

# Beyond Photovoltaics: Semiconductor Nanoarchitectures for Liquid-Junction Solar Cells

Prashant V. Kamat,\* Kevin Tvrdy, David R. Baker, and James G. Radich

Radiation Laboratory and Departments of Chemistry & Biochemistry and Chemical & Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States

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## Contents

1. Evolution of the Photoelectrochemical Cell	6664
1.1. Motivation and Feasibility	6664
1.2. Photoelectrochemistry of Single-Crystal Semiconductor Electrodes	6666
1.3. Photoelectrochemistry of Nanostructured Semiconductor Films	6667
1.4. Charge Rectification Using Composite Semiconductor Films	6668
2. Preparation of Nanostructured Semiconductor Films	6669
2.1. Semiconductor Oxides and Chalcogenides	6669
2.2. Modification of Oxide with Quantum Dots	6670
2.2.1. Coupling with Bifunctional Molecules	6670
2.2.2. Chemical Bath Deposition and SILAR	6670
2.2.3. Other Deposition Methods	6671
3. Electrochemical and Optical Characterization of Nanostructured Semiconductor Films	6672
3.1. Fundamental Characterization	6672
3.2. Photocurrent Action Spectroscopy	6673
3.3. Optical Characterization	6673
3.4. Characterization of Electron Transfer	6673
4. Electron Transport in Metal Oxide Films	6674
4.1. Mechanism of Photoinduced Carrier Transport	6674
4.2. Characterization of Diffusion Length	6675
4.3. One-Dimensional (1-D) Transport Architectures	6675
4.4. Electrolyte Interactions	6676
5. Recent Trends in Liquid-Junction Solar Cells	6676
5.1. Dye Sensitized Solar Cells	6677
5.2. Quantum Dot Sensitized Solar Cells	6678
5.3. Carbon Nanostructure Based Photochemical Solar Cells	6679
6. Future Outlook: A Promise for a Better Tomorrow	6680
7. Acknowledgments	6680
8. Supporting Information Available	6680
9. References	6681

## 1. Evolution of the Photoelectrochemical Cell

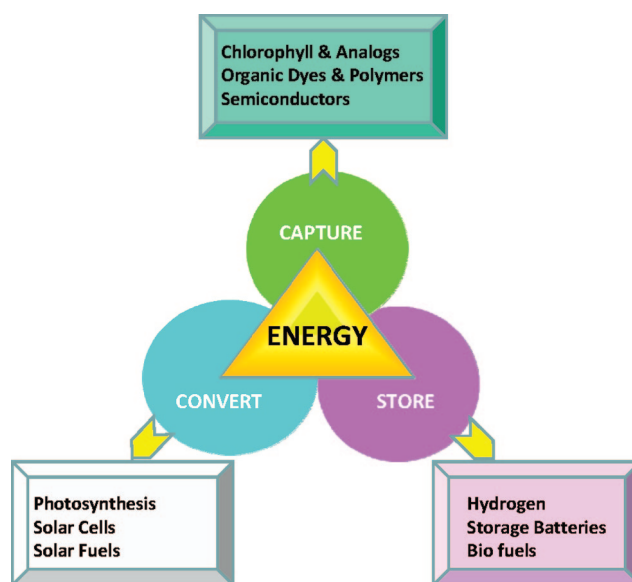
### 1.1. Motivation and Feasibility

The demand for clean energy technologies has spurred academic interest in new and efficient ways to capture and store sunlight.<sup>1–6</sup> Concerted efforts are now being directed toward both the design of light harvesting assemblies,

construction of economically viable solar cells, and the development of efficient energy storage devices (Figure 1). Even in the age of nanotechnology, century-old liquid-junction electrochemical cells play a pivotal role in our daily lives by delivering portable energy to everything from mobile phones to automobiles. More than 50% of energy storage currently employs 150-year-old *lead acid battery* technology. Lithium ion batteries including lithium–air batteries have the potential to overcome the challenges facing lightweight storage batteries. The charge/discharge cycles in these devices are dictated by electrochemical redox processes at the electrodes.

Photosynthetic membranes, conjugated polymers, sensitizing dyes, and semiconductor materials often serve as light harvesting antennas in liquid-junction solar cells, organic hybrid solar cells, or thin film solar cells. While great strides are being made which attempt to mimic natural photosynthesis for next-generation solar cells, current technologies lag behind the development of practical photovoltaic devices. In recent years, the concept of utilizing nanomaterial-based architectures in light energy conversion devices has emerged as an alternative to single-crystalline based photovoltaic devices. Both dye sensitized and quantum dot sensitized solar cells are examples of such devices.

Photoelectrochemical cells are liquid-junction solar cells that typically employ a photoactive electrode that can directly



**Figure 1.** Integration of systems that capture photons, convert light energy into electricity or fuels, and store energy is crucial for harvesting solar energy.

\* To whom correspondence should be addressed. E-mail: pkamat@nd.edu.



Prashant V. Kamat (second from left) is John A. Zahm Professor of Science in the Departments of Chemistry & Biochemistry and Radiation Laboratory, University of Notre Dame. He earned his doctoral degree (1979) in Physical Chemistry from the Bombay University and carried out postdoctoral research at Boston University (1979–1981) and University of Texas at Austin (1981–1983). He joined Notre Dame in 1983 and initiated a successful research project on utilizing semiconductor nanostructures for light energy conversion. His major research interests are in three areas: (1) to understand interfacial processes and catalytic reactions at nanostructured semiconductor interface, (2) to develop semiconductor hybrid assemblies for solar cells and solar fuels, and (3) carbon nanostructure architectures for energy conversion and storage. He has authored more than 350 peer-reviewed journal papers, review articles, and book chapters with more than 20000 citations. He has also edited three books in the area of nanoscale materials.

Kevin Tvrđy (far left) received his Bachelor's degree in Chemistry from the University of Nebraska in 2005, after which he worked for one year at Streck Laboratories as an R&D technician. He is currently pursuing his doctoral degree at the University of Notre Dame in the Department of Chemistry and Biochemistry under the direction of Prashant V. Kamat. His current research centers on the application of ultrafast spectroscopic measurements to better understand and improve upon electron transfer phenomena in photovoltaic devices. In his free time, Kevin enjoys spending time with his wife Jessica outdoors.

David R. Baker (far right) is a Ph.D. candidate in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame, and Radiation Laboratory. He earned his Bachelor's degree in Chemical Engineering at the University of Washington in 2006, where he researched interfacial water phenomena and methylotrophic bacterial populations. His current research focuses on electrode–electrolyte interactions and developing nanoarchitectures within quantum dot solar cells. He has interned with the Jet Propulsion Laboratory and the United States Department of State.

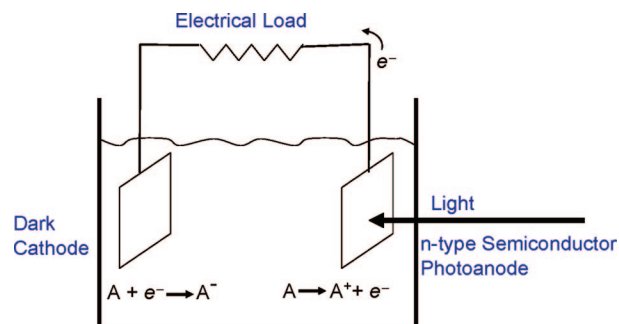
James G. Radich (second from right) is a Ph.D. student in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame where he works under the guidance of Prashant Kamat in the Notre Dame Radiation Laboratory. His current focus is on carbon-based nanostructured composite materials for energy applications. James earned his Bachelor's and Master's degrees in Chemical Engineering from the Dave C. Swalm School of Chemical Engineering at Mississippi State University. He also spent four years working at RespirTek, Inc., a commercial bioenvironmental laboratory. James's research interests are diverse, with past projects focusing on biofuels synthesis, gas hydrates, anaerobic digestion, and novel bioremediation strategies. James has also worked in various government and industrial positions ranging from groundwater assessment/remediation regulator to a refinery process engineer to laboratory director.

convert light energy into electricity.<sup>7–10</sup> Unlike solid state photovoltaic solar cells such as silicon-based photovoltaics, liquid-junction solar cells employ photoactive anode and/or cathode. The redox electrolyte which separates the anode

and cathode regenerates the photoactive component of the electrodes. Thus, the redox electrolyte plays a crucial role in facilitating interfacial electron transfer and maintaining ionic conduction between the two electrodes. A simple schematic illustration (Figure 2) introduced by Wrighton and Bard's groups in the 1970s has become an iconic representation of liquid-junction photoelectrochemical solar cells.<sup>11,12</sup>

During scientific discussions or at scientific meetings, one often encounters criticisms which aim to downplay the potential advancements presented by liquid-junction solar cells due to the alleged problematic or impractical nature of the liquid electrolyte. However, these criticisms fail to recognize the versatility of batteries as energy storage devices, which are simply electrochemical cells that employ redox electrolytes in the form of liquid or paste for ionic conduction between the two electrodes. Whether it is an alkaline battery or lead-acid battery, electrochemical cells dictate the market of portable energy supply. Thus, the presence of electrolytes in liquid-junction solar cells should not be regarded as a hindrance. Given recent electrolyte advances such as the design of ionic liquids and polymer electrolytes, it should be possible to overcome the misgivings surrounding mass implementation of a liquid-junction solar cell.

