PHYSICAL REVIEW B **81**, 081303(R) (2010)

# Efficient carrier multiplication in InP nanoparticles

Stuart K. Stubbs,[1] Samantha J. O. Hardman,[1] Darren M. Graham,[1] Ben F. Spencer,[1,2] Wendy R. Flavell,[1] Paul Glarvey,[3] Ombretta Masala,[3] Nigel L. Pickett,[3] and David J. Binks[1,*]

[1]*School of Physics and Astronomy and the Photon Science Institute, The University of Manchester, Manchester M13 9PL, United Kingdom*

[2]*Cockcroft Institute, STFC Daresbury Laboratory, Warrington, Cheshire WA4 4AD, United Kingdom*

[3]*Nanoco Technologies Ltd., Grafton Street, Manchester M13 9NT, United Kingdom*

(Received 26 October 2009; published 16 February 2010)

Efficient carrier multiplication in InP nanoparticles is reported; ultrafast transient absorption measurements at the band edge were used to determine the number of excitons per photoexcited nanoparticle for a range of both excitation fluences and photon energies. At photon energies greater than $2.1 \pm 0.2$ times the band gap, an average of more than 1 exciton per photoexcited nanoparticle was found even in the limit of vanishing fluence. The average number of excitons generated by an absorbed photon was measured to be $1.18 \pm 0.03$ for excitation photons with energies 2.6 times the band gap.

DOI: 10.1103/PhysRevB.81.081303 PACS number(s): 78.67.Bf, 78.47.D−

## I. INTRODUCTION

In conventional photovoltaic (PV) cells the energy of an absorbed photon ($h\nu$) in excess of the band gap ($E_g$) is dissipated as heat. This loss mechanism is generally regarded as both unavoidable and significant and places a theoretical limit on solar cell efficiency of ~30%.[1] Carrier multiplication (CM), also known as multiple exciton generation, is a phenomenon in which some of this excess energy, ($h\nu$-$E_g$), generates additional electron-hole pairs. CM could thus increase photocurrent and therefore PV efficiency, with recent calculations[2] indicating that a solar cell utilizing CM could have efficiency as high as 44%. CM has been observed in bulk semiconductors for decades[3–5] but is too weak an effect in these materials to have a significant influence on PV performance. However, recently several studies[6–8] have shown that CM quantum yields (QYs), i.e., the average number of electron-hole pairs generated per absorbed photon, in some colloidal nanoparticles (NPs) can be significantly greater than 100% and consequently large enough to have an impact on PV efficiency. The enhancement of CM in NP has been attributed to quantum confinement effects increasing the Coulomb interaction of charge carriers and suppressing competing processes such as phonon mediated cooling.[9–11] There are some reports of little or no CM in ostensibly similar NPs,[12–14] but these seemingly conflicting results may have been reconciled by a recent study which showed that CM is sensitive to the way in which the NP have been prepared.[15] The potential for high CM QY in NPs is further supported by the recent demonstration of a NP-based photoconductive device with >100% internal gain.[16]

Efficient CM has to date been demonstrated in a number of different NPs: PbSe,[17] PbS,[18] PbTe,[19] CdSe,[20] InAs,[21] and Si.[22] There are numerous other materials that could be used for CM, and a number of candidates were evaluated recently[11] by calculating a figure of merit based on the ratio of the biexciton and monoexciton density of states. On this basis, CdSe, PbSe, and InP NP were identified as being particularly well suited to CM. However, of these only CdSe and PbSe NP have been studied with the CM performance of InP NP remaining, until now, uninvestigated. Further, the threshold for CM in InP is expected to be $h\nu = 2.1E_g$ (Ref. 8); in comparison, the thresholds for PbSe and CdSe have been measured to be $2.9E_g$ and $2.5E_g$, respectively.[8] An analysis of the potential efficiency of solar cells utilizing CM shows that a low threshold is critical to PV performance.[2] Finally, InP is a relatively benign substance compared to arsenic, lead, or cadmium. Here we report the demonstration of CM in colloidal InP NP using ultrafast transient absorption measurements. The CM QY is measured for a range of excitation photon energies and the CM threshold thus determined is shown to agree with theory.

