

CENTENNIAL FEATURE ARTICLE

Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters[†]

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The emergence of semiconductor nanocrystals as the building blocks of nanotechnology has opened up new ways to utilize them in next generation solar cells. This paper focuses on the recent developments in the utilization of semiconductor quantum dots for light energy conversion. Three major ways to utilize semiconductor dots in solar cell include (i) metal–semiconductor or Schottky junction photovoltaic cell (ii) polymer–semiconductor hybrid solar cell, and (iii) quantum dot sensitized solar cell. Modulation of band energies through size control offers new ways to control photoresponse and photoconversion efficiency of the solar cell. Various strategies to maximize photoinduced charge separation and electron transfer processes for improving the overall efficiency of light energy conversion are discussed. Capture and transport of charge carriers within the semiconductor nanocrystal network to achieve efficient charge separation at the electrode surface remains a major challenge. Directing the future research efforts toward utilization of tailored nanostructures will be an important challenge for the development of next generation solar cells.

A. Nanoscience Opportunities

New initiatives to harvest incident photons with greater efficiency are needed to meet our demand of clean energy.^{1–4} The single crystal silicon based photovoltaic devices that are commercially available for installation deliver power with a ~15% efficiency. These *first generation* devices suffer from high cost of manufacturing and installation. The *second generation* devices consisting of polycrystalline semiconductor thin films can bring down the price significantly, but their efficiency needs to be enhanced for making them practically viable. Now the focus is on the *third generation* devices that can deliver high efficiency devices at economically viable cost.

In recent years nanomaterials have emerged as the new building blocks to construct light energy harvesting assemblies. Efforts are being made to design organic and inorganic hybrid structures that exhibit improved selectivity and efficiency toward light energy conversion. Of particular interest are the size dependent properties such as size quantization effects in semiconductor nanoparticles and quantized charging effects in metal nanoparticles.^{5–11} Recent efforts to synthesize nanostructures with well defined geometrical shapes (e.g., solid and hollow spheres, prisms, rods, tubes, and wires) and organize them as 2- and 3-dimensional assemblies have further expanded the possibility of developing new strategies for light energy conversion.^{12–30}

Quantum dot based solar cells have drawn a lot of attention during past few years because of the possibility of boosting the energy conversion efficiency beyond the traditional Shockley and Queisser limit of 32% for Si based solar cells.³¹ Three different types of solar cells that capitalize salient properties of semiconductor nanocrystals have emerged: (i) metal–semiconductor or Schottky junction photovoltaic cell, (ii) semiconductor nanostructure–polymer solar cell, and (iii) semiconductor sensitized quantum dot solar cell (Figure 1).

Specific advantages to using semiconductor quantum dots as light harvesting assemblies in solar cells exist.³² First and foremost, their size quantization property allows one to tune the visible response and vary the band offsets to modulate the vectorial charge transfer across different sized particles.³³ In addition, these quantum dots open up new ways to utilize hot electrons³⁴ or generate multiple charge carriers with a single photon.^{35,36} Multiple carrier generation in PbSe nanocrystals has shown that two or more excitons can be generated with a single photon of energy greater than the bandgap.^{35,37,38} These recent developments of photoinduced charge separation semiconductor nanocrystal based assemblies and efforts to utilize them in solar cells are reviewed here.

B. Charge Separation in Semiconductor Composites. Early Studies

Photoinduced charge separation in semiconductor nanoparticles has been studied since the early 1980s.^{5,11,39,40} Although the charge recombination dominates in a nanometer sized semiconductor particle, the charge separation can be greatly improved by coupling it with another semiconductor particle having favorable energetics. In addition, semiconductors such as CdS,^{41–43} PbS,^{44,45} Bi₂S₃,^{44,46,47} CdSe,^{48–50} and InP,⁵¹ which absorb light in the visible, can serve as sensitizers as they are

[†] This year marks the Centennial of the American Chemical Society's Division of Physical Chemistry. To celebrate and to highlight the field of physical chemistry from both historical and future perspectives, *The Journal of Physical Chemistry* is publishing a special series of Centennial Feature Articles. These articles are invited contributions from current and former officers and members of the Physical Chemistry Division Executive Committee and from *J. Phys. Chem.* Senior Editors.

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Prashant V. Kamat is currently a Professor of Chemistry and Biochemistry, a Senior Scientist at Radiation Laboratory, and a Concurrent Professor in the Department of Chemical and Biomolecular Engineering, University of Notre Dame. A native of Binaga, India, he earned masters (1974) and doctoral degrees (1979) in Physical Chemistry from the Bombay University, and carried out his postdoctoral research at Boston University (1979–1981) and University of Texas at Austin (1981–1983). He joined Notre Dame Radiation Laboratory in 1983 and initiated the photoelectrochemical investigation of semiconductor nanoparticles. Dr. Kamat's research has made significant contributions to three areas: (1) photoinduced catalytic reactions using semiconductor and metal nanoparticles, nanostructures, and nanocomposites, (2) developing inorganic–organic hybrid assemblies for utilizing renewable energy resources, and (3) environmental remediation using advanced oxidation processes and chemical sensors. He has directed DOE funded solar photochemistry research for more than 20 years. He has published more than 350 peer-reviewed journal papers, review articles, and book chapters. He has edited two books in the area of nanoscale materials. He was a fellow of Japan Society for Promotion of Science during 1997 and 2003 and was presented the 2006 Honda-Fujishima Lectureship award by the Japan Photochemical Society. In 2008 he was elected a Fellow of the Electrochemical Society.

able to transfer electrons to large bandgap semiconductors such as TiO₂ or SnO₂ (Figure 2). Improved charge separation and enhanced photocatalytic efficiency of such composite nanostructures have been extensively studied by our group^{52–57} and other research groups.^{43,58–64} Readers may refer to earlier reviews to obtain charge transfer and charge rectification in various semiconductor composite systems.^{65–68}

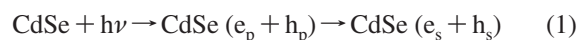
By controlling the particle size of quantum dots one can vary the energetics of the particles. Increased band energies of Q-dots can thus be utilized to promote,⁴⁴ suppress,⁵⁷ or rectify^{48,69} the electron transfer between two semiconductor nanostructures. Such composite structures rectify the flow of charge carriers and improve the photocatalytic performance or photoelectrochemical performance of nanostructure semiconductor based systems. For example, nearly ten times enhancement in the photocatalytic efficiency has been achieved by coupling TiO₂ and SnO₂ systems.^{53,55} Similarly, composites of ZnO–CdS,⁷⁰ TiO₂–SnO₂,⁷¹ SnO₂–CdSe,⁷² and SnO₂–CdS⁵⁶ have been successfully used to promote efficient charge separation and charge propagation in dye-sensitized solar cells.

Most of the early studies on semiconductor nanocrystals reported to-date have been limited to elucidation of photophysical and photochemical properties^{5,73–77} or their use as biological probes.^{78–83} One of the early studies on the TiO₂–CdSe system highlighted the possibility of rectification behavior of the composite system and its usefulness in improving the overall performance of nanostructured semiconductor systems.^{48,69} Transient absorption studies indicated intense bleaching of the excitonic band as the CdS^{84–86} and CdSe⁸⁷ particles were subjected to bandgap excitation. Such bleaching that directly represents charge separation in semiconductor nanocrystal was explained on the basis of band filling model^{86,88} as well as Stark

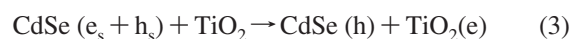
effect.^{89–91} The electrons trapped within TiO₂ nanoparticles following the laser excitation of CdS–TiO₂ system were characterized by femtosecond transient absorption spectroscopy.⁹²

C. Charge Separation in Semiconductor Nanocrystals. Recent Advances

Semiconductor nanocrystals when subjected to bandgap excitation undergo charge separation (Reactions 1 and 2 represent charge separation and recombination of CdSe nanocrystals respectively. Subscripts s and p refer to the electronic states of the electrons (e) and holes (h)).



As the electrons and holes accumulate in the conduction and valence bands, one observes bleaching in the absorption. The charge separated state can be followed by the emission decay or the recovery of the transient bleaching.^{74,75,93–102} Figure 3 compares the emission yield and decay of CdSe quantum dots anchored on glass slides and TiO₂ films. The significant quenching seen in these emission measurements confirms the electron transfer between excited CdSe and TiO₂ as the major deactivation pathway for the observed quenching of emission.



The deactivation of the excited semiconductor nanocrystals can be modulated by applying electrochemical bias.¹⁰³ Mulvaney and co-workers¹⁰⁴ have demonstrated that the photobrightening and charge carrier injection are coupled processes. The photoluminescence (PL) of CdSe/CdS/ZnS semiconductor nanocrystals deposited on gold substrates is reversibly quenched at negative potentials in nitrogen atmosphere. However, when a negative potential is applied to the semiconductor nanocrystalline film in aerated acetonitrile, the PL intensity increased.