Law and Meigs<sup>13</sup> were some of the early investigators to report the effect of water vapor on the photoresponse curves and reverse current characteristics of germanium and silicon p–n junction units. The field of photoelectrochemistry emerged as a competitive energy conversion scheme following the work of Fujishima and Honda<sup>14</sup> in splitting water with a UV-irradiated TiO<sub>2</sub> electrode. The possibility of using nature's feedstock of water and sunlight to generate fuel in the form of hydrogen and oxygen has motivated many



**Figure 2.** Photoelectrochemical cell for conversion of light into electricity. Adapted from ref 11. Copyright 1977 American Chemical Society.

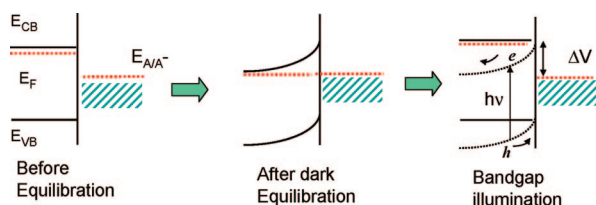
research groups to explore metal oxide based photocatalysis.<sup>5,15–25</sup> The simplicity of the technique was further demonstrated with polycrystalline oxide semiconductors.<sup>26</sup> For detailed discussion on various topics related to photoelectrochemistry, readers are encouraged to refer to a recent books edited by Memming<sup>27</sup> and Archer and Nozik.<sup>28</sup>

The quest to understand charge transfer processes at the semiconductor/electrolyte interface led to the development of various types of liquid-junction solar cells.<sup>16,29–41</sup> Initial efforts were mainly focused on single-crystal semiconductor electrodes.<sup>7,8,31,41–52</sup> Because most of the oxide semiconductors that showed photocatalytic activity were large bandgap semiconductors, attention was quickly driven to small bandgap semiconductors such as Si and CdS. However, these semiconductors underwent photocorrosion in aqueous media. These adverse effects were overcome through the use of either nonaqueous electrolytes or semiconductor surface modifications. Metal chalcogenides such as CdS, CdSe, and CdTe, which exhibit strong absorption in the visible spectrum, became popular choices for photoelectrochemical investigations. The use of sulfide electrolytes was found to be effective in scavenging the photogenerated holes, thus overcoming the issues related to aqueous anodic photocorrosion.<sup>53–59</sup> Early claims<sup>60–62</sup> related to CdS as a water splitting photocatalyst were quickly refuted with the argument that anodic corrosion dominates over hole oxidation of water.<sup>63,64</sup>

## 1.2. Photoelectrochemistry of Single-Crystal Semiconductor Electrodes

A single-crystal semiconductor electrode in contact with a redox couple behaves similarly to a metal junction Schottky interface. The thermodynamic and electronic properties of the chosen redox couple dissolved in the electrolyte solution dictate the properties of the semiconductor/liquid interface. Figure 3 shows the band bending of an n-type semiconductor as its Fermi level equilibrates with a redox couple. The initial difference between the semiconductor,  $E_F$ , and solution Fermi level (redox potential),  $-nE(A/A^-)$ , determines the size of the energy barrier (or extent of band bending) at the semiconductor/liquid junction when the interface reaches equilibrium. Because of the low carrier density, the value of  $E_F$  in the semiconductor changes much more rapidly as the electrons are almost completely depleted at the interface. The extent of band bending thus can be tuned by selecting the redox couple in the liquid.

The region of band bending is referred to as the space charge layer, and the length of that layer (usually 0.1–1  $\mu\text{m}$ )



**Figure 3.** Equilibration of charge at the semiconductor/electrolyte interface in dark leads to band bending. Upon illumination under open-circuit conditions, these charges accumulate leading to the shift in Fermi level. The difference between the semiconductor Fermi level and the redox potential is the maximum theoretically attainable photovoltage. In practice, the values are slightly lower because bands do not become completely flat. (Notation: the bottom of the conduction band at the surface,  $E_{cb}$ , the top of the valence band at the surface,  $E_{vb}$ , the Fermi level,  $E_F$ , and the electrochemical potential of redox couple,  $E_{A/A^-}$ ).

is dictated by carrier density.<sup>65</sup> During bandgap excitation, the space charge layer assists in charge separation as the electrons are driven into the bulk semiconductor and the holes to the electrolyte interface (for p-type semiconductor the situation is reversed; the accumulation layer drives the electrons to the liquid interface and holes are driven into the bulk). Under open-circuit conditions, electrons accumulate within the conduction band, resulting in the flattening of the bands. The shift of Fermi level to more negative potential represents the open circuit photovoltage. At this stage of illumination, the interface attains a steady state equaling the rates of charge separation and charge recombination.

The maximum photovoltage one would expect following the excitation of semiconductor/electrolyte interface is the difference between conduction band and the redox potential of the electrolyte.

$$\Delta V = E_F - E_{A/A^-} \quad (1)$$

The photovoltage thus can be manipulated by varying the redox potential of the couple employed in the electrolyte. Similarly for metal oxide electrodes, surface chemistry in aqueous electrolyte solutions associated with proton-transfer equilibria dominates the interfacial energetics and shifts the conduction band edge to more negative potential with increasing pH. As a result, one observes a linear dependence of photovoltage on pH.<sup>17,66,67</sup> However, this relationship is no longer valid if the Fermi level gets pinned at the interface.<sup>12,68</sup> In addition, the charge transfer kinetics at the interface play an important role in determining the net attainable photovoltage.

The observed charge-transfer rate across an n-type semiconductor/liquid interface is the result of various processes that follow the bandgap excitation of the semiconductor. These processes include recombination of the photogenerated electron–holes within the space charge layer (or depletion layer) and tunneling of the excited electrons (or thermionic emission) across the junction barrier to react with the oxidized form of the redox couple. These processes along with the photogeneration of electrons dictate the accumulation of electrons in the space charge layer. Thus, the undesirable loss of electrons through recombination processes limits the achievable energy-conversion efficiency of a photoelectrochemical system.

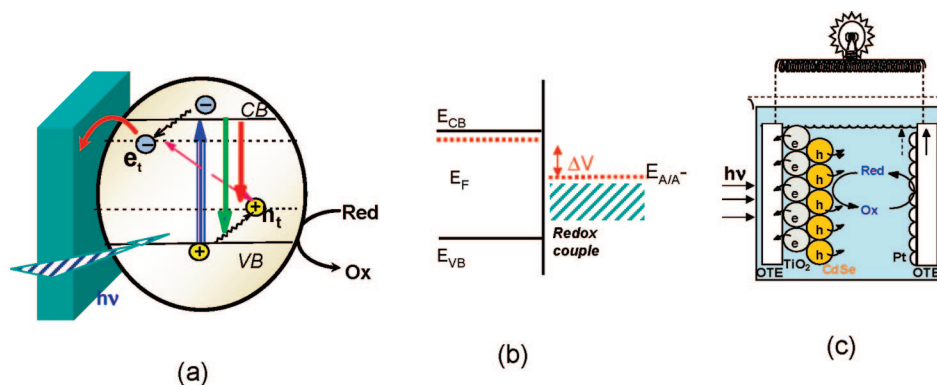
If  $I_0$  is the dark saturation current opposing the photogenerated current density and  $I_{sc}$  is the photocurrent at short circuit, one can express the open-circuit voltage of a Schottky barrier using eq 2<sup>69</sup>

$$V_{oc} = \frac{k_B T}{q} \left( \ln \left( \frac{I_{sc}}{I_0} \right) + 1 \right) \cong \frac{k_B T}{q} \left( \ln \frac{I_{sc} L N_D}{q A D n_i^2} \right) \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $L$  is the diffusion length of the minority charge carrier,  $N_D$  is the dopant density of the bulk semiconductor,  $A$  is the electrode area,  $D$  is the diffusion coefficient of the minority charge carrier, and  $n_i$  is the intrinsic carrier concentration in the semiconductor. Because recombination of charge carriers in the bulk is always nonzero, the largest obtainable  $V_{oc}$  will always be less than the ideal  $\Delta V$  expressed in eq 1 and Figure 3.

