efficiency (IQE) via two independent approaches: first, we measure the fraction of light reflected from the device at each photon energy \( R(\text{hv}) \) using a calibrated silicon or germanium photodiode. The IQE was then calculated as \( \text{IQE}_{\text{Exp}}(\text{hv}) = \frac{1}{1-R(\text{hv})} \). We note that IQE \( (\text{hv}) \) presents the lower bound for the IQE, as parasitic absorbance by other layers and diffuse scattering are neglected. In our second approach, we derive IQE \( (\text{Model}) (\text{hv}) \) by applying an optical transfer matrix model using the refractive indices and the extinction coefficients \( k \) of each device layer measured by ellipsometry (Supplementary Fig. 9). In this case, IQE \( (\text{Model}) (\text{hv}) = \frac{A}{A+1} \), where \( A \) is the calculated fraction of light absorbed. Reassuringly, we identify similar values for IQE \( (\text{Exp})(\text{hv}) \) and IQE \( (\text{Model})(\text{hv}) \) (Fig. 4).

These values at their highest are above 170%, which is comparable to devices incorporating singlet fission materials to generate multiple excitons. We note that the dip in EQE after the first excitonic absorption peak is deeper than would be expected based on the absorption spectrum (Supplementary Fig. 10), leading to a significant dip in the calculated IQE spectrum in the same spectral region. This phenomenon is
It is unlikely to result from charge generation taking place deeper in the device when the absorption coefficient is lower, as these effects should recover in full when the absorption coefficient regains its initial peak value at around 1.4 $E_g$ (see Supplementary Fig. 10 for film absorption).
energy. An ideal MEG system would show sharp increases in quantum efficiency at multiples of the bandgap. However, in common with other reports5,10,34–36, we find a gradual increase in efficiency above 2Eg. The threshold energy at which this increase begins, and the rate of efficiency increase above the threshold are important parameters in comparing materials systems and in determining the gain in power conversion efficiency due to MEG for a device under solar illumination. Beard et al.4 have considered a model in which the rate of MEG increases with energy above threshold, leading to a gradual rise in initial MEG yield as this process competes with rapid cooling. In a device, quantum efficiency enhancement depends not only on the initial yield of multiple excitons, but also on being able to rapidly separate and efficiently collect the additional charge carriers. From our data, we make the following observations: the dependence of IQE on bandgap-normalized energy is remarkably similar for all three NR bandgaps, exceeding 100% at around 2.9Eg in all cases and reaching 150% by 3.4Eg. This is a substantial improvement over the dot devices reported by Semonin et al.3, where the IQE increases much more slowly with energy, not reaching 150% until nearly 5Eg. In our data, it is difficult to accurately determine a threshold energy for MEG, due to the energy-dependent quantum efficiency below 2Eg that is discussed above. Clearly quantum efficiency without the assistance of MEG cannot be >100%, so the MEG threshold must be below 2.9Eg. Taking a quantum efficiency of 75–80% with no MEG contribution, consistent with the IQE values at the first excitonic peak, suggests an MEG threshold below 2.5Eg, and if the energy dependence of IQE in Fig. 5 were solely due to MEG then the threshold would be close to 2Eg. It is interesting to compare the IQE energy dependence with spectroscopic measurements of initial MEG yields in PbSe dots3,36 and rods9,11 in solution, also shown in Fig. 5 and in the Supplementary Fig. 11. Despite the fact that device IQEs are reduced by Auger recombination competing with charge separation, and by regular recombination losses, the IQEs we measure increase more rapidly with energy than the initial MEG yields in solution. This indicates that MEG is enhanced in films, with the 4% enhancement estimated by similar methods for dot devices5. MEG thus contributes a substantive amount to the realistic quantum efficiency without MEG of 80%, leads to enhancements as high as 12.5% for the 0.8 eV sample, compared with the 4% enhancement estimated by similar methods for dot devices5. MEG thus contributes a substantive amount to the IQE without the assistance of MEG of 80%, leads to enhancements as high as 12.5% for the 0.8 eV sample, compared with the 4% enhancement estimated by similar methods for dot devices5. MEG thus contributes a substantive amount to the realistic quantum efficiency without MEG of 80%, leads to enhancements as high as 12.5% for the 0.8 eV sample, compared with the 4% enhancement estimated by similar methods for dot devices5.