Figure 4, panels A and B, shows the ground-state absorption spectra and transient absorption spectra of different size CdSe quantum dots in the visible region recorded 2 ps after 387 nm laser pulse (pulse width 130 fs) excitation. The ultraband excitation initially excites electrons to the higher p-state which then quickly relaxes to low lying s-state. The bleaching at the band edge seen in the transient absorption in Figure 4B provides a means to probe the fate of electrons accumulated in the thermally relaxed s-state. Sargent and co-workers have found dominance of Auger recombination rate in PbS quantum dots if more than one fundamental exciton is excited per dot.¹⁰⁵ Based on the saturation in the bleaching signal they concluded that additional excitons do not contribute to absorption saturation, in contrast to CdSe.¹⁰⁵ The shape of the semiconductor nanocrystal also affects the excited-state dynamics. For example, CdSe nanorod samples with the same length (~30 nm) but with different diameters, 2.5 and 8.0 nm, exhibit 8 times faster intraband energy relaxation for thicker rods than thin rods.¹⁰⁶ The multiple charge carrier generation in semiconductor nanocrystals has also drawn much interest for its possible implementation in solar cells. The details on the photogeneration and recombination of multiexcitons in semiconductor nanocrystals and their implication in solar cells have been reviewed recently by Klimov.¹⁰⁰

When in contact with another semiconductor, the excited CdSe quantum dots are capable of injecting electrons into TiO₂ nanoparticles.^{49,108} The TiO₂ particle has a band gap of 3.2 eV, exhibiting absorption in the UV region with onset around 390

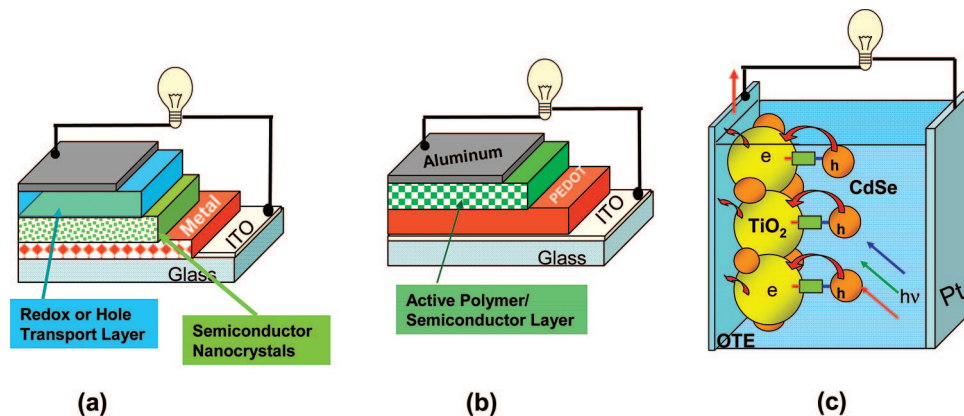


Figure 1. Schematic diagram showing the strategies to develop quantum dot (semiconductor nanocrystal) based solar cells: (a) metal–semiconductor junction, (b) polymer–semiconductor, and (c) semiconductor–semiconductor systems.

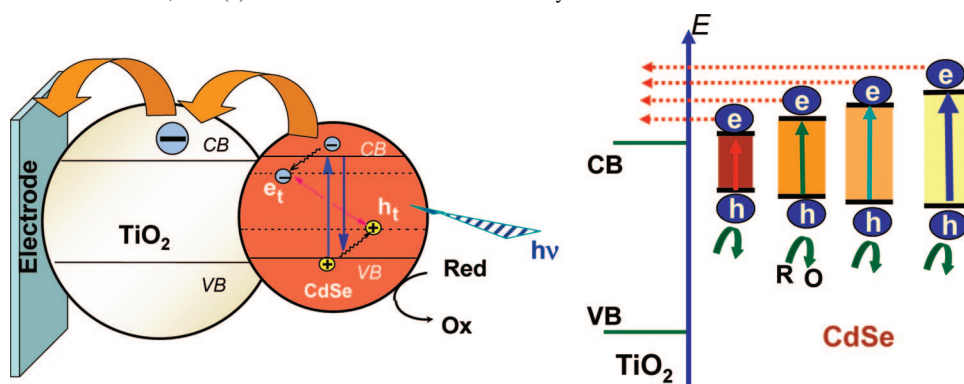


Figure 2. Charge injection of excited CdSe quantum dot into TiO₂ nanoparticle. The scheme on the right shows the modulation of energy levels (and hence the charge injection) by size control.

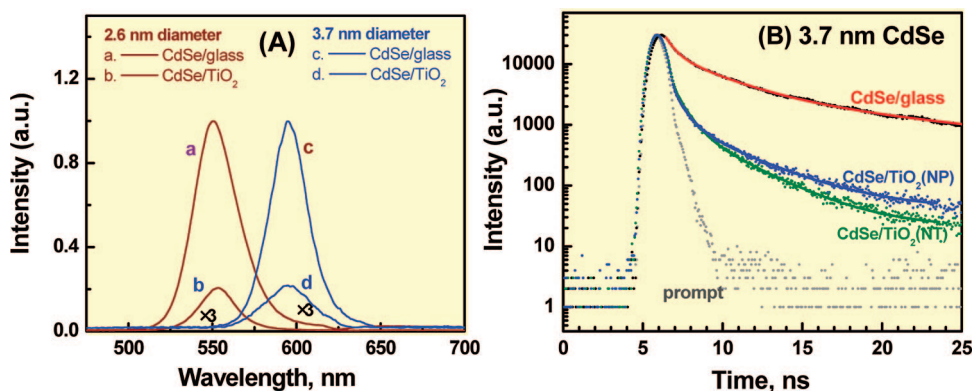


Figure 3. (A) Emission spectra of 2.6 and 3.7 nm diameter CdSe quantum dot film deposited on glass and OTE/TiO₂ (nanoparticle) films. (B) Emission lifetimes of 3.7 nm CdSe quantum dots deposited on glass, TiO₂ nanoparticle film and TiO₂ nanotubes (monitoring wavelength 580 nm). (From ref 33.)

nm. By employing mercaptopropionic acid (MPA) as a linker molecule, it is possible to bring together TiO₂ and CdSe nanoparticles. For 7.5 nm diameter CdSe colloids the conduction band is estimated to be -0.8 V vs NHE¹⁰³ and it shifts to negative potentials with decreasing particle size (e.g., -1.57 V vs NHE for 3.0 nm particles). Because of the small electron effective mass $m_e = 0.13m_0$ versus the significantly larger hole mass $m_h = 1.14m_0$, most of the band gap increase is seen as a shift in the conduction band to more negative potentials (vs NHE).⁹³ Thus, CdSe quantum dots with their increased band gaps are expected to have favorable conduction band energies for injecting electrons into TiO₂ (reaction 3).

The effect of the TiO₂ interaction with excited CdSe quantum dots can be seen from the bleaching recoveries recorded in Figure 4, panels C and D. The additional deactivation pathway

of electron transfer to TiO₂ causes a faster recovery of the bleaching (Figure 4D). With decreasing particle size the bleaching recovery occurs at a faster rate. The rate constant can be estimated by comparing the bleaching recovery lifetimes in the presence and absence of TiO₂ (expression 4).

$$k_{et} = 1/\tau_{(\text{CdSe}+\text{TiO}_2)} - 1/\tau_{\text{CdSe}} \quad (4)$$

Electron transfer kinetics can be evaluated in terms of Marcus theory^{109,110} for a nonadiabatic reaction in the classical activation limit. The theory implies that the logarithm of the electron transfer rate is a quadratic function with respect to the driving force, $-\Delta G$. This expression has been successfully applied by Hupp¹¹¹ and others^{112,113} to investigate charge recombination kinetics in dye-sensitized SnO₂ and TiO₂ systems. As the driving force, $-\Delta G$, (viz., energy difference between the acceptor and