The electron transfer from an excited semiconductor into the redox couple at the interface has been described by the





**Figure 4.** (a) Photoinduced charge separation in a single semiconductor nanoparticle, (b) electron accumulation within the particle shifts its Fermi level to negative potentials, and (c) a schematic showing a regenerative photoelectrochemical cell.

Marcus–Gerischer model.<sup>42,70–73</sup> According to this model, the standard driving force for charge transfer,  $\Delta G^{o'}$ , at n-type semiconductors is described by eq 3:<sup>74,75</sup>

$$\Delta G^{o'} = E_{cb} - E_{A/A^-}^o \quad (3)$$

where  $E^{o'}$  is the formal potential for the  $A/A^-$  redox couple and  $E_{cb}$  is the energy of the conduction-band edge. The measured charge-transfer rate constant has a complex dependence on  $\Delta G^{o'}$ , as shown by eq 4:<sup>73,75</sup>

$$k_{ct} = k_{ct,max} \exp\left[-\frac{(\Delta G^{o'} + \lambda)^2}{4\lambda k_B T}\right] \quad (4)$$

where  $k_{ct,max}$  is the maximum rate constant observed at the optimum value of  $\Delta G^{o'}$ , and  $\lambda$  is the reorganization energy involved with a change in the nuclear configurations of the solvated species  $A$  and  $A^-$ . Thus the Marcus–Gerischer model predicts that values of  $\ln[k_{ct}]$  should show a parabolic dependence on  $\Delta G^{o'}$ . In other words, one should observe smaller values of  $\ln[k_{ct}]$  for  $\Delta G^{o'}$  values smaller or greater than  $\lambda$ . Experimentally, one can test the validity of this model by varying the driving force  $\Delta G^{o'}$  and employing different redox couples in the electrolyte phase. Few examples in the literature show the validity of such relationships.<sup>74,76</sup> Because of the sensitivity of the semiconductor surface to adsorbed species or complexation of dangling bonds with the chemical species in solution, it is difficult to establish this relationship for all semiconductor electrodes.

### 1.3. Photoelectrochemistry of Nanostructured Semiconductor Films

A nanostructured semiconductor film is capable of generating photocurrent when employed as an electrode in a photoelectrochemical cell.<sup>77–79</sup> Nanostructured semiconductor films exhibit photoelectrochemical characteristics similar to those of a polycrystalline semiconductor material while retaining the properties of individual particles (e.g., photoemission or electron storage capabilities). The formation of an ideal space charge layer in semiconductor nanocrystallites with particle diameters <10 nm is less likely. Because nanostructured semiconductor films consist of a three-dimensional network of nanoparticles, one cannot strictly employ the mechanistic considerations that are employed with single-crystal or polycrystalline semiconductor electrodes. The explanation for the origin of both particulate-type photoelectrochemical behavior and polycrystalline-type

photoelectrochemical behavior of the nanostructured semiconductor films remains an intriguing phenomenon.

Under bandgap illumination, semiconductor nanoparticles undergo charge separation to form electron–hole pairs (Figure 4). Upon scavenging holes with a suitable redox couple, photogenerated electrons transport through the nanoparticulate film and are harvested at a conducting electrode. The electrons reach the counter electrode via the external circuit and regenerate holes present within the redox couple. The chemical composition of the electrolyte is unchanged while converting incident light into electricity. Thus, the basic principle behind the operation of a photoelectrochemical cell consisting of nanostructured semiconducting electrodes is similar to that of a single-crystal semiconductor electrode cell. A properly designed semiconductor particulate system and a suitably matched redox couple can produce a long-lived charge separated state and contribute to the efficient photoelectrochemical performance of a nanostructured semiconductor film.

One of the early reports on the electrochemical aspects of UV-irradiated  $\text{TiO}_2$  particle suspensions was published by Bard and co-workers.<sup>80</sup> Later, attention was drawn to the photoelectrochemistry of nanostructured  $\text{TiO}_2$  films,<sup>81–85</sup> especially in the context of the dye sensitization process.<sup>86</sup> Initial studies carried out with metal oxides and metal sulfide films indicated that differing rates of electron or hole transfer into the electrolyte results in the accumulation of one of the charge carriers within the film.<sup>77,87–90</sup> For example, in the presence of a hole scavenger, electrons accumulate in a nanocrystalline  $\text{TiO}_2$  film and subsequently propagate through numerous grain boundaries. The chance of recombining with holes will be significantly reduced if photogenerated holes are scavenged by hydroxide ions. Thus, presence of a hole (or electron) scavenger becomes crucial in maximizing the efficiency of photocurrent generation in irradiated semiconductor particulate films.

The kinetic-based model was first pointed out by Hodes and co-workers to explain the n-type behavior of nanocrystalline CdSe films.<sup>91–94</sup> The observation of p-type photoreponse in some films indicated that the direction of the current flow is determined by the semiconductor/electrolyte interface and not by the field in the bulk of the film. Similarly, lack of charge rectification behavior in thin semiconductor films was also demonstrated in electrochemically deposited thin CdSe films (<1  $\mu\text{m}$ ).<sup>95,96</sup> The photoelectrochemical properties of these films are susceptible to surface adsorbed species such as oxygen,<sup>89,97</sup> charge recombination at the grain boundaries,<sup>77,87</sup> and leakage of electrons

into the solution instead of generating photocurrent.<sup>96</sup> These early studies pointed out that nanostructured semiconductor films do not possess a well-defined space charge layer region similar to that of single-crystal or polycrystalline semiconductor electrodes.

On the other hand, it is possible to observe cell characteristics typical of Schottky behavior in nanostructured semiconductor films. A model has been developed to analyze observed photovoltage and photocurrent in ZnO films.<sup>98,99</sup> For a photoelectrochemical cell operating on a Schottky-barrier principle,  $V_{oc}$  can be related to  $I_{sc}$  by eq 5:<sup>50</sup>

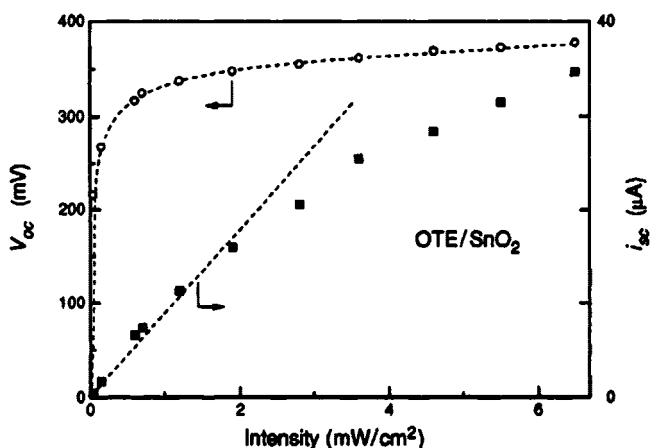
$$V_{oc} = \frac{nk_B T}{q} [\ln(I_{sc}/I_0) + 1] \quad (5)$$

where  $q$ ,  $n$ , and  $I_0$  are, respectively, the electric charge, the diode quality factor, and the reverse saturation current.