Conclusion

We have demonstrated working photovoltaic devices based on high-quality CdCl2-treated PbSe NRs of three different bandgaps. EQE values clearly exceeded 100%, and maximum EQEs of 122% were found for the smallest bandgap devices. Estimated IQE values were found to increase rapidly above 2Eg, reaching values as high as 170% at only 3.5Eg. This behaviour is superior to that seen in solution-based measurements of MEG yields, and indicates potential for substantial efficiency gains in MEG-based solar cells.

Methods

PbSe nanorod synthesis. The synthesis of PbSe NRs was carried out following modified versions of previously reported methods (see Supplementary Note 1)5.

Briefly, PbO (1.76 g, 7.8 mmol), oleic acid (6.2 ml, 19.7 mmol, 5.6 g) and octadecene (41.8 ml, 127.6 mmol, 32.6 g) were combined in a three-neck flask and degassed at 110 °C under vacuum (10−2 mbar or better) for 2 h. Subsequently, the reaction flask was flushed with nitrogen and heated to 160 °C. In parallel, CdCl2 (0.16 g, 0.9 mmol), tetradecylphosphonic acid (33 mg, 0.12 mmol) and oleylamine (8.13 ml, 30.4 mmol, 8.1 g) were combined in a separate three-neck flask and degassed under vacuum (10−2 mbar or better) at 110 °C for 12 h. The solution was flushed with nitrogen and set to 100 °C. A solution of selenium (1.92 g, 23.8 mmol) in tris(diethylamino)phosphine (TDP, 24.0 ml, 87.6 mmol; 20.8 g) was rapidly injected into the lead precursor solution. The bandgap of the PbSe NRs was tuned
by adjusting the reaction temperature while the overall reaction time was kept constant at 2.5 min. For bandgaps of 1.05, 0.95 and 0.80 eV, reaction temperatures of 120, 130 and 140 °C were chosen, respectively. For the in situ CdCl₂ treatment, 2.7 ml of the CdCl₂/tetradecylphosphonic acid solution was injected into the reaction flask of the NRs, 10 s before the crystal growth was quenched. The reaction was quenched by adding 20 ml of ice-cold n-hexane and by placing the reaction flask in an ice-water bath. The NRs were isolated from the reaction mixture by flocculating to turbidity using a 1-buthanol/ethanol/hexane solvent system. The purified QDs were then redispersed in octane at a concentration of ~100 mg ml⁻¹ and stored under argon.

**Figure 4** | Internal quantum efficiency (IQE) of photovoltaic devices. NRs with bandgaps of 1.05 eV (a), 0.95 eV (b) and 0.80 eV (c). IQE₆x₆ₜ(hv) and IQE₆x₆₏₆₇(hv) were determined, respectively, using reflectance measurements and optical modelling as described in the text. (d–f) The measured reflection (coloured curve) and modelled absorbed fraction for bandgaps of 1.05, 0.95 and 0.80 eV, respectively. Error bars show the standard deviation of multiple independent solar cells (six cells for 1.05 eV, five cells for 0.95 eV and five cells for 0.80 eV). The range of grey curves shown for the modelled results illustrate the effect of changing the active layer thickness in the model by the experimental error of ±10 nm.

**Figure 5** | Comparison IQEs with literature. IQEs of devices consisting of PbSe NRs with bandgaps of 1.05, 0.95 and 0.80 eV and MEG quantum yields of PbSe QDs in devices and PbSe NRs in solution. Error bars show the standard deviation of multiple independent solar cells (six cells for 1.05 eV, five cells for 0.95 eV and five cells for 0.80 eV). A comparison including MEG quantum yields of PbSe QDs in solution and PbSe QDs in films can be found in Supplementary Figure 1.
modified version of a literature reported layer-by-layer deposition method. Briefly, PbSe NRs were spin coated on the substrate at a concentration of 25 mg mL\(^{-1}\) in octadecane for 15 s. Subsequently, the native oleic acid ligand was exchanged with ethane dithiol (20 mM in acetonitrile) in a second spin-coating step using the same spinning conditions. To remove residual ligand and un-exchanged NRs consecutive spin-rinsing steps using pure acetonitrile and octane were performed. This cycle was repeated four times. For the final NR layer, hydrazine (1 M in acetonitrile) instead of EDT as the exchanging ligand was used. The NR films were encapsulated by affixing a glass coverslip on the NR layer using carbon tape as spacer unit and epoxy glue as sealant. TEM samples were prepared as reported elsewhere by drop casting a ca. 1 mg mL\(^{-1}\) solution in octane on a TEM Grid (200 Mesh Cu, Agar Scientific) in a nitrogen-filled glove box.