## II. EXPERIMENTAL

The dynamics of excitons at the band edge were measured using a transient absorption spectrometer. The probe beam was a white light continuum generated in a 2-mm-thick sapphire window by 0.8 $\mu$J laser pulses split from the output of a Ti:Sapphire ultrafast regenerative amplifier (Spectra Physics Spitfire Pro) operating at a center wavelength of 800 nm with ~100 fs pulse length and 1 kHz repetition rate. The probe beam was split into a reference beam, which bypassed the sample, and a sample beam which was focused to a spot size of ~1 mm at the sample position. The NP samples, in hexane, were contained in 10 mm path-length quartz cuvettes, and could be stirred at up to 1000 rpm. The reference and sample beams were balanced in the absence of any sample photoexcitation before being passed through a monochromator and detected with a pair of silicon photodiodes. The majority of the output from the regenerative amplifier was used to produce, via an optical parametric amplifier (Light Conversion, TOPAS) and subsequent harmonic generation stages, a pump beam with photon energies ranging from $h\nu = 2.8$ to 5.2 eV. The pump beam was modulated with a mechanical chopper synchronized to the second subharmonic of the laser repetition rate. A digital lock-in amplifier was phase-locked with the mechanical chopper and amplified any difference in signal between the reference and sample

 

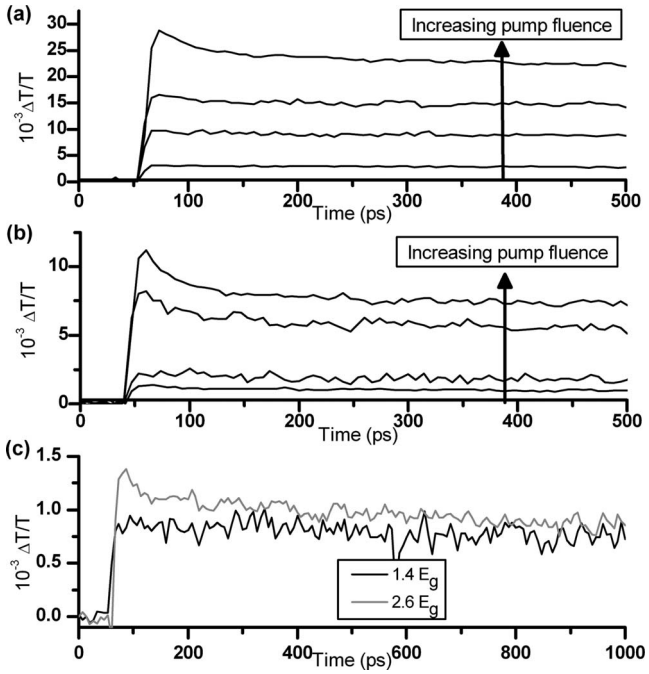


FIG. 1. Pump-induced fractional transmittance transients, $\Delta T/T$, for the large core NP for various absorbed pump fluences for (a) $h\nu=1.4E_g$ and (b)$h\nu=2.6E_g$, and (c) for low fluence pump pulses only at both photon energies.

probe beams. The time delay between pump and probe beam was controlled by a motorized optical delay line.

Three InP NP samples with different InP core diameters (designated large, medium, and small cores from here on) were used and each comprised an InP core, a ZnS inner shell, a ZnO outer shell, and a undecylenic acid passivating layer. The fabrication method is described in detail elsewhere,[23] but briefly, the InP cores were synthesized by the reaction of $In_2(acetate)_3(myristate)_3$ with tris(trimethylsilyl)phosphine. The ZnS shell was then added by reaction of anhydrous zinc acetate and octanethiol with the InP cores after etching with HF. The ZnO outer shell was then formed by the slow addition of 1-octadecanol to a heated solution of the NP, which was followed by centrifugation and purification to produce the completed NP. The absorption edges were found to be at 2.0, 2.1, and 2.4 eV and the photoluminescence (PL) peaks were centered at 1.9, 2.0, and 2.2 eV for the large, medium, and small core NPs, respectively.[24]

## III. RESULTS AND DISCUSSION

We investigated pump-induced changes in transmission of the large core NP using a probe wavelength of 620 nm (2.0 eV). Figures 1(a) and 1(b) show the transmittance transients at pump photon energies of $h\nu=2.8$ and 5.2 eV, i.e., $1.4E_g$ and $2.6E_g$, for a range of excitation fluences. At the highest fluence in each case, there is an initial decay to a plateau which persists for the rest of the transient. A monoexponential fit to this initial decay feature yielded a time constant of $41\pm3$ ps, which is similar to the biexciton lifetime measured previously for InP NP.[25] For $h\nu=1.4E_g$, as the fluence was decreased the initial feature reduced in magnitude and was not evident at the lowest fluences. This feature is thus attributed to decay of biexcitons created by the absorption in a single NP of more than one photon per pump pulse; note there is insufficient excess photon energy for CM to occur in this case. In contrast, for $h\nu=2.6E_g$ the biexcitonic decay feature persists at pump fluences at which it had disappeared for $h\nu=1.4E_g$; Fig. 1(c) compares low fluence transients for these two photon energies. The persistence of the initial feature at low fluences for $h\nu=2.6E_g$ is attributed to biexcitons created by CM.