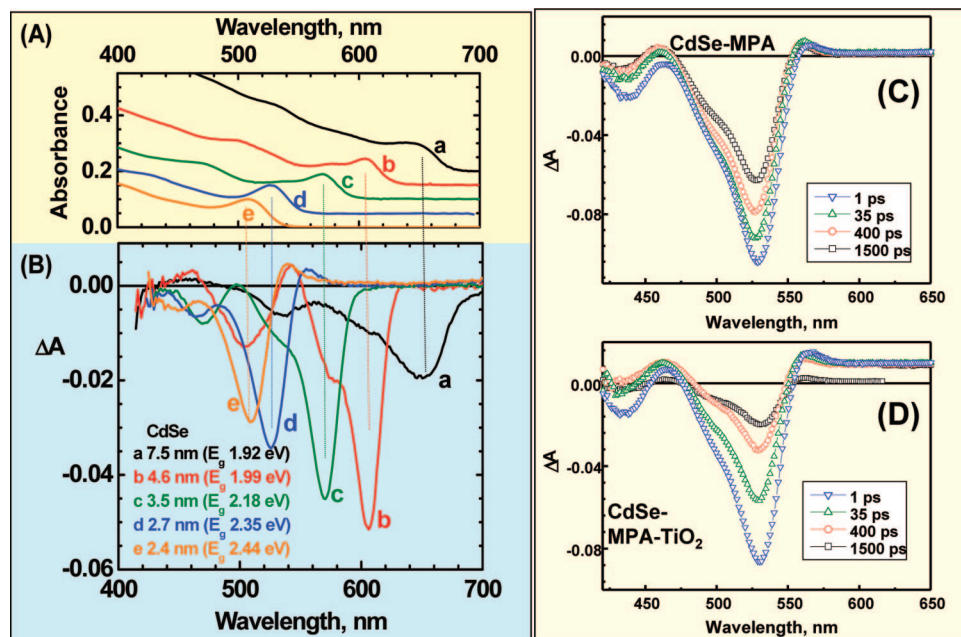


Figure 4. (A) Absorbance spectra of CdSe quantum dots in toluene. (Y-axis offset is introduced for clarity.) (B) Transient absorption spectra recorded 2 ps following the 387 nm laser pulse excitation of different size CdSe quantum dots in 1:1 ethanol:tetrahydrofuran (THF). Time resolved spectra recorded following laser pulse excitation of 3 nm CdSe quantum dots in the (C) absence and (D) presence of TiO₂ are also shown. (From refs 107 and 49.)

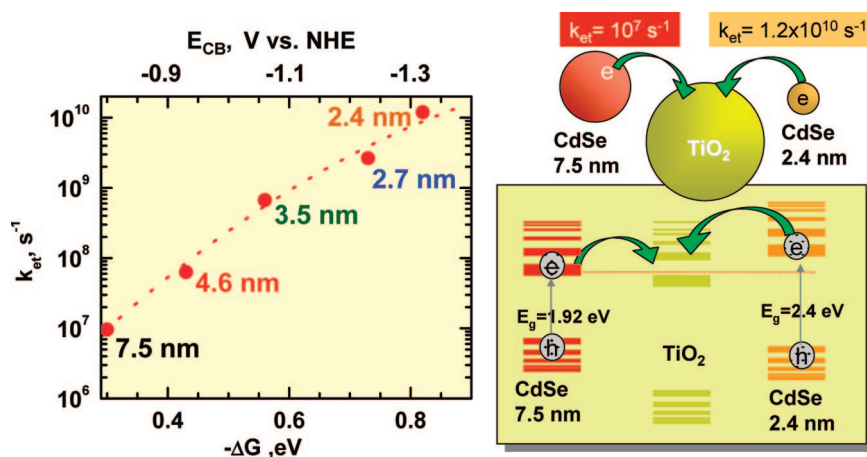


Figure 5. Left: The dependence of electron transfer rate constant on the energy difference between the conduction bands. Right: Scheme illustrating the principle of electron transfer from two different size CdSe quantum dots into TiO₂ nanoparticle. (From ref 107.)

donor systems) increases, the rate of ET increases, reaching a maximum when the driving force equals the reorganization energy (i.e., when the activation free energy $\Delta G^* = 0$). Similar observation has also been confirmed recently by Lian and co-workers during the investigation of CdSe QDs adsorbed with Re(CO)₃Cl(dcbpy) (dcbpy) 4,4'-dicarboxy-2,2'-bipyridine.¹¹⁴

The driving force for the electron transfer between CdSe and TiO₂ is dictated by the energy difference between the conduction band energies. The conduction band of TiO₂ is at -0.5 V versus NHE.¹¹⁵ If we assume the larger CdSe particles have band energy close to the reported value of -0.8 V vs NHE,¹⁰³ we can use the increase in bandgap as the increase in driving force ($-\Delta G$) for the electron transfer. Since the shift in the conduction band energy is significantly greater than the shift in valence band energy for quantized particles,⁹³ we can expect the conduction band of CdSe QDs to become more negative (on NHE scale) with decreasing particle size. Figure 5 shows the energy gap dependence of $\log(k_{et})$. As the particle size decreases, we see an enhanced electron transfer rate. The driving force of

0.8 eV is at or close to the reorganization energy and hence we expect a normal Marcus region in which the rate of electron transfer increases with the driving force. This small energy difference attained by decreasing particle size is sufficient to increase the electron transfer rate by nearly 3 orders of magnitude.

The fastest electron transfer in the CdSe–TiO₂ system was observed with 2.4 nm-CdSe quantum dots. The rate constant of $\sim 1.2 \times 10^{10}$ s⁻¹ in this experiment reflects an average lifetime of 83 ps. Other femtosecond transient studies have reported similar electron transfer rates between excited CdS/CdSe QDs and TiO₂ on a time scale of 2–50 ps.^{116,117} Size-dependent electronic properties of semiconductor QDs are regarded as one of the most attractive features for attaining a band gap gradient in quantum dot solar cells. The dependence of the charge injection rate constant on particle size demonstrates the possibility of modulating the electron transfer rate between CdSe and TiO₂ particles by making use of size quantization effects.

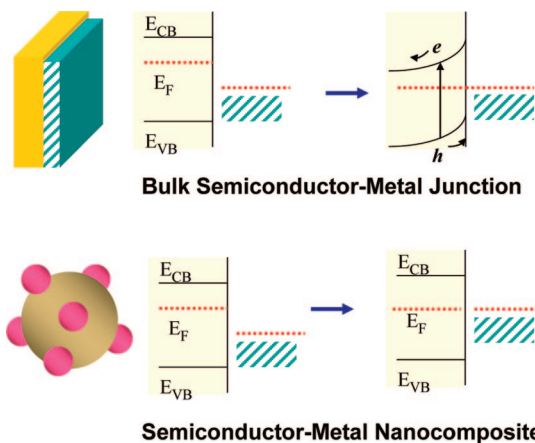


Figure 6. Fermi level equilibration at bulk metal-nanocrystal (top) and metal nanoparticle-semiconductor nanoparticle junction (bottom).

D. Toward the Development of Next Generation Solar Cells

a. Semiconductor–Metal (or Schottky) Junction Solar Cell. When a semiconductor comes in contact with a metal surface it undergoes Fermi level equilibration. For a bulk semiconductor (e.g., single crystal) the conduction and valence bands bend to form a space charge region. The space charge layer, which is dependent on the carrier density, can extend up to a few microns. When such semiconductor-metal junction is subjected to bandgap excitation (e.g., in photovoltaic cell), the band bending rectifies the flow of photogenerated charge carriers to produce photocurrent in a solar cell. In the case of semiconductor nanocrystals, the electrons are confined and the individual nanocrystal remains isoenergetic. As a result of this size limitation the bands remain flat and the charge separation is essentially dictated by the Fermi level equilibration (Figure 6). Different degrees of electron accumulation can make the nanocrystal attain different Fermi levels and thus create an energy gradient to drive the electrons toward the collecting electrode.^{118–120}

The Fermi level (E_F) of the semiconductor is directly related to the number of accumulated electrons as illustrated in expression 5.

$$E_F = E_{CB} + kT \ln n_c N_c \quad (5)$$

E_{CB} is the conduction band energy level versus NHE, n_c is the density of accumulated electrons, and N_c is the charge carrier density of the semiconductor.

If the metal in contact with the semiconductor quantum dot is also in the particulate form we can expect electron storage within the particles. For example, Au nanoparticles possess the property of storing electrons in a quantized fashion.^{121,122} The double-layer charging around the metal nanoparticle facilitates storage of the electrons within the gold nanoparticle. When the semiconductor and metal nanoparticles are in contact, the photogenerated electrons are distributed between the semiconductor and metal nanoparticles.^{123–126} Since the electron accumulation increases the Fermi level of the metal to more negative potentials, the resultant Fermi level of the composite shifts closer to the conduction band of the semiconductor.

For example, if one accumulates more electrons in the TiO₂ or TiO₂/Au system a negative shift in the Fermi level of the TiO₂ is expected to occur. By shifting the Fermi level closer to the conduction band it would therefore be possible to improve the energetics of the semiconductor particle systems.

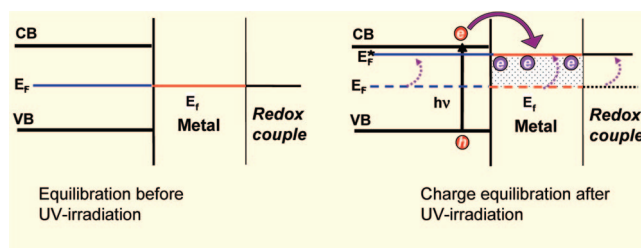


Figure 7. Equilibration of semiconductor-metal nanocomposites with the redox couple before and after UV-irradiation. Electron storage in metal nanostructure causes Fermi level to shift closer to conduction band of the semiconductor. (From ref 127.)