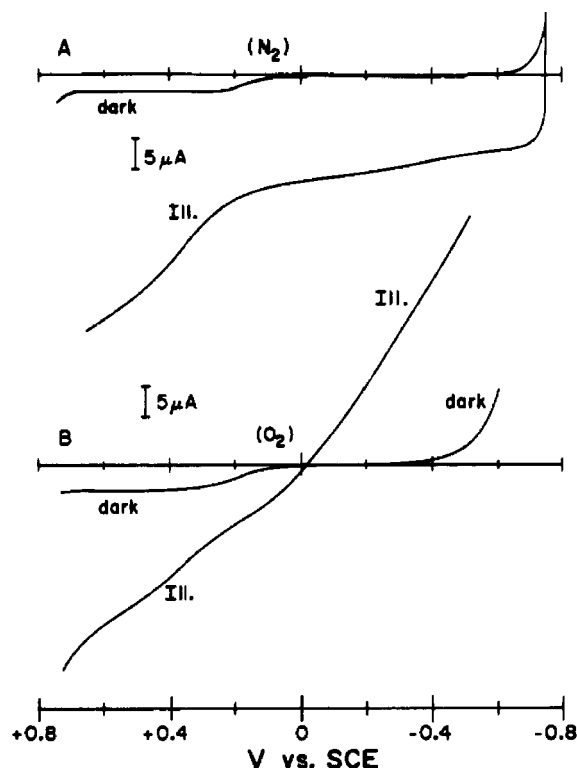
Photovoltage dependence on incident light intensity,  $I_{inc}$ , of SnO<sub>2</sub> films can be analyzed from the plot of  $V_{oc}$  versus  $I_{sc}$  at various intensities (Figure 5). The linearity of the  $V_{oc}$  on the natural logarithm of  $I_{sc}$  at lower light intensities suggests the validity of eq 5 in evaluating the photoelectrochemical performance of a nanocrystalline SnO<sub>2</sub> film. The diode quality factor,  $n$ , and reverse saturation current,  $I_0$ , can be determined from a plot of  $\ln[I_{sc}]$  vs  $V_{oc}$ .

The generation of photocurrent as a result of charge separation is strongly dependent on the applied potential. Applied anodic bias shifts the pseudo Fermi level in such a way that it resembles that of a potential gradient within the nanocrystalline film and drives the photogenerated electrons and holes in opposite directions. With increasing negative potential, the pseudo-Fermi level increases resulting in accumulation of electrons. At potentials corresponding to the flat band potential, the photocurrent drops to zero as all the photogenerated charge carriers are lost to recombination. The  $I$ - $V$  characteristics of a nanocrystalline TiO<sub>2</sub> film in the nitrogen purged and oxygenated solutions are shown in Figure 6.

Equation 6, similar to an equation employed for a p-n junction solar cell, has been derived to fit the experimental data of current-voltage ( $I$ - $V$ ) characteristics of nanostructured TiO<sub>2</sub> films:<sup>88</sup>



**Figure 5.** Open-circuit photovoltage ( $V_{oc}$ ) and short circuit photocurrent ( $I_{sc}$ ) of a nanocrystalline SnO<sub>2</sub> film (note that short circuit current is proportional to incident light intensity) (electrolyte, 0.02 M NaOH; counter electrode, Pt; excitation at 290 nm). From ref 87. Copyright 1994 American Chemical Society.



**Figure 6.**  $I$ - $V$  characteristics of nanostructured TiO<sub>2</sub> film (RE: SCE, scan rate 5 mV/s) in: (A) N<sub>2</sub> saturated and (B) O<sub>2</sub> saturated aqueous solution of 0.05 M NaOH. The traces were recorded in dark and under illumination with UV-light. From ref 89. Copyright 1993 American Chemical Society.

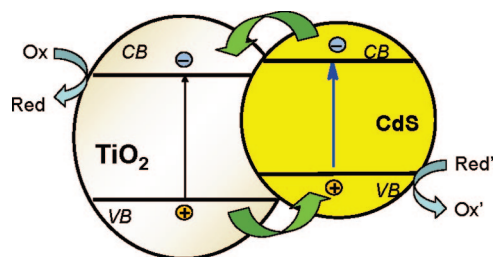
$$I = I_L - I_S(e^{qV/k_B T} - 1) \quad (6)$$

where  $I_L$  is the photocurrent due to the incident light and  $I_S$  is the saturation current.

#### 1.4. Charge Rectification Using Composite Semiconductor Films

The feasibility of designing composite films of two or more semiconductor nanoparticles presents the possibility to improve charge separation within those films. For example, rectification of electron flow in a nanostructured TiO<sub>2</sub> film was demonstrated by coating that film with a thin layer of CdSe.<sup>95,96</sup> Uekawa et al.<sup>100</sup> also succeeded in developing a p-n junction diode for achieving charge rectification. The advantage of using coupled semiconductor films in photoelectrochemical cells is 3-fold: (i) to extend the photoresponse by coupling a large-bandgap semiconductor with a small-bandgap semiconductor, (ii) to retard the recombination of photogenerated charge carriers by injecting electrons into the lower lying conduction band of the large bandgap semiconductor, and (iii) to improve the selectivity by carrying out reduction and oxidation at two different particles. A schematic diagram showing the principle of charge separation in a composite semiconductor film is shown in Figure 7.

An early demonstration of this concept came from Nozick and co-workers,<sup>101</sup> who developed a simple photochemical diode by sandwiching p- and n-type semiconductors. This concept was later extended to water photoelectrolysis.<sup>102</sup> The feasibility of sensitizing a large bandgap semiconductor such as ZnO by coating with a CdS film was demonstrated by Gerischer and Lübke.<sup>103</sup> During these early years, considerable interest was also shown in developing coupled semi-



**Figure 7.** Schematic diagram illustrating the principle of charge separation between two semiconductor nanoparticles. Coupling of such semiconductor nanoparticles improves charge rectification and the selectivity of reduction and oxidation processes at the interface.

conductor systems. These include CdS–TiO<sub>2</sub>,<sup>103–106</sup> SnO<sub>2</sub>–TiO<sub>2</sub>,<sup>107,108</sup> CdS–PbS,<sup>109</sup> CdS–ZnO,<sup>98,105,110</sup> CdS–AgI,<sup>106</sup> Cd<sub>3</sub>P<sub>2</sub>–TiO<sub>2</sub> and Cd<sub>3</sub>P<sub>2</sub>–ZnO,<sup>111</sup> ZnO–ZnS,<sup>112</sup> ZnO–ZnSe,<sup>113</sup> CdS–HgS,<sup>114,115</sup> TiO<sub>2</sub>–CdSe,<sup>95,96,116,117</sup> SnO<sub>2</sub>–CdS,<sup>118</sup> and SnO<sub>2</sub>–CdSe.<sup>119</sup> These early efforts have led to the development of many new semiconductor heterostructures and hybrid systems. In the following sections, we focus on the current methodologies for constructing and characterizing photosensitive electrodes, charge transfer processes, and recent developments in the area of nanostructured semiconductor liquid-junction cells.

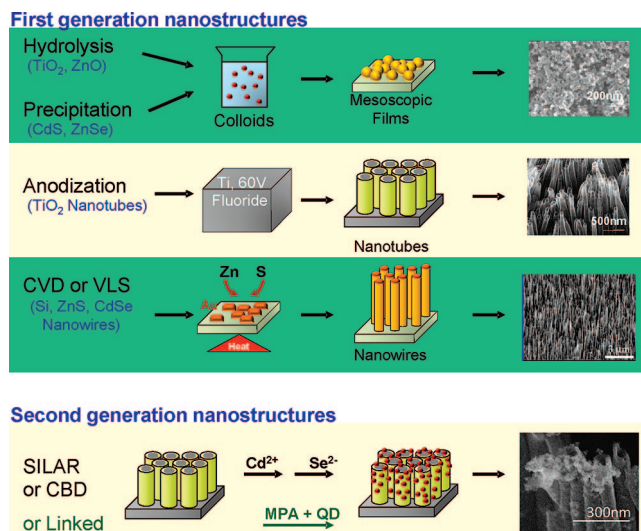
## 2. Preparation of Nanostructured Semiconductor Films

The methodology used in the preparation of nanostructured semiconductor films is an important factor in the performance of next-generation photoelectrochemical cells. Depending on the desired functionality of the film, the choice of preparation technique varies. There are many properties of nanostructured films which strongly impact device performance: surface area, morphology, grain boundary density, and robustness among others can all be optimized to fit specific applications. Generally, these properties are somewhat exclusive of each other. For example, high surface area films consisting of nanocrystalline particles yield high grain boundary densities, and this effect will increase charge carrier recombination through loss of carrier mobility.<sup>120–122</sup> Thus, a variety of thin film preparation techniques have been developed and employed for the wide range of devices. Some popular methods employed in the construction of first- and second-generation nanostructured semiconductor films on conducting surfaces are illustrated in Figure 8.

