

Communication

**Quantum Dot Solar Cells. Electrophoretic Deposition
of CdSe/C Composite Films and Capture of
Photogenerated Electrons with *n*C Cluster Shell**

Patrick Brown, and Prashant V. Kamat

J. Am. Chem. Soc., **2008**, 130 (28), 8890-8891 • DOI: 10.1021/ja802810c • Publication Date (Web): 18 June 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 5 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Quantum Dot Solar Cells. Electrophoretic Deposition of CdSe–C₆₀ Composite Films and Capture of Photogenerated Electrons with nC₆₀ Cluster Shell

Patrick Brown and Prashant V. Kamat*

Radiation Laboratory, Department of Chemistry and Biochemistry, Department of Chemical and Biomolecular Engineering, and Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

Received April 16, 2008; E-mail: pkamat@nd.edu

Recent efforts have focused on the utilization of semiconductor quantum dots for designing next generation solar cells.^{1–5} These quantum dots are unique compared to bulk semiconductors or organic sensitizers. Quantum dots such as CdSe, PbSe, and InAs with their tunable band gaps offer improved light harvesting capability through the design of rainbow solar cells.^{6–8} They also offer the possibility of generating multiple charge carriers under high energy excitations.^{9,10} The challenge now is to capture these photogenerated electrons as quickly as they are generated and transport them to the electrode surface in an efficient manner.

A common strategy to utilize semiconductor quantum dots in solar cells is to couple them with another large bandgap semiconductor such as TiO₂, ZnO, or SnO₂. For example, the electron transfer from excited CdSe into the less negative conduction band of TiO₂ is size dependent and can be increased by 3 orders of magnitude by decreasing the particle size from 7.6 to 2.3 nm.¹¹ The size dependent property has also been successfully used for tuning photoresponse and modulating the efficiency of quantum dot solar cells.²

C₆₀ is widely used to capture and transport electrons in organic solar cells.^{12–14} The electron accepting property of fullerenes has also been utilized for photocurrent generation in porphyrine-C₆₀-based cluster films.¹⁵ It would be interesting to see whether C₆₀ can be effective for harvesting electrons from photoexcited CdSe quantum dots. In a previous study effort was made to dropcast CdSe quantum dots and C₆₀ mixture on a conducting surface for the purpose of demonstrating photovoltaic performance.¹⁶ The poor interaction between the two components resulted in relatively low photocurrent generation. We present here a new approach of capping the CdSe quantum dots with a molecular shell of electron acceptor C₆₀ and discuss the ways to improve the capture of photogenerated electrons in quantum dots.

Thin films of SnO₂ and TiO₂ were cast on optically transparent electrodes (OTE). A TOPO-capped CdSe quantum dot (4 nm in diameter) suspension in toluene was synthesized by the earlier reported procedure.¹⁷ C₆₀ (SES Research, Houston, Texas) was dissolved in toluene. A known amount of toluene solutions of CdSe and C₆₀ were first mixed in a vial. This mixed suspension was injected into an acetonitrile solution with the aid of a microsyringe to form CdSe–nC₆₀ composite clusters. The brown-colored solution was transferred to an electrophoretic cell containing two parallel electrodes. Application of a 50 V/cm field resulted in the deposition of CdSe–nC₆₀ clusters on the positive electrode. Individual clusters of CdSe and nC₆₀ were also deposited in a similar way. Photoelectrochemical measurements were carried out in a 3-arm cell using a Pt counter electrode (see Supporting Information for other experimental details).

Electrophoretic deposition is a convenient technique to deposit films of CdSe.¹⁸ In the present study CdSe and CdSe–nC₆₀ clusters were directly deposited as films from quantum dots and clusters dispersed in an acetonitrile/toluene (4:1) mixed solvent. Figure 1A shows the AFM image of CdSe–nC₆₀ composite clusters deposited on OTE. The micrographs show distribution of spherical clusters of 200 nm diameter.

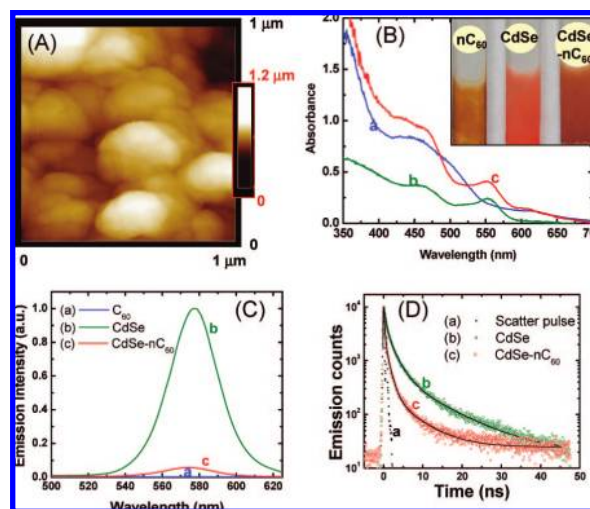


Figure 1. (A) AFM image of CdSe–nC₆₀ composite clusters deposited on OTE, (B) absorption spectra, (C) emission spectra, and (D) emission decay: (a) C₆₀, (b) CdSe, and (c) CdSe–nC₆₀ mixed clusters in toluene/acetonitrile.