The fractional change in transmission at the absorption edge is proportional to the total number density of excitons in the sample[26] and its initial peak, $\Delta T(0)/T$, corresponds to the number density created by the pulse (and consequently absorbed pump fluence). The ratio of $\Delta T(0)/T$ to the value after several biexciton lifetimes, $R$, yields the average number of excitons created per initially photoexcited NP.[8] In the limit of vanishing fluence, $J$, the probability of a NP absorbing more than one photon is negligible and thus $R(J\rightarrow 0)$ equals the average number of excitons created per absorbed photon, i.e., the CM QY. For five different pump photon energies, $R$ was evaluated for the large core NP over a range of pump fluences by fitting a monoexponential decay to the measured transient for a period after the initial maximum equal to five biexciton lifetimes.

Figures 2(a)–2(e) show $R$ as a function of $\Delta T(0)/T$ for $h\nu=1.4E_g$, $2.0E_g$, $2.2E_g$, $2.4E_g$, and $2.6E_g$. In each figure, $R$ is significantly greater than one for larger values of $\Delta T(0)/T$ and decreases as the absorbed pump fluence is reduced, consistent with the generation of biexcitons by the successive absorption of photons by a single NP. At the lowest values of $\Delta T(0)/T$ accessible by our experiment, $R$ tends to unity for $h\nu<2.2E_g$ but is significantly greater than one for $h\nu>2.2E_g$. The existence of a significant number of biexcitons at absorbed pump fluences where the probability of absorption of multiple photons by a single NP during a pump pulse is negligible indicates that CM is efficient in these NP for $h\nu>2.2E_g$. The efficiency of the CM process can be quantified by finding the value of $R$ in the limit of vanishing $\Delta T(0)/T$, which was done by fitting the following function[22] to the data in each of Figs. 2(a)–2(e):

$$R\left(\frac{\Delta T(0)}{T}\right)=k\delta\frac{\Delta T(0)}{T}\left[1-\exp\left(-\frac{k}{QY}\frac{\Delta T(0)}{T}\right)\right]^{-1}. \quad (1)$$

where $k$ is a constant of proportionality relating the number of photons absorbed per NP, $\sigma_{pump}J$, to $(QY)^{-1}\times\Delta T(0)/T$, and $\delta$ is a correction factor, calculated to be 1.01 from PL decay transients,[24] that compensates for the small drop in single exciton population over the measurement window. Figure 2(f) shows that for the large core NP the number of additional excitons produced, i.e., QY-1, increases significantly when $h\nu>2E_g$, reaching $0.18\pm0.03$ at $h\nu=2.6E_g$, the maximum photon energy used.

A model has been proposed[21,27,28] which requires that one or other of the charge carriers *individually* must possess sufficient energy to create an additional exciton. In this

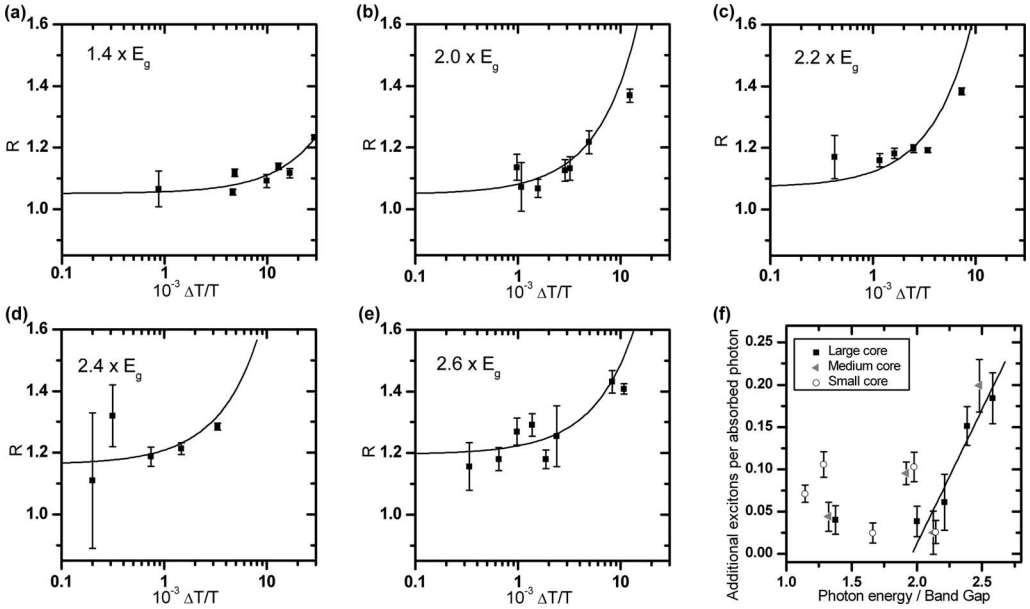


FIG. 2. Average number of excitons generated per photo-excited large core NP, $R$, as a function of fractional change in transmission for pump photon energies (a) 1.4, (b) 2.0, (c) 2.2, (d) 2.4, and (e) 2.6 times $E_g$. The average number of additional excitons created per absorbed photon as a function of $h\nu/E_g$ for the different NP is shown in (f).