The preparation of nanostructured semiconductor films is classified below with five categories: (i) colloidal synthesis and its subsequent deposition as thin films, (ii) chemical precipitation on an electrode surface, (iii) electrochemical deposition, and (iv) chemical vapor deposition (CVD). Essentially, the colloidal method is a two-step process (synthesis and deposition) but enjoys the flexibility of fine-tuning the nanocrystal properties during synthesis. Chemical bath, electrochemical, and chemical vapor deposition methods on the other hand integrate the synthesis and deposition of the nanocrystals into simultaneous steps. The salient features of these methods are briefly discussed below.

### 2.1. Semiconductor Oxides and Chalcogenides

The preparation of colloidal suspensions of semiconductor nanocrystals allows for the control of parameters such as particle size, particle concentration, and method of deposition. With this ability to control the properties of the film on the



**Figure 8.** Schematic illustration of preparing semiconductor nanostructures by solution-based, electrochemical, or chemical vapor deposition methods. These first-generation nanostructures can be further coupled, or grown, with a different semiconductor particle to produce a second-generation structure. SEM images are adapted from refs 125, 715. Copyright 2008 American Chemical Society.

particulate level, the colloidal synthesis of many different types of nanoparticles has become popular. Metal chalcogenides are of particular interest, especially given the size-tunable<sup>123–125</sup> effects that quantum confinement has on material bandgap and the inclusion of such materials as tunable sensitizers (electron donors) in metal oxide (electron acceptors) nanostructured assemblies.<sup>126–132</sup> Electron injection from the sensitizer to the metal oxide is a key driving force for photocurrent generation, thus careful construction of each individual layer is required for high-performance devices. For this reason, colloidal deposition methods for metal oxide and sensitizer should be considered separately.

The synthetic procedure for metal oxides commonly involves preparation of ultrasmall semiconductor particles (particle diameter 2–10 nm) in polar solutions by controlled hydrolysis. Viscous gels with suspended nanoparticles, also known as sol–gels,<sup>133–144</sup> can also be achieved by using high viscosity liquid polymers such as polyethylene glycol. Colloidal suspensions of SnO<sub>2</sub> and TiO<sub>2</sub> are also commercially available. A thin film of nanostructured metal oxide material can then be created using a variety of techniques such as spin-coating,<sup>145</sup> spray pyrolysis,<sup>145–148</sup> doctor blade,<sup>149–151</sup> electrophoretic,<sup>152–169</sup> and template assisted<sup>170–178</sup> deposition methods on top of a conducting glass substrate (referred as optically transparent electrode, OTE) or other preferred surface. The film is then annealed at 200–450 °C in air for 1–2 h. Annealing is important to reduce grain boundaries and enhance crystallinity (and thus electrical conductivity) regardless of the deposition method. Sol–gel techniques have proven useful in the development of nanostructured semiconductor membranes with either 2-D<sup>179</sup> or 3-D configurations.<sup>84,180–184</sup> Organic template mediated synthesis has been employed to develop nanoporous tin sulfide materials.<sup>185</sup> Other methods of producing nanostructured electrode materials include preparation of semiconductor nanoclusters in polymer films<sup>62,186–196</sup> and Langmuir–Blodgett films.<sup>197–201</sup>

This simple approach of arranging preformed metal oxide colloids on a desired surface produces a thin semiconductor film with excellent stability in both acidic and alkaline media



(pH range 1–13). A variety of nanostructured semiconductor films (0.1–10  $\mu\text{m}$  thick) of the metal oxides  $\text{SnO}_2$ ,<sup>87</sup>  $\text{ZnO}$ ,<sup>98,99,202–209</sup>  $\text{TiO}_2$ ,<sup>95,97,100,201,210–218</sup>  $\text{WO}_3$ ,<sup>219,220</sup> and  $\text{Fe}_2\text{O}_3$ ,<sup>221</sup> have been prepared from colloidal suspensions. These thin metal oxide films exhibit interesting photochromic, electrochromic, photocatalytic, and photoelectrochemical properties. It may be necessary to optimize the concentration of precursor colloid or add external binding agents to achieve the desired integrity of the nanostructured film.

Synthetic procedures for chalcogenide semiconducting sensitizers vary,<sup>222–226</sup> but most methods typically involve dissolution of precursors in large organic surfactants such as trioctylphosphine oxide (TOPO) and dodecylamine (DDA) while reacting under heat in an inert atmosphere.<sup>227–229</sup> Core/shell<sup>230–236</sup> nanoparticles and quantum dots are easily obtained with subsequent precursor injections combined with the use of organic surfactants to control nucleation and crystal growth with high precision, allowing for size-controlled nanocrystal colloids. Additionally, optical and electronic properties of metal chalcogenide semiconductor nanocrystals can be tuned with metal ion doping (e.g., manganese-doped  $\text{ZnSe}$  or  $\text{ZnS}$ ).<sup>237–241</sup> Nanowires,<sup>242–244</sup> nanocubes,<sup>245</sup> nanospheres,<sup>224</sup> and other morphologies<sup>79,246</sup> can be realized by taking advantage of anisotropies and other preferred crystal growth characteristics and with additional coordinating compounds. Recently, more interest has been devoted to synthesizing these materials in water for potential biomedical imaging and other applications.<sup>235,247–253</sup>

Colloidal nanoparticles typically retain some of the surfactant molecules (i.e., TOPO, DDA) used to control nucleation and growth as ligands bound to their surface. The colloidal suspension is stabilized through the use of appropriate ligands, and selection of such ligands is dependent on the deposition method as well as the end application. Ligand type can affect the properties of the colloid in many ways, including photoluminescent intensity<sup>225,254–258</sup> and lifetimes,<sup>259–261</sup> as well as suspension stability<sup>262–265</sup> among others. Also, proper selection of ligands can greatly influence the ease with which ligand exchange reactions proceed during further processing of the colloid.<sup>255,258,259,266–272</sup>

One-dimensional architecture of oxide films (e.g.,  $\text{TiO}_2$  and  $\text{ZnO}$ ) has also been the subject of many investigations. Both bottom-up and top-down approaches have been extensively studied in this regard. For example,  $\text{TiO}_2$  nanotube array can be readily synthesized from the electrochemical anodization of Ti film in a fluoride medium<sup>273,274</sup> or a nanorod array<sup>275</sup> can be assembled on a conducting glass electrode via hydrothermal synthesis. The  $\text{TiO}_2$  nanotube arrays can be disassembled in solution with sonication and then reassembled on a conducting electrode surface.<sup>276</sup> Additionally, the  $\text{TiO}_2$  nanotube arrays can be transformed into ternary semiconductor oxides by treating them by hydrothermal synthesis.<sup>277,278</sup> For detailed discussion on the synthesis and characterization of 1-D arrays of semiconductor nanostructures, readers are advised to refer to recent review articles.<sup>243,244,279–281</sup>

## 2.2. Modification of Oxide with Quantum Dots

### 2.2.1. Coupling with Bifunctional Molecules

The surface modification of oxide films with sensitizing dyes and semiconductors can be achieved in a number of ways. Direct adsorption is the simplest technique for adsorbing sensitizers to metal oxides<sup>145,151,282–285</sup> and involves

immersion of a metal oxide film into a concentrated solution of colloidal sensitizer.

