

Photosensitization of nanocrystalline TiO₂ by self-assembled layers of CdS quantum dots

Laurence M. Peter,^{a*} D. Jason Riley,^b Elizabeth J. Tull^b and K. G. Upul Wijayantha^a

^a Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY.

E-mail: l.m.peter@bath.ac.uk

^b School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS

Received (in Cambridge, UK) 15th February 2002, Accepted 26th March 2002

First published as an Advance Article on the web 12th April 2002

CdS quantum dots can be self-assembled on high surface area nanocrystalline TiO₂ electrodes; spectroscopic and photoelectrochemical studies indicate that the size, and hence the absorption edge, of the CdS particles can be controlled; efficient photosensitization of the TiO₂ electrode by the Q-particles has been achieved.

Nanocrystalline semiconductor materials^{1,2} exhibit a wide range of novel chemical and physical properties that are finding application in devices such as solar cells,^{3,4} photocatalytic coatings,⁵ electrochromic windows⁶ and supercapacitors.⁷ If the particle size becomes sufficiently small, quantum confinement of electrons leads to a size-dependent separation between the valence and conduction bands, which are split into discrete exciton-like states. These ultra-small particles are referred to as quantum dots (Q-dots).

The dye-sensitized nanocrystalline TiO₂ solar cell pioneered by O'Regan and Grätzel^{8,9} achieves peak light harvesting efficiencies approaching 100% by adsorption of the sensitizer dye on high-surface-area nanocrystalline TiO₂. The most widely used dye is *cis*-di(thiocyanato)-*N,N*-bis(2,2'-bipyridyl dicarboxylate)ruthenium(II), which is anchored to the TiO₂ surface by the carboxylate groups. Current approaches to enhancing cell efficiency involve tuning the absorption spectrum and redox properties of different dyes.^{3,4,10,11} This generally involves rather difficult synthetic routes. An alternative strategy that we are exploring is based on replacing the sensitizer dye by semiconductor Q-dots. The electronic levels of the Q-dots (*i.e.* the electronic affinity and optical bandgap) can be tuned by changing the particle size without changing the chemical composition. The present communication demonstrates efficient sensitization of nanocrystalline TiO₂ electrodes by self-assembled layers of CdS Q-dots.

CdS was chosen as a model system for proof of concept because quantum confinement effects in CdS have been widely studied^{12–14} and methods of controlling the size of CdS Q-dots are well-established.¹⁵ Previous studies have shown that CdS Q-dots can be grafted onto planar surface-functionalized SnO₂-coated glass electrodes.^{12,13,16} In the present study, this methodology was developed to achieve self-assembly of CdS Q-dots on nanocrystalline TiO₂ electrodes. Efficient photosensitization and control of Q-particle size were demonstrated by measurement of the photocurrent response of the electrodes in a redox electrolyte.

TiO₂ films were prepared on fluorine-doped tin oxide coated glass substrates by the well-established sol-gel method.^{4,17} Typical film thicknesses were in the range 2.0–5.0 µm and the mean particle size of the TiO₂ was approximately 40 nm. The coated substrate was cut into pieces to ensure that identical films were used for the self-assembly of layers containing different Q-particle sizes. CdS Q-dots were self-assembled on the TiO₂ films by arrested precipitation. 3-mercaptopropionic acid (3-MPA) was chosen as the stabiliser in order to facilitate assembly on the TiO₂ substrate via the carboxylic moiety. The size of the Q-dots was adjusted by controlling the concentration of 3-MPA following the approach used by Fischer and Henglein.¹⁵ The required amount of 3-MPA in THF was transferred to a cleaned 50 mL volumetric flask. 500 µL of 0.1

M Cd(ClO₄)₂ in THF were added and diluted to 50 mL with anhydrous THF. The nanocrystalline TiO₂ electrode was placed face up at the bottom of a 250 mL conical flask, which was sealed with a rubber septum, and the precursor solution was added. A hypodermic needle was inserted into the septum to bubble dry nitrogen through the solution. The solution was stirred while passing nitrogen, and after 20 min the flow was stopped and the needle removed. 2 mL of H₂S were then slowly injected into the solution through the septum while continuing stirring. The flask was covered with a black cloth and stirring was continued for 1 h. At the end of this process, the nanocrystalline TiO₂ film had turned yellow. The resultant CdS-modified electrode was washed with THF and dried. To form multilayers of CdS, the self-assembly procedure was repeated a number of times. The film colour became more intense with each deposition cycle.