**Photovoltaic device fabrication.** Solar cells were prepared on indium tin oxide (ITO)-patterned glass substrates cleaned in an ultrasonic bath with ethanol, acetone and isopropanol. A ca. 55-nm ZnO layer (Supplementary Figure 8) was deposited using a sol–gel method suggested by Lloyd et al.\(^{39}\) and modified by Beck et al.\(^{21}\). Briefly, 250 μl of diethylzinc in hexane (1 M) was diluted in 750 μl anhydrous tetrahydrofuran in a nitrogen-filled glove box. The solution is spun-cast in air at 4,000 r.p.m. for 30 s. The ZnO films were then allowed to rest at room temperature under ambient environment for 15 min and were then annealed at 130 °C for 5 min. PbSe NRs were deposited following a sequential layer-by-layer spin-coating technique as described above. The samples were then transferred into a thermal evaporator and molybdenum oxide (MoO\(_x\)) was deposited using a sol–gel method suggested by Lloyd et al.\(^{39}\) and modified by Beek et al.\(^{26}\), and was used. For wavelengths between 1,500 and 800 nm, a set of InGaAs detectors were employed, (Thorlabs SM1PD2A) and for wavelengths between 900 and 350 nm a set of silicon diodes (Thorlabs SM03PD1A) were used. A Keithley 2635 source measure unit was used to measure the short-circuit current as a function of wavelength. The incident light was focused to a spot size of ca. 1 mm\(^2\) using a set of lenses to illuminate the individual pixel of size 5.5 cm\(^2\). Current–voltage characteristics were measured under AM 1.5G conditions using an Abet Sun 2000 solar simulator, at an intensity equivalent to 100 mW cm\(^{-2}\). Internal quantum efficiency measurements were performed using a Beeket 2635 source measure unit located in an in situ Helios dual-beam FEG scanning electron microscopy (SEM)/focused ion beam (FIB) microscope, fitted with an Omniprobe micromanipulator for in situ lift-out technique,\(^{40}\) and the thinning step of the lamellar specimen was performed with decreasing beam current to reduce sample damage and improve sputtering of the material. The cross-sectional specimen was analysed through high-angle dark-field scanning TEM, using a Fischione detector on a FEI Tecnai F20 microscope, operated at 200 kV. Energy dispersive X-ray spectroscopy mapping of the cross-sectional specimen was performed using a FEI Tecnai Osiris TEM/scanning TEM equipped with a field-assisted thermionic emitter gun, operating at 200 kV. The microscope is also equipped with four Bruker silicon drift detectors for high collection efficiency and high count rates.

**Ellipsometry.** For ellipsometry, all samples were prepared as described above but on silicon substrates. The only exception is ITO, which was measured on glass as received from Psiotec. The samples were measured on a Woollam Vase VB-400 ellipsometer in reflection mode (ITO in transmission mode) using monochromatic light from a xenon lamp guided through a monochromator. The data for the QD sample was fitted using a combination of a Cauchy and a Gaussian model. The ITO data were fitted with a combination of a Drude and a Lorentz oscillator and the MoO\(_x\) was fitted with a Lorentz oscillator.

**Transfer matrix modelling of IQE.** Reflectance was modelled as per literature sources\(^{27,41}\). The \(n\) and \(k\) values were measured in-house as described in the ellipsometry section above and are presented in Supplementary Figure 9. This program calculates the field profile, excitation generation profile and generated current from the wavelength dependent complex indices of refraction in devices using a transfer matrix method described in detail in refs 27,28. It assumes the light source located in an \(n = 1\) environment (air) and that the first layer is a thick substrate, so that incoherent reflection at the air/1st layer interface is taken into account before the coherent interference is calculated in the remaining layers. Film thicknesses were measured using a DEKTAK profilometer. Error in the model is given as \(\pm 10\%\) of the active layer.

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