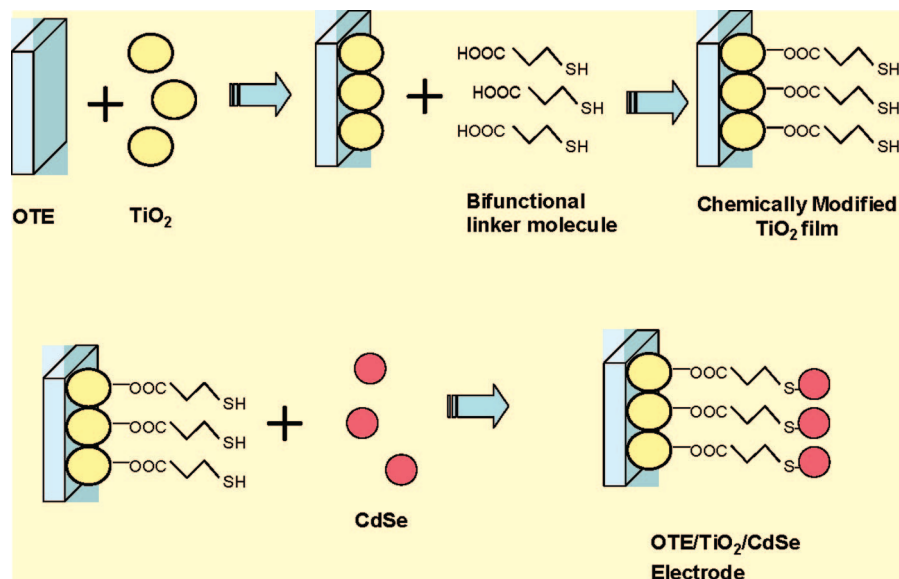
The use of bifunctional molecules to link quantum dots to metal oxide surfaces has proven to be an effective means for their sensitization as well.<sup>124,125,282,286–288</sup> Electron transfer and transport properties are highly dependent on the length of the bifunctional molecule.<sup>289–292</sup> This chemical binding approach has been used to successfully link  $\text{TiO}_2$  nanoparticles to  $\text{CdS}$  and  $\text{CdSe}$ <sup>285,290,293,294</sup> as well as to gold nanoparticles.<sup>295,296</sup> Modification of the  $\text{TiO}_2$  film with bifunctional molecules of the form  $\text{HOOC-R-SH}$  (e.g., mercaptopropionic acid, MPA, thiolacetic acid, TAA, and mercaptohexadecanoic acid, MDA) can be carried out by simply immersing a nanostructured  $\text{TiO}_2$  electrode in an acetonitrile-based linker molecule solution.<sup>290</sup>  $\text{TiO}_2$  has a strong affinity for the carboxylate group of the linker molecules, as demonstrated previously with a variety of sensitizing dyes.<sup>212,297</sup> Following application of the linker to the  $\text{TiO}_2$  surface, the electrode is then immersed in a suspension of  $\text{CdSe}$  quantum dots. Thiol and amine groups have been shown to bind strongly to  $\text{CdSe}$  nanoparticles.<sup>298–303</sup> Figure 9 illustrates the principle behind anchoring  $\text{CdSe}$  quantum dots onto a nanostructured  $\text{TiO}_2$  film.

### 2.2.2. Chemical Bath Deposition and SILAR

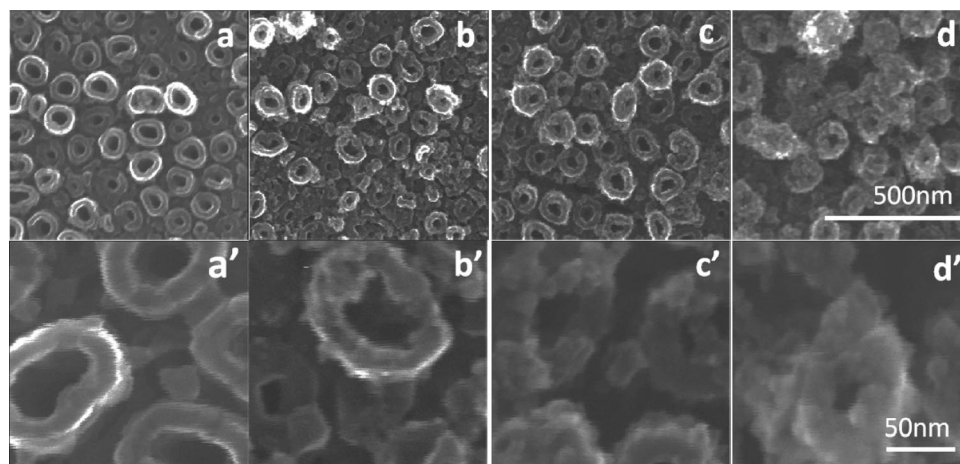
Traditionally, chemical bath deposition (CBD) methods involve precursor baths which contain ions of both precursor species. Precipitation is controlled by the rate of nucleation at the surface of the oxide, and CBD methods usually involve the decomposition of at least one compound responsible for providing the precursor in ionic form at a rate slower than the rate of nucleation to prevent solution precipitation. Thus, decomposition kinetics can dictate the overall rate of deposition. As chemical synthesis-deposition methods evolved, a successive ionic layer adsorption and reaction (SILAR) procedure began to gain popularity as a modified CBD method whereby successive submersions of the electrode into separate precursor solutions produces an ionic layer precipitation effect. These controlled chemical precipitation synthetic routes for depositing the semiconductor nanoparticles directly on the surface of a desired substrate can yield photoelectrochemically active films. For a detailed history and overview of CBD methods, the reader is referred to Hodes<sup>37,304</sup> and references therein.

Compared with other sensitization techniques, SILAR has the advantage of being a faster, more reproducible, and less expensive way to deposit sensitizing materials. A highly efficient  $\text{CdSe}$  SILAR method<sup>305</sup> involving the use of  $\text{Se}^{2-}$  as the selenium precursor greatly reduces the time required to produce a film when compared to the decomposition SILAR reaction involving sodium selenosulfate.<sup>306–309</sup> However, deposition under inert atmosphere is required in the former as a result of selenide instability in air.  $\text{CdS}$  sensitized electrodes have historically been prepared using SILAR, given the simple, air-stable precursor solutions of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$ . For example, by successively dipping a  $\text{ZnO}$  film in  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  solutions, one can cast a thin film of  $\text{CdS}$  nanocrystallites. The yellow coloration of the film indicates formation of  $\text{CdS}$  on the metal oxide surface. The scanning electron micrograph (Figure 10) shows the formation of  $\text{CdS}$  islands on  $\text{TiO}_2$  nanotubes, followed by a  $\text{CdS}$  film using repeated cycles of the SILAR technique.<sup>310</sup>

The excitonic peaks in the absorption spectrum typically associated with quantum dots are not preeminently observed



**Figure 9.** Linking CdSe QDs to TiO<sub>2</sub> surface with a bifunctional surface modifier. From ref 290. Copyright 2006 American Chemical Society.



**Figure 10.** SEM image of (a, a') TiO<sub>2</sub> nanotube electrode before modification and after CdS deposition cycles (b, b') 5 cycles, (c, c') 10 cycles, and (d, d') 20 cycles. The micrographs show two different magnifications as indicated by the representative scale bars. Reprinted with permission from ref 310. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

for semiconductor films prepared by SILAR or CBD methods. A larger distribution of particle size is responsible, although quantum effects can still be realized in the films through proper control of the processing conditions.<sup>305,311</sup>

Such a chemical precipitation technique is especially useful for designing coupled or multicomponent semiconductor films. Just as core–shell quantum dots present unique properties depending on the relative band positions of the core–shell compounds, layers of quantum-confined materials with key band alignments help further the development of high efficiency photovoltaic devices. Moreover, cosensitization and/or doping of the semiconductor thin film for specific roles in the light absorption, charge separation, and carrier lifetime extension is easily obtained with SILAR.

SILAR and CBD are processes capable of high-throughput and convenient operation. Additionally, the highest reported efficiencies of photoelectrochemical quantum dot solar cells are those produced by SILAR.<sup>305,312,313</sup> SILAR and CBD exhibit some loss of control over certain properties (particle size distribution, surface passivation, etc.) of the nanocrystallites that is provided by colloidal synthesis and subsequent deposition. However, the ability to rapidly generate a variety

of semiconductor thin films may lead to SILAR methods being used preferentially for large-scale manufacturing.