The apparent Fermi levels of the TiO₂ and TiO₂/Au nanoparticle systems can be determined by attaining a Nernstian equilibrium with a known redox couple (viz., C₆₀/C₆₀^{•−}).¹²⁷ The apparent Fermi level (E_{F^*}) was correlated to the concentration of the redox species by using expression 6.^{126,128,129}

$$E_{F^*}(\text{TiO}_2(e)) = E_{fb} = E^{\circ}_{\text{Ox/Red}} + 0.059 \log\left(\frac{[\text{Ox}]_{\text{eq}}}{[\text{Red}]_{\text{eq}}}\right) \quad (6)$$

where E_{F^*} and E_{fb} are the apparent Fermi level and the flat band potential of TiO₂ (or TiO₂/Au), respectively, and $E^{\circ}_{\text{Ox/Red}}$ is the standard reduction potential of the redox couple (viz., $E^{\circ}(\text{C}_{60}/\text{C}_{60}^{\bullet-}) - 0.25$ V versus NHE). By determining the equilibrium concentration of C₆₀^{•−} in the UV-irradiated TiO₂ and TiO₂/Au suspension from the absorption at 1075 nm ($\epsilon = 16\,000 \text{ M}^{-1} \text{ cm}^{-1}$), we can obtain the values of E_{F^*} (expression 6). In the absence of a noble metal, the apparent Fermi level of TiO₂ is around −230 mV versus NHE for TiO₂ particulate system. As the TiO₂ particles come in contact with Au nanoparticles, the apparent Fermi level shifts to negative potentials.

A similar shift in the Fermi level of the composite system was also observed for the ZnO–Au systems.^{124,125} The negative shift in the Fermi level is an indication of improved charge separation and more reductive power for the composite system. Figure 7 illustrates the shift in the Fermi level of the composite as a result of charge equilibration between semiconductor and metal nanoparticles.

The particle size of the metal also influences the shift in apparent Fermi level. The apparent Fermi levels for TiO₂/Au system were determined to be −250, −270, and −290 mV vs. NHE for 8, 5, and 3 nm size gold nanoparticles respectively. Since the energy levels in the gold nanoparticles are discrete, one expects a greater shift in the energy level for each accumulated electron in smaller size Au nanoparticles than in larger ones. Thus, the composite with smaller Au nanoparticles is expected to be more reductive than the one with larger Au nanoparticles. These observations parallel the size-dependent catalytic properties of gold nanoparticles deposited on titania in earlier studies.¹³⁰

Efforts have been made to self-assemble gold nanoparticles and CdS or CdSe quantum dots using thiol linkers and characterize their photophysical and charge transfer properties.^{131–133} Charge injection and charge transport in thin disordered films of CdSe nanocrystals between metal electrodes have been probed by monitoring current–voltage characteristics of photovoltaic devices.¹³⁴ The rectifying behavior of such a device pointed out that high work function materials such as gold and indium–tin oxide are poor electron injectors in agreement with the estimated conduction and valence band levels of the nanocrystals. Willner and co-workers,^{135–137} who studied the

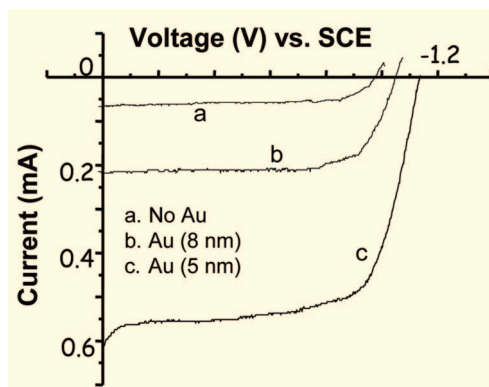


Figure 8. I – V characteristics of (a) TiO_2 , (b) TiO_2/Au (8-nm diameter), and (c) TiO_2/Au (5-nm diameter) composite film. Measurements were performed in a three-arm cell with Pt as counter electrode, a saturated calomel electrode as reference, and 3 mL of 0.05 M NaOH as electrolyte. UV light from xenon lamp ($\lambda > 300$ nm) was used as the excitation source. (From reference 125.)

photoelectrochemical performance of self-assembled CdS nanocrystals on gold surfaces have observed that redox properties of bridging unit such as dianiline play an important role in transporting the electrons from the semiconductor nanoparticles to the electrode. A recent study highlights hybrid gold-tipped CdSe nanorods (nanodumbbells) for visible light photocatalysis.¹³⁸ Under visible light irradiation, charge separation takes place between the semiconductor and metal parts of the hybrid particles which in turn induces photocatalytic reduction. Excited state deactivation processes of CdS or CdSe particles can provide further insight into energy^{139,140} and electron transfer^{141,142} pathways between the excited semiconductor and metal nanocomposites.

The beneficial effect of Fermi level equilibration between semiconductor-metal nanoparticles can be seen from the photoelectrochemical behavior of nanostructured semiconductor films.^{125,126,143} Figure 8 shows the current–voltage characteristics of TiO_2 and TiO_2/Au films cast on conducting glass electrodes, which were recorded in a photoelectrochemical cell using 0.05 M NaOH solution as the electrolyte.

The zero-current potential, which corresponds to apparent flat band potential of the nanostructured semiconductor film, shifts to negative potentials with the deposition of Au nanoparticles. The shifted apparent flat band potentials are observed at -1.04 and -1.14 V versus SCE for electrodes modified with 8 and 5 nm gold nanoparticles respectively. The observed photocurrents at positive bias are significantly higher for the composite films involving Au nanoparticles. These photoelectrochemical measurements further confirm the effect of noble metals in improving the energetics of the semiconductor nanostructures.

Although Schottky junction based quantum dot solar cells are yet to be exploited fully, their importance is being realized in recent findings. For example, Sargent and co-workers have reported solution-processed infrared responsive photovoltaic devices based on PbS quantum dots.^{105,144–146} One such example involves spin casting of thin films of PbS quantum dots (total thickness of 210–250 nm) on ITO (indium tin oxide) substrates and then treating with a surface modifier (e.g., benzenedithiol treatment). A metal contact layer consisting of 100 nm Mg/190 nm Ag was then made by thermal evaporation through a shadow mask.¹⁴⁷ Using a contact area of 3.1 mm² a power conversion efficiency of 3.6% in the infrared and 1.1% under simulated solar illumination at 100 mW/cm² was reported.¹⁴⁷ Further advances in this area could lead to the development of low-cost, large-area, physically flexible solar cells.

b. Organic Solar Cell. The solution processibility and attractive photoconversion efficiency have focused significant attention on organic semiconductor materials for constructing solar cells.¹⁴⁹ The heterojunctions of regioregular polymers (e.g., poly(3-hexylthiophene) or P3HT) and a soluble fullerene derivative (for example, [6,6]-phenyl C-61-butyric acid methyl ester fullerene or PCBM) have been found to be quite effective in delivering power conversion efficiencies up to 5%.^{150–161} The morphology of the heterogeneous junction is very sensitive to the treatment procedure adopted during the film casting and annealing process. It has been proposed that an initial crystallization of P3HT chains, followed by diffusion of PCBM molecules to nucleation sites to form aggregates of PCBM is responsible for morphology evolution in these cells.^{157,162,163} Local film structures with device performance have been mapped using photoconductive atomic force microscopy (pcAFM) with 20 nm resolution¹⁴⁸ and electrostatic force microscopy (EFM).¹⁶⁴ The schematic of the conductive-AFM set up to image the photocurrent distributions in organic thin films is shown in Figure 9.

The use of semiconductor nanocrystals in organic photovoltaic cells has been the focus of many recent research efforts.^{159,166–172} The blend of polymer and CdSe quantum dots, for example, facilitates charge separation and the generation of photocurrents under visible light irradiation.¹⁶¹ Blends of conjugated polymers and semiconductor nanoparticles have also been probed to investigate the photoinduced charge transfer processes.^{170,171} Alivisatos and co-workers^{165,169} have shown that CdSe nanorods, when combined with poly(3-hexylthiophene), create charge transfer junctions with high interfacial area (see for example Figure 10). These researchers succeeded in optimizing the overlap between the cell absorption and solar spectrum. By improving the polymer–semiconductor interface it should be possible to increase the carrier mobilities and hence the overall photoconversion efficiency. The details on the mechanism of photocurrent generation and recent advances in organic solar cells can be found in recent reviews.^{149,152,153,155,160,161,173–176}

c. Quantum Dot Sensitized Solar Cells (QDSSC). As discussed in section B above, by coupling a short bandgap semiconductor such as CdSe with another semiconductor with favorable energetics, it is possible to maximize the efficiency of charge separation through charge rectification.⁶⁹ Suitable matching of the conduction and valence bands of the two semiconductors allows accumulation of electrons and holes in two separate particles, thus allowing enough time to capture one of the charge carriers at the electrode surface. For example, chemically or electrochemically deposited or self-assembled CdS and CdSe nanocrystallites have been shown to inject electrons into wider gap materials such as TiO_2 ,^{41,49,177–187} SnO_2 ,^{56,72,188} and ZnO.^{70,189,190} This process is often referred to as type II mechanism, which is analogous to dye sensitization of semiconductor films, the dye being replaced by a short bandgap semiconductor (Figure 11). In a recent study nitrogen doped TiO_2 nanoparticle (TiO_2/N) films have been modified with CdSe quantum dots.¹⁸⁶ CdSe linked to TiO_2/N nanoparticles was found to increase the photocurrent and power conversion of the films compared to standard TiO_2/N films without quantum dot sensitization.