The inset in Fig. 1 shows the UV-VIS spectra of colloidal suspensions of CdS Q-dots formed at 3-MPA concentrations of 7.5×10^{-5} M (380 µL of 0.01 M 3-MPA) and 0.38 M (1745 µL of pure 3-MPA). Approximate values of the optical bandgaps were obtained as indicated in the figure. The colloid prepared using the lower concentration of 3-MPA appears to have a bandgap of around 2.53 eV, whereas the higher concentration of 3-MPA gives particles with a bandgap of approximately 2.88 eV. Assuming that the particles are spherical and using the effective mass approximation,¹⁸ these bandgaps correspond to particle radii of 3.1 and 1.9 nm for the 3-MPA concentrations of

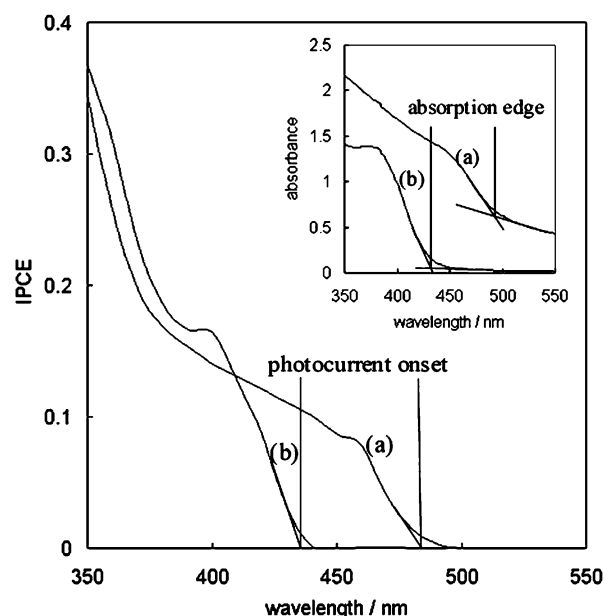


Fig. 1 Normalized photocurrent excitation spectra showing the incident photon to current conversion efficiency (IPCE) of TiO₂ electrodes sensitized using bilayers of the two different sizes of CdS Q-particles. The size of the particles estimated from the photocurrent onset wavelengths are (a) 2.9 and (b) 1.9 nm. The inset shows absorbance spectra of CdS colloidal suspensions prepared using (a) 7.5×10^{-5} M and (b) 0.38 M 3-MPA. Approximate positions of the optical bandgap are shown.

7.5×10^{-5} M and 0.38 M, respectively. Consideration of the UV–VIS spectra of colloids prepared using a range of 3-MPA concentrations indicates that the particle radius (R) is related to the stabiliser concentration by an equation analogous to the one proposed by Fischer and Henglein for alkane thiols.¹⁵

$$\log\{R/\text{nm}\} = -0.065 \log\{[3\text{-MPA}]/\text{M}\} + 0.236 \quad (1)$$

Dynamic light scattering studies of the sols indicate that clusters of nanoparticles are formed at low 3-MPA concentrations. In the UV–VIS experiments, scattering from the clusters precludes accurate identification of the bandedge of the particles. As shown below, more reliable values of the bandgap can be obtained from the photocurrent excitation spectra of the modified TiO₂ electrodes.

To assess if the particles deposited on the TiO₂ substrate were of the same size as those in the parent sol, UV–VIS spectra of the CdS modified TiO₂ films were recorded. Values of the absorption edge similar to those of the parent sol were observed, although reliable values were difficult to obtain due to light scattering by the TiO₂. It was found that more accurate values of the bandgap could be obtained from the photocurrent excitation spectra of the modified TiO₂ electrodes, and this was the method of choice for determining the bandedge of the particles on the substrate.

Photoelectrochemical experiments were made using a 1 M Na₂SO₃ aqueous electrolyte solution (buffered at pH 12) as a hole scavenger. A conventional three electrode arrangement was used with an Ag|AgCl|3 M KCl reference electrode and Pt foil counter electrode. The monochromatic incident light was chopped at 3 Hz, and the photocurrent was detected by a lock-in amplifier. Fig. 1 shows plots of the incident photon to current conversion efficiency (IPCE) as a function of excitation wavelength for TiO₂ electrodes coated with the two sizes of CdS particles discussed above. The spectra shown are both for TiO₂ electrodes on which two layers of CdS particles were deposited. When recording the spectra, the potential was held in the photocurrent saturation region at -0.3 V vs. Ag/AgCl. The difference in the photocurrent onset energies can be seen clearly. The bandgap energies obtained by linear extrapolation of the edges from the IPCE spectra are 2.53 and 2.88 eV. These values are probably more reliable than those derived from the UV–VIS spectra of the colloidal suspensions. Calculation of the particle size from these spectra indicate that the particles on the electrode surface prepared in the presence of 7.5×10^{-5} and 0.38 M of 3-MPA are 2.9 and 1.9 nm, respectively. It is also of note that both the IPCE spectra display clearly the first exciton peak, which is generally regarded as evidence for a monodisperse Q-dot system.¹⁸

The inset in Fig. 2 illustrates the photocurrent voltage behaviour of an electrode modified with CdS particles of radius 2.9 nm. The photocurrent onset occurs at -0.8 V vs. Ag/AgCl, and a well-defined saturation region is observed at more positive potentials. Studies of CdS nanoparticles self-assembled on planar tin oxide electrodes¹⁶ and on single crystal CdS electrodes¹⁹ indicate that the conduction band edge of the 2.9 nm CdS lies at a potential of -1.0 V vs. Ag/AgCl in the same electrolyte. The observation that the photocurrent falls to zero at potentials positive of the conduction band edge of the nanoparticles indicates that electron accumulation in the titanium dioxide layer decreases the photoconversion efficiency as the result of back reaction with photogenerated holes in the CdS.