These clusters are larger than nC₆₀ clusters (~90 nm in diameter, see Supporting Information Figure S1). One expects hundreds of CdSe nanoparticles to be entrapped by C₆₀ in these clusters.

Figure 1B,C compare the absorption and emission spectra of C₆₀, CdSe, and CdSe–nC₆₀ clusters films cast on a conducting glass electrode. The absorption of CdSe exhibits the characteristic excitonic peak at 563 nm and the nC₆₀ clusters exhibit broad absorption in the visible. Detailed characterization of C₆₀ clusters can be found elsewhere.^{19,20} The absorption spectrum of CdSe–nC₆₀ composite clusters shows an additive effect with photoresponse <600 nm along with an excitonic peak at 552 nm.

The emission spectrum (Figure 1C) exhibits the characteristic emission band of CdSe quantum dots with a maximum at 580 nm. More than 95% of the CdSe emission is quenched as the excited CdSe quantum dots interact with nC₆₀ in the cluster. Although both energy and electron transfer mechanisms can dictate the luminescence quenching, the electron accepting property of C₆₀ is expected to favor the electron transfer pathway.

If indeed the observed emission quenching (Figure 1D) involves electron transfer, we should be able to capture these generated photoelectrons at the conducting glass electrode surface. We evaluated the photocurrent response of these electrodes by inserting them in a photoelectrochemical cell. Figure 2A shows the photocurrent action spectra presented in terms of incident charge carrier generation efficiency (IPCE) at different excitation wavelengths. Both CdSe and CdSe–nC₆₀ electrodes show an onset of photocurrent generation at 600 nm. This wavelength closely matches the onset of CdSe absorption. The characteristic excitonic peak of 4 nm CdSe quantum dots at 560 nm can also be seen in the photocurrent action spectrum. The

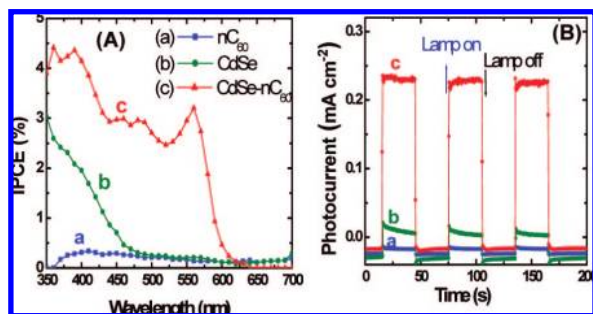


Figure 2. (A) Dependence of incident photon to current generation efficiency (IPCE) on the incident wavelength and (B) the photocurrent response of the electrodes to ON–OFF cycles of illumination: (a) nC_{60} , (b) CdSe quantum dots, and (c) CdSe– nC_{60} clusters on SnO_2 film electrodes. The electrolyte was 0.1 M Na_2S in water.

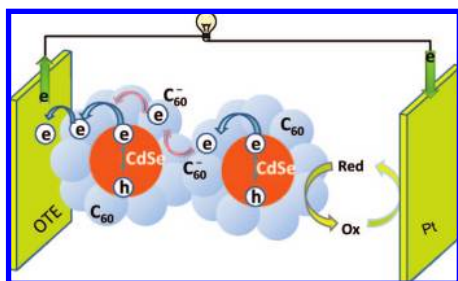


Figure 3. Photocurrent generation at CdSe– nC_{60} composite clusters.

maximum open circuit photovoltage and photocurrent observed with white light illumination ($\lambda > 300$ nm; incident light, 100 mW/cm²) were 0.3 V and 0.25 mA/cm², respectively. The observed photocurrents are 2–3 orders of magnitude greater than the one obtained with dropcast films of CdSe and C_{60} .¹⁶ Figure 2B shows the reproducibility and stability of the photocurrent response of these films. The Na_2S electrolyte scavenges the holes from CdSe, thus enabling the regeneration of the CdSe in the film.⁸ The CdSe– nC_{60} composite clusters exhibit an incident photon to photocurrent generation efficiency (IPCE) of ~4%, which is significantly higher than those of CdSe or nC_{60} films. The IPCE response of CdSe– nC_{60} is not a simple additive effect arising from individual components, but reflects the synergy arising from the excited interaction between CdSe and nC_{60} .

Since nC_{60} is a good electron acceptor ($E^0 = -0.2$ V vs NHE) one expects a quick electron transfer from excited CdSe into nC_{60} . The electron stabilization in nC_{60} clusters and its ability to generate photocurrent is described in an earlier study.^{15,21} The contribution of C_{60}^- generation from direct excitation of nC_{60} in S^{2-} electrolyte is expected to be small. The lower IPCE values in Figure 2 support such an argument. The C_{60} anion stabilized within the cluster then transports its electrons to the collecting electrode surface. Figure 3 illustrates the photoinduced electron transfer between CdSe and C_{60} followed by the electron transport through the C_{60} network to the collecting surface of OTE, which is previously coated with SnO_2 nanoparticles. Since the conduction band of SnO_2 is at 0 V vs NHE, it facilitates capture of electrons from C_{60}^- quite efficiently (see Scheme S1 for energy level diagram).