Short bandgap semiconductor quantum dots such as CdSe, InP, InAs, PbS, and PbSe with their tunable band edge offer new opportunities for harvesting light energy in the visible region of the solar spectrum.^{32,45,51,108,191} Alivisatos and co-workers¹⁹² fabricated planar donor–acceptor (D–A) heterojunctions by sequentially spin casting films of CdTe and then

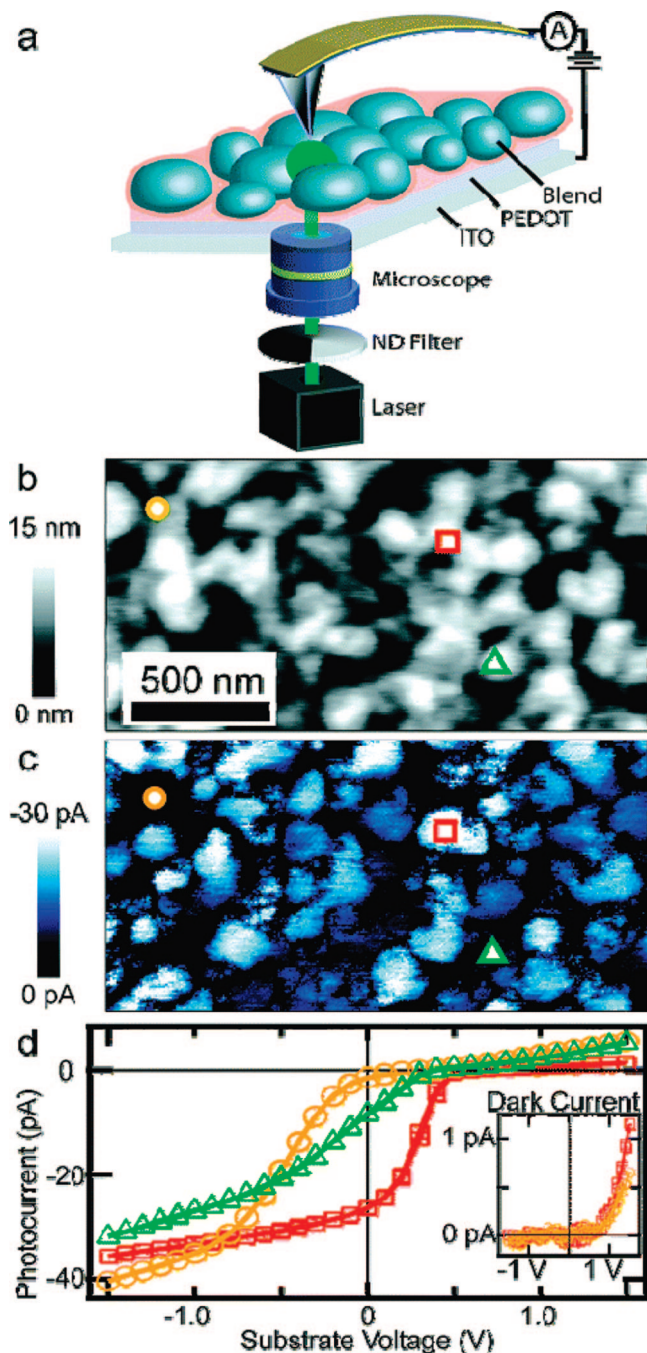


Figure 9. (a) Schematic of a conductive AFM set up to probe photovoltaic blend film. Current is collected with a metal-coated AFM tip. (b) AFM height image of an MDMO-PPV:PCBM 20:80 film spin-coated from xylenes. (c) Photocurrent map measured with zero external bias and an illumination intensity of $\sim 10^4$ W m $^{-2}$ at 532 nm. (d) Local current–voltage data acquired at the three locations indicated in b and c. Inset: Local current–voltage data without illumination. (From ref 148.)

CdSe on indium tin oxide (ITO) glass. The photoaction spectrum revealed features from both the CdSe and CdTe absorption spectra, thus confirming the contributions from both components. External quantum efficiencies approaching 70% and power conversion efficiency of 2.9% were reported. Efficient quenching of photoluminescence and a reduced emission lifetime for CdTe nanocrystals support a spatial charge separation of the photoexcited electron–hole pairs due to tunneling of charge carriers through the thin organic layer between CdTe and CdSe nanocrystals.¹⁹³

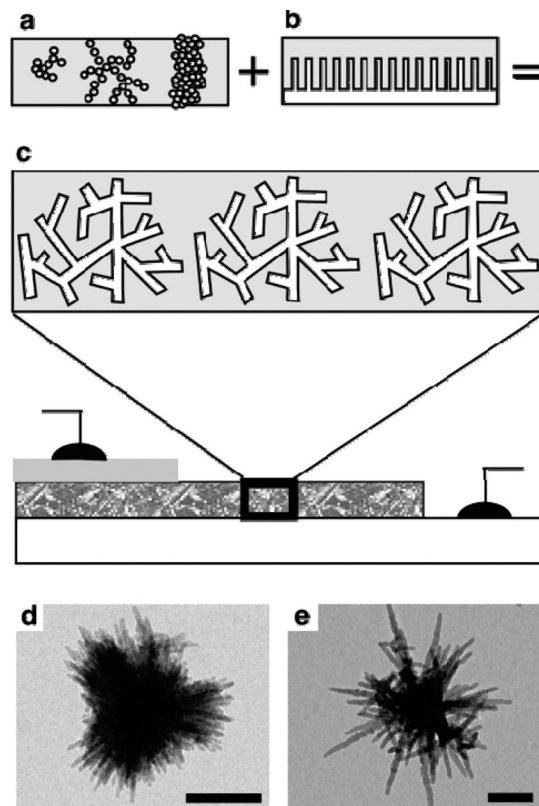


Figure 10. Hyperbranched nanocrystal solar cells (a) with the controlled morphology of templated approaches (b). Defects such as islands and aggregates detrimental to the performance of conventional spin-cast hybrid cells are eliminated in hyperbranched particle composites (c). The hyperbranched particles span the entire thickness of the active film, thereby enhancing electron transport. In panels (d) and (e), transmission electron micrographs show the 3-D structure of CdSe and CdTe hyperbranched nanocrystals, respectively. Scale bar, 100 nm. (From ref 165.)

In order to explore the salient features of quantum dots in photoelectrochemical cells, we assembled TiO $_2$ and CdSe nanoparticles using bifunctional surface modifiers of the type HS-R-COOH. Such an approach has been used to successfully link TiO $_2$ nanoparticles to CdS^{136,194,195} as well as to gold nanoparticles.^{135,196} In a typical procedure, OTE/TiO $_2$ electrode (optically transparent electrode modified with TiO $_2$ particulate film) is immersed in an acetonitrile solution of HOOC-R-SH (viz., mercaptopropionic acid) solution for 2–4 h.⁴⁹ The electrode after washing thoroughly with acetonitrile is then immersed in a toluene suspension of CdSe quantum dots. TiO $_2$ has a strong affinity for the carboxylate group of the linker molecules, as demonstrated previously with a variety of sensitizing dyes.^{197,198} Thiol and amine groups, on the other hand, bind strongly to CdSe nanoparticles.^{133,199–203} The coloration of the electrode confirms anchoring CdSe quantum dots onto a nanostructured TiO $_2$ film. Spin casting and electrophoretic deposition are also convenient methods to deposit films of CdSe quantum dots.^{204–206} These electrodes can then be inserted into a photoelectrochemical cell for evaluating their photoresponse and I–V characteristics.