### 2.2.3. Other Deposition Methods

Electrochemical deposition is also a convenient technique for casting thin films of II–VI compound semiconductors, viz., CdS, CdSe, CdTe, and several mixed semiconductor films.<sup>90,91,96,314</sup> Electrochemically deposited films are strongly adherent to the substrate and are comprised of aggregated nanocrystallites. The nanocrystal size distribution (isolated or aggregated) can be controlled by deposition current and temperature. Recent work in electrochemical deposition techniques explores various substrates,<sup>315</sup> including graphene,<sup>316</sup> as well as various morphologies such as ZnO nanorods.<sup>317</sup> Electrophoretic<sup>318–324</sup> and ultrasonic-assisted<sup>325,326</sup> deposition of colloidal quantum dots are other approaches which can be used to deposit known amount of CdSe quantum dots on electrode surfaces. TiO<sub>2</sub> crystallites can also be deposited on conductive surfaces by anodic oxidative hydrolysis of TiCl<sub>3</sub>.<sup>211</sup> Likewise, anodic corrosion can be



used to electrochemically etch a Ti foil to produce one-dimensional (1-D) TiO<sub>2</sub> nanotubes.<sup>276,310</sup>

CVD is a technique involving the reaction of gas phase precursors at nucleation sites on a substrate, all located within a thermal reactor. All precursors may be in the gas phase, or one precursor may be present on the substrate to assist in nucleation. The development of this method is centered around semiconductor thin films.<sup>327–332</sup> Once more, metal oxides<sup>333–339</sup> and sensitizing semiconductors<sup>340–347</sup> can be prepared following CVD processing, and recent work involves structural and morphological varieties of semiconductors that may boost future photoelectrochemical solar cell performance.

As progress is made in new synthesis techniques such as grafting,<sup>271,348</sup> spray pyrolysis,<sup>349</sup> or molecular beam epitaxy,<sup>350,351</sup> thin film engineering for photoelectrochemical solar cells continues to illuminate further understanding of charge-separation and charge-transfer mechanisms as well as the possibility of high-efficiency devices in the future. The method of synthesis and deposition of nanostructured semiconductor thin films contributes significantly to the performance of the device in many ways that are still not fully understood. To better understand those contributions, as well as set benchmarks by which nanostructured liquid junction and other photovoltaic devices may be measured, a device's individual and assembled properties must be characterized. The following section discusses such characterization in detail, specifically highlighting measurements which are of greatest importance to liquid-junction solar cells.

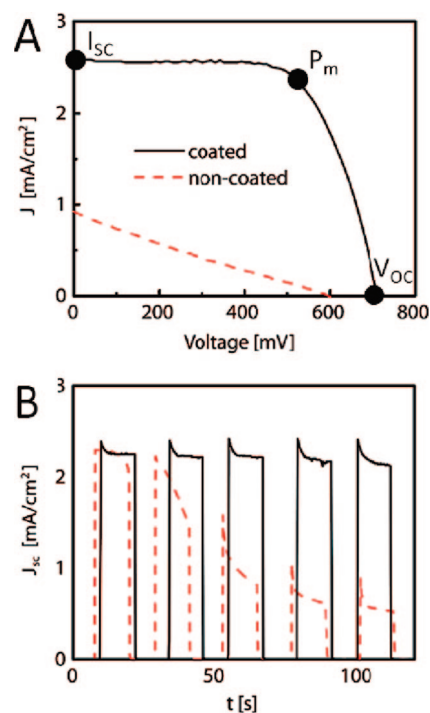
### 3. Electrochemical and Optical Characterization of Nanostructured Semiconductor Films

#### 3.1. Fundamental Characterization

Once assembled, nanostructured semiconducting photovoltaics can be characterized and modeled<sup>352</sup> in a variety of ways. Perhaps the most relevant characterization is the current vs voltage, or  $I$ – $V$ , plot.<sup>353</sup> A representative  $I$ – $V$  curve is shown in Figure 11A.<sup>354</sup> This curve was obtained by shining one-sun (100 mW/cm<sup>2</sup>) of AM1.5 light at a quantum dot sensitized solar cell and measuring values of current produced under various applied potentials for devices coated (solid) and not coated (dashed) with an amorphous layer of TiO<sub>2</sub>. This single characterization provides all the quantitative information necessary to integrate a solar cell, in series or parallel with others, into a circuit which can then fulfill specified power needs.<sup>355</sup> There exist several points along the  $I$ – $V$  curve which are of practical importance and from which relevant cell parameters can be determined.

The first point, open circuit voltage ( $V_{oc}$ ), represents the maximum voltage obtainable from the cell,<sup>356</sup> which occurs at zero current. Second, short circuit current ( $I_{sc}$ ) is the current obtained from the cell at zero voltage. Ultimately, a solar cell is constructed with the intent to generate power, which is the product of voltage and current. Therefore, each point where  $V_{oc} > 0$  and  $I_{sc} > 0$  on the  $I$ – $V$  curve represents extractable power from the cell. The point along the  $I$ – $V$  curve, which maximizes power is labeled  $P_m$ .<sup>357</sup> Approximate points for  $V_{oc}$ ,  $I_{sc}$ , and  $P_m$  are labeled in Figure 11A (solid line).

Fill factor,  $ff$ , is a computed value, ranging from 0 to 1, which reports on a cell's performance relative to its  $V_{oc}$  and  $I_{sc}$  (eq 7).



**Figure 11.** Examples of fundamental solar cell characterization. (A)  $I$ – $V$  plot and (B)  $I_{sc}$  versus time trajectories for quantum dot sensitized solar cells with (solid) and without (dashed) an amorphous layer of TiO<sub>2</sub> used to reduce carrier losses. From ref 354. Copyright 2009 American Chemical Society.

$$ff = \frac{P_m}{I_{sc} \times V_{oc}} \quad (7)$$

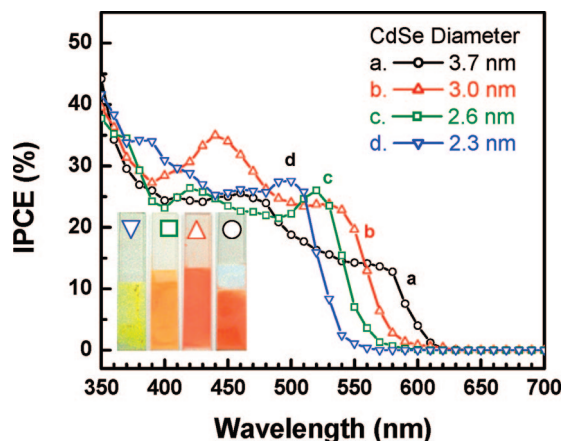
Fill factors of the  $I$ – $V$  curves shown in Figure 11A are 0.66 (solid) and 0.23 (dashed), respectively. These values are always below unity because of losses in the cell due to electron–hole recombination, internal resistances, and other sources.<sup>151,357–362</sup> Specific mechanisms for these and other losses are discussed in greater detail in Section 4.

A second important calculated factor is power conversion efficiency,  $\eta$ , which is a direct comparison of the electrical power produced by the cell relative to incident photonic power:

$$\eta = \frac{P_m}{I \times A} \times 100\% \quad (8)$$

where  $\eta$  ranges from 0 to 100%,  $A$  is the area of experimental irradiance,  $I$ , which, at standard “one-sun” conditions is 100 mW/cm<sup>2</sup> with an AM1.5 spectral profile. Power conversion efficiency serves as the bottom line method to quantify solar cell performance regardless of the materials used to construct the device.<sup>363–365</sup>

If a specific cell is a candidate for widespread implementation, its long-term stability must be characterized.<sup>366,367</sup> Although consumers largely expect solar cells to last for years, such a measurement in a laboratory environment is oftentimes not feasible. However, cells which show appreciable degradation over time often do so on scales of minutes or hours, a more reasonable time scale for researchers to undertake. The stability of the cells characterized by the  $I$ – $V$  curves in Figure 11A is highlighted in Figure 11B as  $I_{sc}$  vs time.<sup>354</sup> While  $I$ – $V$  curve parameters and their stability with time remain at the core of solar-cell charac-



**Figure 12.** Demonstration of the use of IPCE measurements to identify the species responsible for photocurrent generation. In this case, CdSe quantum dots show a size dependent photocurrent spectral response which correlates directly with their size dependent absorption. From ref 125. Copyright 2008 American Chemical Society.

terization, other measurements can be made which elucidate specific areas of device performance, making step-by-step optimization possible. A closer look at some of those measurements and how they specifically pertain to nanostructured liquid-junction solar cells is given in the remainder of the section.