Although the possibility of direct electron transfer between excited CdSe and SnO_2 film exists, we consider its contribution to the overall photocurrent generation as minimal. First, the CdSe quantum dots are surrounded by C_{60} moieties, thus minimizing the direct contact between CdSe and SnO_2 . In addition, when we replaced SnO_2 with TiO_2

nanoparticles as support, the photocurrent generation was totally suppressed (see Figure S2). Since the conduction band of TiO_2 is -0.5 V vs NHE it can accept electrons from CdSe but not from C_{60}^- . The absence of photocurrent generation in the OTE/ TiO_2 /CdSe– C_{60} electrode thus rules out the possibility of direct electron transfer from excited CdSe into oxide particles.

The emission decay profile (Figure 1D) supports the quenching of the CdSe quantum dots by nC_{60} clusters. The multiexponential decay shows that the electron transfer occurs over a wide range of time. On the basis of the average emission lifetimes of CdSe in the absence ($\langle\tau\rangle = 4.2$ ns) and presence ($\langle\tau\rangle = 1.7$ ns) of nC_{60} clusters, we obtain an average electron transfer rate constant of 2.93×10^9 s⁻¹ (see Supporting Information). These results show the approach of capturing photogenerated electrons from CdSe quantum dots with an electron acceptor shell is quite effective.²²

The observed photocurrent generation efficiency with CdSe– nC_{60} films is 2 orders of magnitude greater than CdSe films alone. When CdSe quantum dots are assembled as thin films we see limited success in transporting photogenerated charge carriers to generate photocurrent. Fast capture of electrons at the quantum dot interface remains a major challenge if one is interested in exploiting multiple charge carrier generation for photocurrent generation. The strategy of encapsulating CdSe quantum dots in nC_{60} clusters paves the way for developing new and effective strategies toward light energy harvesting.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Science of the Department of the Energy. This is contribution NDRL-4762 from the Notre Dame Radiation Laboratory.

Supporting Information Available: Experimental details, AFM images, and emission lifetime analysis are presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kamat, P. V. *J. Phys. Chem. C* **2007**, *111*, 2834.
- (2) Kongkanand, A.; Tvrđy, K.; Takechi, K.; Kuno, M. K.; Kamat, P. V. *J. Am. Chem. Soc.* **2008**, *130*, 4007.
- (3) Ginger, D. S.; Greenham, N. C. *Synth. Met.* **1999**, *101*, 425.
- (4) Leschikies, K. S.; Divakar, R.; Basu, J.; Enache-Pommer, E.; Boecker, J. E.; Carter, C. B.; Kortshagen, U. R.; Norris, D. J.; Aydil, E. S. *Nano Lett.* **2007**, *7*, 1793.
- (5) Diguna, L. J.; Shen, Q.; Kobayashi, J.; Toyoda, T. *Appl. Phys. Lett.* **2007**, *91*.
- (6) Nozik, A. J. *Physica E* **2002**, *14*, 115.
- (7) Wang, Z. L. *J. Phys. Chem.* **2000**, *104*, 1153.
- (8) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2006**, *128*, 2385.
- (9) Schaller, R. D.; Agranovich, V. M.; Klimov, V. C. *Nat. Phys.* **2005**, *1*, 189.
- (10) Ellingson, R. J.; Beard, M. C.; Johnson, J. C.; Yu, P.; Micic, O. I.; Nozik, A. J.; Shabaev, A.; Efros, A. L. *Nano Lett.* **2005**, *5*, 865.
- (11) Robel, I.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2007**, *129*, 4136.
- (12) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510.
- (13) Sariciftci, N. S.; Heeger, A. J. *Synth. Met.* **1995**, *70*, 1349.
- (14) Tada, K.; Onoda, M. *Adv. Funct. Mater.* **2004**, *1*, 139.
- (15) Hasobe, T.; Imahori, H.; Kamat, P. V.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1216.
- (16) Biebersdorf, A.; Dietmüller, R.; Suscha, A. S.; Rogach, A. L.; Poznyak, S. K.; Talapin, D. V.; Weller, H.; Klar, T. A.; Feldmann, J. *Nano Lett.* **2006**, *6*, 1559.
- (17) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183.
- (18) Islam, M. A.; Herman, I. P. *Appl. Phys. Lett.* **2002**, *80*, 3823.
- (19) Kamat, P. V.; Barazzouk, S.; Thomas, K. G.; Hotchandani, S. *J. Phys. Chem. B* **2000**, *104*, 4014.
- (20) Kamat, P. V.; Barazzouk, S.; Hotchandani, S. *Adv. Mater.* **2001**, *13*, 1614.
- (21) Thomas, K. G.; Biju, V.; George, M. V.; Guldi, D. M.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 8864.
- (22) Boulesbaa, A.; Issac, A.; Stockwell, D.; Huang, Z.; Huang, J.; Guo, J.; Lian, T. *J. Am. Chem. Soc.* **2007**, *129*, 15132.

JA802810C