The absorption spectra of TiO $_2$ films following surface binding of four different sized CdSe quantum dots are shown in Figure 12. The absorption spectra of four different size CdSe particles anchored on TiO $_2$ particulate films and TiO $_2$ nanotubes which exhibit excitonic transitions at 580, 540, 520, and 505 nm are similar to the one observed in the solution spectra and correspond to diameter 2.3, 2.6, 3.0, and 3.7 nm. The size

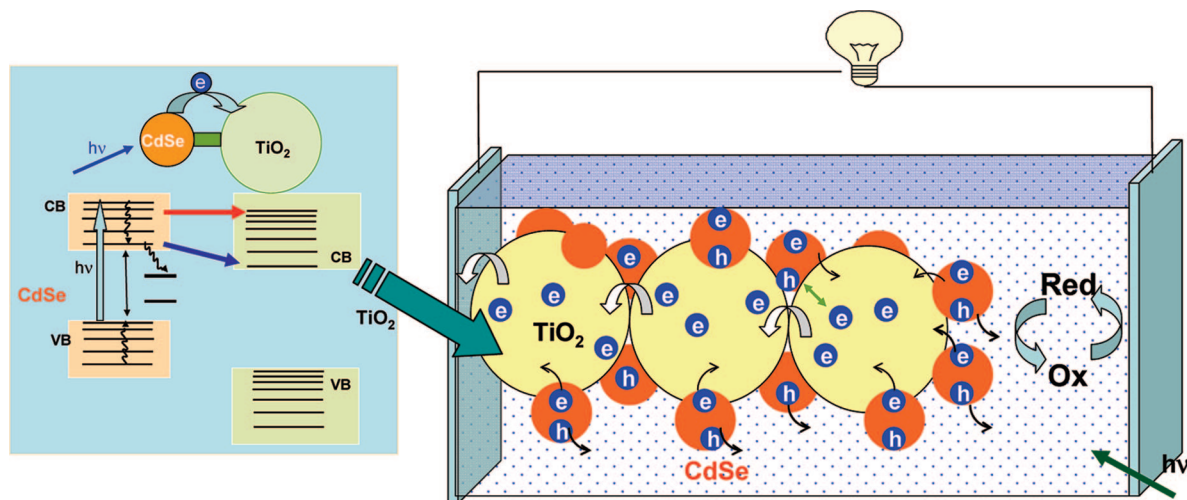


Figure 11. Principle of operation of quantum dot sensitized solar cell (QDSSC). Charge injection from excited CdSe quantum dots into TiO₂ nanoparticles is followed by collection of charges at the electrode surface. The redox electrolyte (e.g., sulfide/polysulfide) scavenges the holes and thus ensures regeneration of the CdSe.

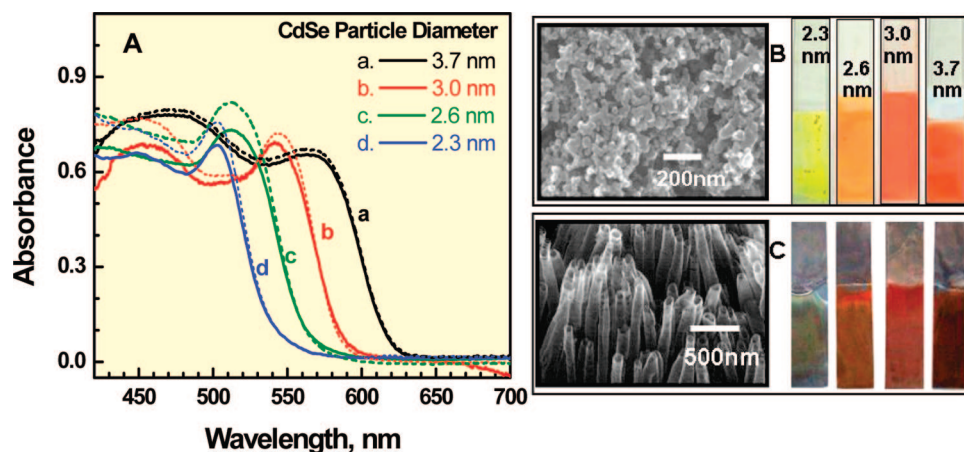


Figure 12. (A) Absorption spectra of (a) 3.7, (b) 3.0, (c) 2.6, and (d) 2.3 nm diameter CdSe quantum dots anchored on nanostructured TiO₂ films OTE/TiO₂(nanoparticle)/CdSe (solid lines) and Ti/TiO₂(nanotubes)/CdSe (dashed lines). The scanning electron micrographs (SEM) of TiO₂ particulate (B) and TiO₂ nanotube (C) films along with photographs of CdSe deposited TiO₂ films are also shown. (From ref 33.)

dependent coloration offers an opportunity to tune the coloration of the TiO₂ films and this in turn enables one to selectively modulate the absorption of incident light.

An important point that emerges from the absorption spectra is the fact that the native quantization property of CdSe nanocrystals is retained even after their binding to the TiO₂ surface. The ability to achieve relatively high coverage of CdSe quantum dots on TiO₂ surface shows the penetration of small size CdSe quantum dots into the porous network within the TiO₂ film and allows a uniform coverage throughout the film. Such monolayer coverage of the CdSe particles is analogous to the mesoscopic TiO₂ films modified with sensitizing dyes.

d. Size Dependent Photoelectrochemical Response. The photoelectrochemical response of OTE/TiO₂/CdSe films to monochromatic light irradiation can be analyzed in terms of incident photon to charge carrier efficiency (IPCE), also referred to as external quantum efficiency. IPCE was determined from short circuit photocurrents (J_{sc}) monitored at different excitation wavelengths (λ) using the expression

$$IPCE\% = \frac{1240 \times J_{\text{shortcircuit}} (\text{A/cm}^2)}{\lambda (\text{nm}) \times I_{\text{incident}} (\text{W/cm}^2)} \times 100\%$$

where I_{incident} is the power of energy of the monochromatic light incident on the electrode. The IPCE action spectra for OTE/

TiO₂(NP)/CdSe and Ti/TiO₂(NT)/CdSe electrodes (NP and NT represent nanoparticle and nanotube films) are presented in Figure 13. The photocurrent action spectra obtained with 3.7, 3.0, 2.6, and 2.3 nm CdSe particles exhibit current peaks at 580, 540, 520, and 505 nm, which closely match the absorption plots in Figure 12. These observations confirm that the photocurrent generation at OTE/TiO₂(NP)/CdSe and Ti/TiO₂(NT)/CdSe electrodes originates from the individual CdSe quantum dots and that their size quantization property is responsible for tuning the performance of quantum dot solar cells.³³ In particular, the ability to modulate the photoresponse by varying the size of CdSe particles affords the possibility to tune the performance of quantum dot solar cells. Similar observation of band-edge tuning was reported for CdSe quantum dots⁵⁰ and bismuth sulfide quantum dots⁴⁷ adsorbed on TiO₂ particles.

Comparison of IPCE at the excitonic peaks shows an interesting dependence on the particle size. The higher IPCE values obtained with 2.3 and 2.6 nm CdSe quantum dots indicated that the smaller size particles are more energetic in their excited-state and are capable of injecting electrons into TiO₂ at a faster rate. Arguments have been made in the literature for injection of hot electrons from the quantized semiconductor particles.^{34,207} Careful analysis of the ultrafast kinetic measure-

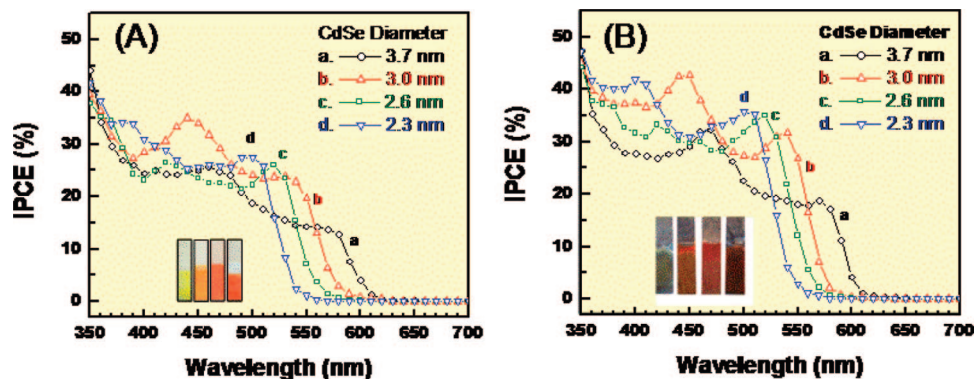


Figure 13. Photocurrent action spectra recorded in terms of Incident photon to charge carrier generation efficiency (IPCE) of (A) OTE/TiO₂(NP)/CdSe and (B) Ti/TiO₂(NT)/CdSe electrodes (electrodes are shown in the inset). The individual IPCE responses correspond to (a) 3.7, (b) 3.0, (c) 2.6, and (d) 2.3 nm diameter CdSe quantum dots anchored on nanostructured TiO₂ films. 0.1 M Na₂S solution was used as redox electrolyte. (From ref 33.)

ments needs to be pursued to establish the contribution of hot electron injection in such systems.

It is also interesting to note that the maximum IPCE obtained with CdSe quantum dots linked to TiO₂ particles and tubes are different. The maximum IPCE values in the visible region (Figure 13) range from 25% to 35% for OTE/TiO₂(NP)/CdSe electrodes while they vary from 35% to 45% for OTE/TiO₂(NT)/CdSe electrodes. These IPCE values are relatively higher than those reported in the literature for the sensitization of TiO₂ films (IPCE 25%)²⁰⁸ and ZnO nanorods (IPCE = 18%)²⁰⁹ with CdSe quantum dots.²⁰⁸ Higher power conversion efficiency has also been reported by Toyoda and co-workers using TiO₂ inverse opal structures²¹⁰ and coating with ZnS.²¹¹ Other studies have also observed enhancement in photocurrent response using TiO₂ nanotubes,^{187,212,213} nanowires,²¹² and nanobelts.²¹⁴ High external quantum efficiencies (>70%) in ferro-/ferricyanide solutions have been obtained for ZnO/CdSe core-shell nanowire arrays annealed at 400 °C.¹⁹⁰ Structural transition in nanocrystalline CdSe nanowire shell, from cubic zinc blende to hexagonal wurtzite structure seems to play an important role in enhancing photocurrent generation. These results demonstrate the necessity of optimizing nanostructure assemblies in an orderly fashion.