Fig. 2 shows the influence of increasing the number of CdS Q-particle layers. Spectra are displayed for TiO₂ electrodes that had undergone one, two and five CdS deposition cycles. In each cycle the concentration of 3-MPA was maintained at 7.5×10^{-5} M. It is apparent that the IPCE of the electrode increases with the number of CdS layers. The high values of the IPCE confirm the basic strategy of replacing the sensitizer dye by surface-assembled size-selected Q-particles. Even for a single deposition cycle, it was observed that the IPCE is twenty times higher than the values observed for CdS self-assembled on flat SnO₂

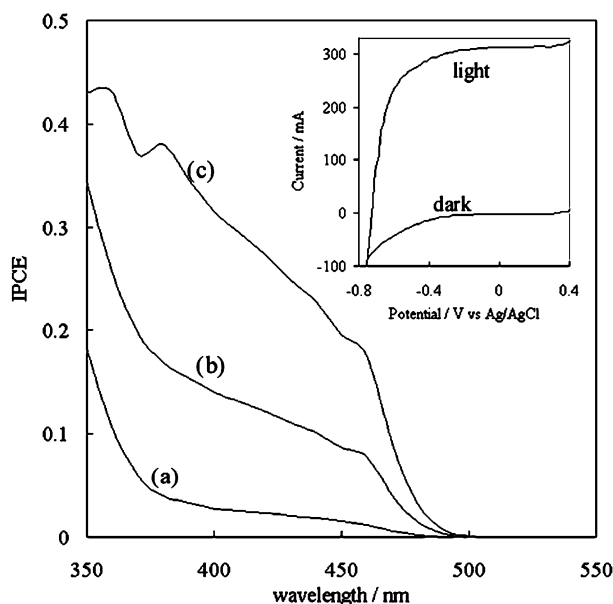


Fig. 2 IPCE spectra of TiO₂ electrodes modified with 2.9 nm CdS Q-particles; (a) one deposition cycle, (b) two deposition cycles and (c) five deposition cycles. The inset shows the current–voltage plot for the nanocrystalline TiO₂ electrode sensitized by self-assembled CdS Q-dots. The curves were recorded, using 1 M Na₂SO₃ aqueous electrolyte solution (buffered at pH 12), in the dark and under illumination with a tungsten lamp.

electrodes in the same electrolyte, indicating that the Q-dots are deposited on the internal surface area of the TiO₂.

Further work is in progress to extend our self-assembly strategy to other Q-particles and to identify reversible redox electrolytes so that stable regenerative photovoltaic cells can be fabricated.

This work is supported by the UK Engineering and Physical Sciences Research Council (EPSRC). The authors wish to thank Dr Robert Potter (Johnson Matthey) for materials and helpful discussions.

Notes and references

- 1 J. Z. Zhang, *J. Phys. Chem. B*, 2000, **104**, 7239.
- 2 G. Hodes, in *Electrochemistry of Nanomaterials*, Wiley-VCH, Weinheim, 2001.
- 3 M. Grätzel, *Proc. Indian Acad. Sci.-Chem. Sci.*, 1995, **107**, 607.
- 4 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, V. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
- 5 K. Vinodgopal and P. V. Kamat, *Sol. Energy Mater. Sol. Cells*, 1995, **38**, 401.
- 6 D. Cummins, G. Boschloo, M. Ryan, D. Corr, S. N. Rao and D. Fitzmaurice, *J. Phys. Chem. B*, 2000, **104**, 11449.
- 7 O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich and S. Sampath, *Chem. Mater.*, 1997, **9**, 2354.
- 8 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
- 9 B. O'Regan, J. Moser, M. Anderson and M. Grätzel, *J. Phys. Chem.*, 1990, **94**, 8720.
- 10 M. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel and B. A. Murrer, *Chem. Commun.*, 1998, 719.
- 11 M. Grätzel, *J. Phys. Chem.*, 1993, **97**, 6272.
- 12 S. G. Hickey and D. J. Riley, *J. Phys. Chem. B*, 1999, **103**, 4599.
- 13 S. Drouard, S. G. Hickey and D. J. Riley, *Chem. Commun.*, 1999, 67.
- 14 R. Vogel, K. Pohl and H. Weller, *Chem. Phys. Lett.*, 1990, **174**, 241.
- 15 C. H. Fischer and A. Henglein, *J. Phys. Chem.*, 1989, **93**, 5578.
- 16 S. G. Hickey, D. J. Riley and E. J. Tull, *J. Phys. Chem. B*, 2000, **104**, 7623.
- 17 L. M. Peter and K. G. U. Wijayantha, *Electrochim. Acta*, 2000, **45**, 4543.
- 18 L. Brus, *J. Phys. Chem.*, 1986, **90**, 2555.
- 19 H. Inoue, D. J. Elliot, M. Tada, T. Nagamura, F. Grieser, H. Sakaguchi and D. N. Furlong, *Colloids Surf. A*, 2000, **169**, 233.