case, and since the excess photon energy, $h\nu$-$E_g$, is partitioned between the hole and electron according to the inverse of their effective masses, the CM threshold $h\nu_{th}=(2+m_e/m_h)E_g$ (assuming that the hole effective mass, $m_h$ is greater than that of the electron, $m_e$).[8] Using the effective mass ratio of bulk InP, $m_h/m_e=8$, this energy partition model predicts the threshold to be $h\nu_{th}=2.1E_g$. A linear fit to the data points for the large core NP corresponding to photon energies >4.0 eV (i.e., $>2E_g$) is shown in Fig. 2(f). The average value of the data for $h\nu<2E_g$ is $0.04\pm0.01$; taking this offset into account yields a threshold of $h\nu_{th}=(2.1\pm0.2)E_g$ which is consistent with the energy partition model. The gradient of the linear fit corresponds to the CM slope efficiency and was $0.3\pm0.1$.

Some authors[16] suggested that photoionization of NP (directly to a trap site or Auger assisted) might be significant for large $h\nu$ and lead to the formation of trions with decay constants similar to those of biexcitons which may thus confuse the measurement of CM efficiency. However, the absorption transients observed in this study were unaffected by sample stirring[24] which suggests that photoionization is not significant. In order to further support this conclusion we studied the dependence of $R$ on pump fluence and $h\nu$ for the small and medium core NP,[24] with the probe wavelength for these NP set to 515 (2.4) and 595 nm (2.1 eV), respectively. As Fig. 2(f) shows, the QY for each of the different NP depends on $h\nu/E_g$ and not on $h\nu$ alone. This suggests that the biexciton feature we observed for the large core NP is caused by CM and not by photoionization (which would be determined by $h\nu$ only). The bulk band gaps of ZnO and ZnS are 3.4 and 3.9 eV, respectively,[29] and so the inner and outer shells of the NP may directly absorb some of the high energy photons used in this study. An exciton created in this way may relax to the InP band edge by either phonon emission or CM, in which case this alternate initial state may affect the rise time of the $\Delta T/T$ signal, or it may produce some other change in the NP. However, a comparison of transients created by pumping below and above the band gaps of ZnO and ZnS showed no discernable difference[24] indicating that absorption by the shell layers does not have a significant effect on the data.

The CM threshold for InP NPs determined here is not significantly different from the minimum required by the conservation of energy, as was also the case for InAs NPs.[21] In contrast, the thresholds found for the other NPs for which CM has thus far been demonstrated are all in excess of this minimum. Many of these experimentally measured CM thresholds are in broad agreement with the energy partition model[11] which predicts $h\nu_{th}\approx3E_g$ for lead chalcogenide NP. A low threshold is crucial to the development of solar cells with efficiency enhanced by CM; the theoretical efficiency limit for a solar cell based on NP with $h\nu_{th}=3E_g$ is 34%, which is only marginally greater than the theoretical limit for conventional cells.[2] The slope efficiency of CM in InP is similar to the value found for InAs[21] at about one-third of the value observed for the lead and cadmium chalcogenide NP and about a fifth of the value measured for Si NP. The relatively low slope efficiency observed for InP is at odds with its CM figure of merit, which was calculated to be similar to that of PbSe and CdSe.[11] However, it is not yet apparent whether the measured slope efficiency reflects an intrinsic property of InP NP or whether it can be increased by improved NP design; clarification of this is an important issue. The optimum $E_g$ for exploitation of the solar spectrum using CM has been calculated to be ~0.9–1.1 eV[2] which compares to a typical range of 1.5–2.0 eV for InP NP.[26] However, the effective $E_g$ of NP can be reduced by use of a type II core/shell structure. This type of structure also has the advantage that the spatial separation of the electron and hole that it produces increases the lifetime of the excitons thereby

increasing the probability that photo-generated carriers may be extracted from the NP before recombination.[27]

Efficient CM in InP nanoparticles has been demonstrated with the average number of excitons generated per absorbed photon observed to be as high as 1.18. The minimum photon energy necessary for CM was $2.1E_g$, as required by the conservation of energy. Above this minimum, CM increased at a rate equivalent to 0.3 additional excitons per photon energy increase equal to $E_g$. The low threshold for CM coupled with the benign nature of InP as compared to many solar cell materials makes it a strong candidate as a NP in 3rd generation solar cells if a CM enhanced photocurrent can be harvested.

## ACKNOWLEDGMENTS

The work described in this Rapid Communication was carried out with the financial support of both the United Kingdom Engineering and Physical Sciences Research Council, under Grant No. EP/E036287/1, and the Northwest Science Fund (NWDA).

*Corresponding author; david.binks@manchester.ac.uk

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