The maximum photocurrents obtained with 3.0 nm CdSe particles were 2.0 and 2.4 mA/cm² for OTE/TiO₂(NP)/CdSe and Ti/TiO₂(NT)/CdSe electrodes respectively under visible light irradiation ($\lambda > 420$ nm, 80 mW/cm²). The open-circuit photovoltage for these two electrodes using Na₂S redox electrolyte and Pt as counter electrode were 600 and 580 mV respectively. The fill factor for these photoelectrochemical cells was estimated as ~0.4. We estimated the overall power conversion efficiency as 0.6% and 0.7% for OTE/TiO₂(NP)/CdSe and Ti/TiO₂(NT)/CdSe electrodes respectively. In a recent study, an overall conversion efficiency of over 1.7% at 0.1 sun and 1% at full sun intensity with a cobalt(II/III)-based redox system was reported for CdSe sensitized TiO₂ solar cells.⁵⁰

Two opposing effects dictate the overall photocurrent generation at OTE/TiO₂/CdSe electrodes. Decreasing particle size has a favorable effect as the shift in conduction band to negative potentials favors the charge injection processes by increasing the driving force. The increase in the photocurrent seen with 3.7 and 3.0 nm diameter CdSe particles supports this argument. On the other hand decreasing particle size results in the absorption blue-shift and thus causes relatively poor absorption of incident visible photons (e.g., 2.3 nm diameter particles harvest less visible photons than 3.0 nm diameter particles).

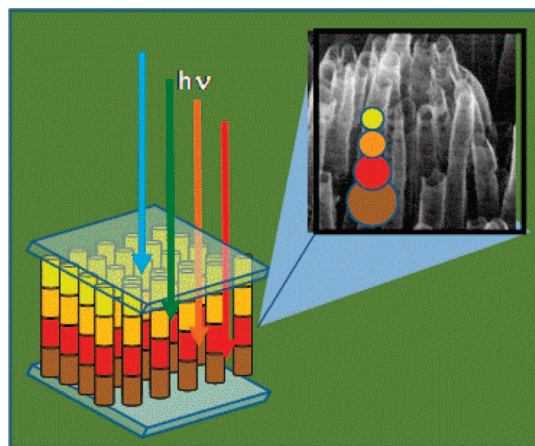


Figure 14. Artistic impression of a rainbow solar cell assembled with different size CdSe quantum dots on TiO₂ nanotube array. (From ref 33.)

Since smaller semiconductor quantum dots exhibit higher photoconversion efficiency but absorb less lower energy photons than larger size particles we can anchor the quantized particles on a nanotube array to maximize the capture of the incident light while collecting and transmitting electrons through the TiO₂ tube network (Figure 14). It is true that the excess energy of electrons of small size particles is lost once they are transferred to the TiO₂ manifold. Such a rainbow cell configuration, however, allows one to couple the faster electron injection rate of small size particles and greater absorption range of large particles effectively.

E. Emerging Strategies to Capture and Transport Photogenerated Electrons

Fast capture of electrons at the quantum dot interface remains a major challenge for efficient harvesting of light energy. Such an issue is of great importance if one is interested in exploiting multiple charge carrier generation for photocurrent generation. The strategy of encapsulating CdSe quantum dots with an electron acceptor shell or decorating on a semiconductor nanotube assembly can provide new ways to enhance the capture and transport of photogenerated electrons. Figure 15 illustrates two strategies to develop carbon nanostructure-semiconductor nanocrystal based light harvesting assemblies.

a. Fullerene Clusters As Electron Acceptors. Fullerenes exhibit rich photochemistry and act as electron shuttles in photochemical solar cells.²¹⁵ They also play an important role

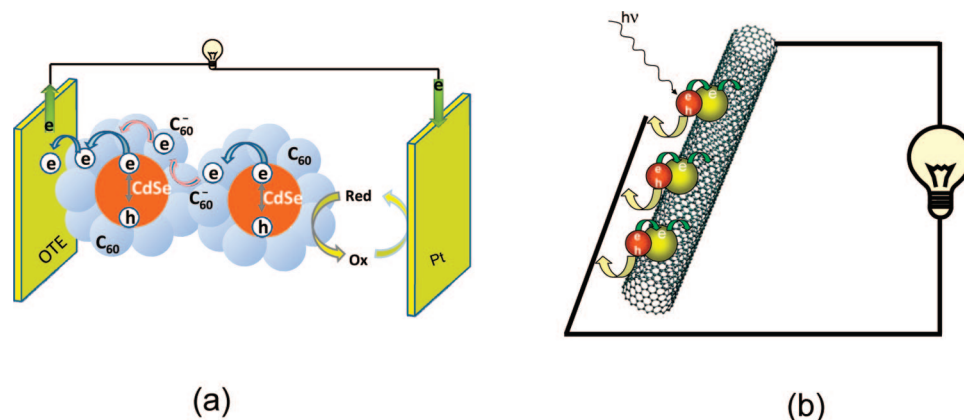


Figure 15. Photocurrent generation using (a) CdSe- nC_{60} composite clusters and (b) single wall carbon nanotubes.

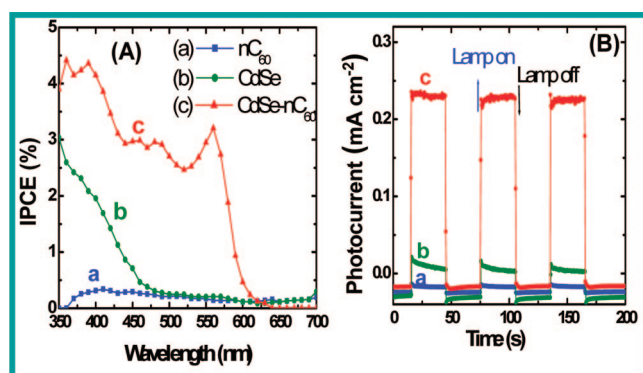


Figure 16. (A) Dependence of incident photon to current generation efficiency (IPCE) on the incident wavelength and (B) the photocurrent response of the electrodes to ON-OFF cycles of illumination. (a) nC_{60} , (b) CdSe quantum dots, and (c) CdSe- nC_{60} clusters on SnO_2 film electrodes. The electrolyte was 0.1 M Na_2S in water. (From ref 206.)

in improving the performance of organic photovoltaic cells.^{216–218} C_{60} and its derivatives are widely used to capture and transport electrons in organic solar cells.^{149,219–221} The electron accepting property of fullerenes has also been utilized for photocurrent generation in porphyrine- C_{60} based cluster films.²²² It would be interesting to see whether C_{60} can be effective for harvesting electrons from photoexcited CdSe quantum dots. In a previous study effort was made to dropcast CdSe quantum dots and C_{60} mixture on a conducting surface for the purpose of demonstrating photovoltaic performance.²²³ The poor interaction between the two components resulted in relatively lower photocurrent generation. A new approach of capping the CdSe quantum dots with a molecular shell of electron acceptor C_{60} was attempted recently to improve the capture of photogenerated electrons in quantum dots in a photoelectrochemical cell.²⁰⁶ A similar approach of capturing photogenerated electrons from CdSe quantum dots with different electron acceptors has been demonstrated by spectroscopic methods.²²⁴

CdSe and CdSe- nC_{60} clusters were directly deposited as films from quantum dots and clusters dispersed in an acetonitrile:toluene (4:1) mixed solvent. Figure 16A shows the photocurrent action spectra presented in terms of incident charge carrier generation efficiency (IPCE) at different excitation wavelengths. Both CdSe and CdSe- nC_{60} electrodes show an onset of photocurrent generation at 600 nm matching the onset of CdSe absorption. The 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 were 2–3 orders of

magnitude greater than the one obtained with dropcast films of CdSe and C_{60} .²²³ Figure 16B 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.⁴⁹ 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 are described in an earlier study.^{216,222,225,226} The C_{60} anion stabilized within the cluster is able to transport electrons to the collecting electrode surface. Figure 15a 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. In addition, coupling of semiconductor quantum dots with sensitizing dyes (e.g., Ru-polypyridine complexes) to promote energy and/or electron transfer can provide new ways to harvest a wider spectrum of incident light energy.^{114,224,227}

b. Carbon Nanotubes as Conduits for Charge Transport. Unique electrical and electronic properties, wide electrochemical stability window, and high surface area have prompted many researchers to employ carbon nanostructures such as single wall carbon nanotube (SWCNT) assemblies for energy conversion devices.^{228–230} The photon harvesting property of carbon nanotubes has been discussed in detail in recent review articles.^{231,232} The use of a nanotube support to anchor semiconductor particles provides a convenient way to capture photogenerated charge and transport them to the electrode surface. Efforts to synthesize semiconductor-CNT composite films have shown significant progress in recent years.^{233–241} Early studies mainly focused on establishing synthetic strategies and characterization of the composite systems. These include carbon nanotubes in contact with TiO_2 ,^{242,243} SnO_2 ,²⁴⁴ ZnO ,²⁴⁵ CdSe,^{237,239,246} CdS,^{234,247–249} CdSe/pyrene,²⁵⁰ and CdS/ TiO_2 .²⁴⁹

Of particular interest is the semiconductor-CNT composite that is capable of generating photocurrent from visible light with unusually high efficiency.^{234,248} Excited state interaction between TiO_2 ,^{251–254} ZnO ,²⁴⁵ and CdS^{234,248,249} and carbon nanotubes has been investigated in detail by monitoring the luminescence quenching or by Fermi-level equilibration. Excitation of CdS deposited on SWCNT films produced photocurrent with a maximum incident photon to current generation efficiency of 0.5% and thus provides evidence for the electron transfer pathway in the composite. The ability of the CdS-SWCNT

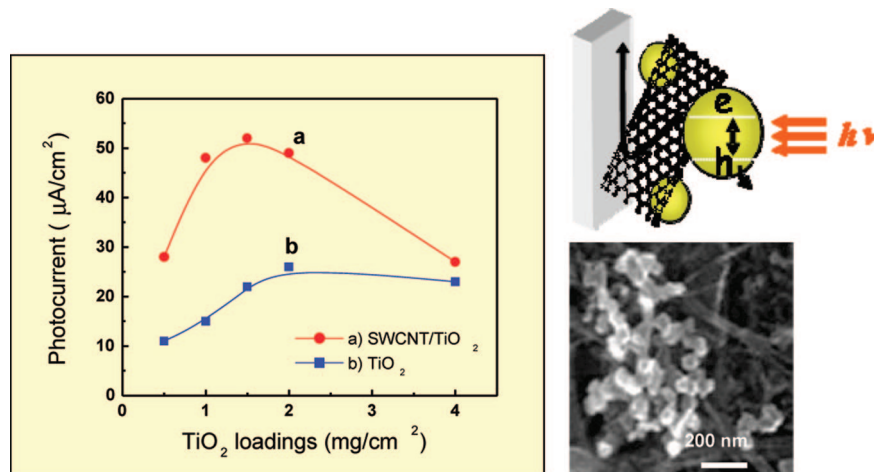


Figure 17. Left: Photocurrent response as a function of the amount of TiO_2 deposited on carbon fiber electrode (CFE): (a) In the presence and (b) absence of SWCNT scaffold. SWCNT concentration was maintained constant at 0.2 mg/cm^2 while TiO_2 loading was varied. Right: Scheme showing the electron transport through SWCNT and SEM image of the SWCNT– TiO_2 composite. (From ref 251.)

nanocomposite system to undergo photoinduced charge separation opens up new ways to design light harvesting assemblies.

The role of SWCNT in enhancing the photoelectrochemical performance of TiO_2 film can be probed by varying the ratio of TiO_2 /SWCNT in the composite film. A commercially available TiO_2 (Degussa P-25) suspension in water was drop cast on carbon fiber electrode (CFE) with and without SWCNT. Figure 17 compares the photocurrent observed with CFE/ TiO_2 and CFE/SWCNT/ TiO_2 electrodes at different loading of TiO_2 particles. In the case of the CFE/ TiO_2 film, we observe an increase in photocurrent with increased TiO_2 loading (at loadings below 2 mg/cm^2) as more of the excited TiO_2 particles undergo charge separation and participate in the photocurrent generation. At higher TiO_2 loadings we observe saturation in the photocurrent showing the limitations of light absorption within the TiO_2 film. It is interesting to note that the photocurrent observed at these TiO_2 loadings with SWCNT support is significantly greater than the photocurrent observed without the SWCNT support. The usefulness of SWCNT support architecture in improving the photocurrent generation in TiO_2 based photoelectrochemical solar cells is discussed elsewhere.^{251,255} Two dimensional carbon nanostructures such as graphene sheets offer new ways to disperse semiconductor and metal nanoparticles.^{256,257} Utilization of such nanocomposites in energy conversion devices has yet to be tested for the effectiveness of graphene as a support carbon nanomat.

c. Nanowire and Nanotube Array Based Solar Cells.

Semiconductor nanowires with high aspect ratio are now being grown as vertically aligned arrays on electrode surfaces to increase the light absorption and to facilitate efficient radial collection of carriers.^{258,259} Most of the recent studies have focused on the utilization of ZnO ,^{190,209,260} SnO_2 ,¹⁸⁸ and TiO_2 nanowires.²⁶¹ The 1-D array of these large bandgap semiconductors can be readily modified with CdS or CdSe quantum dots for extending the photoresponse into the visible.^{33,209,262} The operation of TiO_2 nanotube array based semiconductor cells has already been discussed in the earlier section. By comparing the behavior of nanorod array and planar Si²⁶³ and Cd(Se, Te)²⁶⁴ photoelectrodes Spurgeon et al. concluded that the fill factors of the nanorod array photoelectrodes were generally superior to those of the planar junction devices.

Silicon nanowires are emerging as another class of light harvesting semiconductors.^{264–269} If semiconductor nanorods having radial p-n junctions are arranged in a vertically aligned

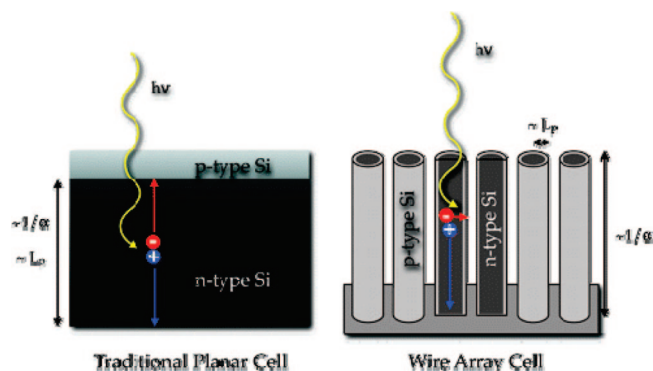


Figure 18. Schematic drawing of the difference between a traditional planar solar cell and a wire array solar cell. In the planar cell, the minority carrier diffusion length (L_p) must be comparable to the absorption length ($1/\alpha$). In the wire array cell, the minority carriers can diffuse radially to the junction, while light is still absorbed along the axial dimension of the wire. (From ref 263.)

array, the light can be absorbed along the long axis of the rod and the charge carriers can diffuse a short distance radially to the junction (Figure 18).²⁶³ Such electrodes have been shown to exhibit significantly higher photocurrent than the control Si electrode during the operation of a photoelectrochemical solar cell. Silicon nanowires grown on Si(111)/Au substrates were controllably p-type doped by addition of tri-Me boron. These p-Si nanowire arrays gave a photovoltage of 220 mV in $[\text{Ru}(\text{bpy})_3]^{2+}$ solution when illuminated by white light.²⁷⁰ Coaxial silicon nanowire solar cells based on p-type/intrinsic/n-type (p-i-n) elements yield a maximum power output of up to 200 pW per nanowire device and an apparent energy conversion efficiency of up to 3.4% under one solar equivalent (1-sun) illumination.²⁷¹ Such interconnected p-i-n silicon nanowire based photovoltaic elements have been projected as the potential nanopower sources to drive functional nanoelectronic sensors and logic gates. Scanning photocurrent microscopy of single Si nanowire devices has indicated the minority carrier diffusion lengths of $2.2 \mu\text{m}$.²⁷¹ Efforts are being made in several research groups to obtain fundamental understanding of charge separation and recombination processes in semiconductor nanowires^{272–280}

F. Concluding Remarks

The orphan status of solar energy as a major source of our energy chain is expected to change as the demand for clean

energy increases. During the last two decades significant advances have been made in designing photoactive nanostructure architectures and inorganic–organic hybrid assemblies. Many of the newly synthesized nanomaterials hold the promise of being able to meet the global challenge of supplying clean energy. Quantum dot and carbon nanostructure based solar cells are still in their infancy. The recent advances in utilizing quantum dots or semiconductor nanocrystals as light energy harvesters provide unique opportunities for the development of next generation solar cells. Developing new and revolutionary viable strategies to organize ordered assemblies on electrode surfaces will be the key to improving the performance of quantum dot solar cells. Commercialization of large scale solar cells based on nanostructure architecture has yet to be realized. With the recent surge in interest of renewable energy we can expect major breakthroughs in developing economically viable solar energy conversion devices in the near future.

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