### 3.2. Photocurrent Action Spectroscopy

While measuring  $I_{sc}$  under AM1.5 illumination indicates how a device will perform in a real-world setting, making  $I_{sc}$  measurements using monochromatic light is a useful way to pinpoint how sensitizing species are contributing to broadband photocurrent.<sup>368,369</sup> The incident-photon-to-carrier efficiency (IPCE), also called external quantum efficiency (EQE), is determined by measuring the photocurrent at various excitation wavelengths and using the expression:

$$\text{IPCE}(\lambda) = \frac{1240 \times I_{sc}(\lambda)}{\lambda \times I(\lambda)} \times 100\% \quad (9)$$

where  $I_{sc}(\lambda)$  is the wavelength dependent short-circuit photocurrent density in  $\text{A}/\text{cm}^2$ ,  $I(\lambda)$  is the wavelength dependent incident light intensity in  $\text{W}/\text{cm}^2$ , and  $\lambda$  is the excitation wavelength in nm. Figure 12 illustrates the ability of IPCE characterization to identify the main sensitizer responsible for photocurrent generation, which in this case is assigned to CdSe quantum dots.<sup>125</sup> IPCE measurements have been used to better understand the nature of the sensitizing material in both dye sensitized<sup>370–373</sup> and quantum dot sensitized<sup>117,125,282,286,374–376</sup> solar cells.

### 3.3. Optical Characterization

Although measuring photovoltaic properties of solar cells offers the most direct insight into device performance, optical techniques offer the opportunity to characterize and optimize isolated cell components. A common example of this is a comparison between UV–vis absorbance traces of sensitizers in solution and those which have been adsorbed onto a photovoltaic substrate, such as a nanoparticulate  $\text{TiO}_2$  film. Such characterization provides a way to determine the aggregation of a dye on the nanostructured surface,<sup>377–387</sup> track the successive addition of semiconductor through

chemical bath deposition<sup>388–390</sup> or SILAR,<sup>305,310,391</sup> or confirm the transfer of electronic properties between colloidal quantum dots present in solution and those attached to substrates.<sup>125,268,288,376,392,393</sup>

In addition to steady state absorption, it is also useful to compare the steady state emission properties of electrodes constructed with electron accepting supports to those constructed of insulating nanostructures. This comparison provides a qualitative measurement of the presence of electron transfer from the sensitizing species to the support species and has been used extensively with dye<sup>297,384,394–400</sup> and quantum dot<sup>324,401–403</sup> sensitized working electrodes.

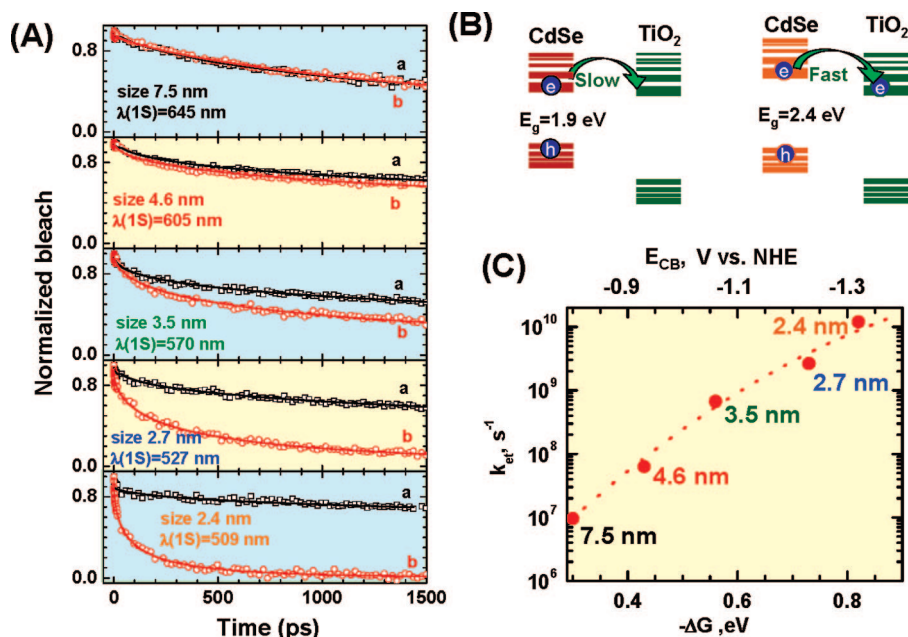
### 3.4. Characterization of Electron Transfer

A more quantitative method to probe electron transfer from the sensitizer to the nanostructured support involves making time-resolved spectroscopic measurements such as emission lifetime or transient absorption. In both strategies, the sensitizer is first placed in an excited state with a pump pulse of known temporal width. This is followed, with known delay time, by either detection of an emitted photon (emission lifetime) or analysis of the sample's excited state absorption spectrum (transient absorption). In both cases, fitting of measured signal versus delay time to a kinetic model<sup>404</sup> allows one to extract the average lifetime of the excited state of the sensitizer. If, however, the sensitizer is placed in a system whereby it readily donates an electron to a neighboring material, the observed lifetime will decrease due to the additional excited state depopulation pathway of electron transfer. By making the assumption that electron transfer is the only additional pathway introduced, an apparent electron transfer rate of the donor/acceptor pair can be calculated:

$$k_{et} \cong \frac{1}{\tau_{D/A}} - \frac{1}{\tau_D} \quad (10)$$

where  $\tau_{D/A}$ ,  $\tau_D$  and  $k_{D/A}$ ,  $k_D$  are the average excited state lifetimes and rate constants of the donor/acceptor, and isolated donor, respectively, the latter of which is a linear combination of constituent rate constants and may include radiative ( $k_r$ ), nonradiative ( $k_{nr}$ ), and electron transfer ( $k_{et}$ ) processes. An example of different kinetic traces in the absence and presence of an acceptor using ultrafast transient absorption spectroscopy is shown in Figure 13.

Alternatively, a second method commonly used to characterize electron transfer kinetics involves tracking directly the presence of injected electrons in the electron accepting species. This strategy, which is complementary of the electron donor spectroscopic tracking described in the previous paragraph, was first used by Lian and co-workers to investigate electron transfer from dye molecules to  $\text{TiO}_2$  substrates.<sup>405,406</sup> A similar experimental transient absorption spectroscopy setup is needed to use both electron transfer elucidation techniques, with the primary difference being the wavelength of the probe pulse needed to track either the electron donating or electron accepting species. When tracking the electron accepting species, commonly metal oxide nanoparticles, many studies have used near-infrared probe pulses which elucidate the presence of reduced metal oxide particles.<sup>407–411</sup> Microwave conductivity<sup>397,412–416</sup> and terahertz spectroscopy<sup>417–419</sup> techniques are also useful in identifying the charge separation, charge trapping, and charge injection processes in semiconductor nanostructures.



**Figure 13.** (A) Illustration of differences in transient absorption kinetic traces between CdSe quantum dots anchored to electron accepting (TiO<sub>2</sub>, red traces) and nonaccepting (SiO<sub>2</sub>, black traces) metal oxide nanoparticles. From top to bottom: difference in transient signal as a function of CdSe quantum dot size, ranging from 7.5 to 2.4 nm in diameter. (B) Energy level diagram and (C) dependence of electron transfer rate constant on the energy difference between the conduction bands of CdSe and TiO<sub>2</sub>. From ref 459. Copyright 2007 American Chemical Society.

Spectroscopic methods provide direct determination of electron transfer rate constants in systems comprised of dyes anchored to TiO<sub>2</sub> nanoparticles, the rates of which have been found to vary widely depending on both dye species and TiO<sub>2</sub> treatment.<sup>420–438</sup> Among the values reported for electron transfer rates in dye-sensitized TiO<sub>2</sub> systems, the fastest rate constant was reported by Huber et al. as  $2 \times 10^{14} \text{ s}^{-1}$  in an alizarin sensitized system.<sup>423</sup> Generally, rates of electron transfer in these systems fit well with simulated models.<sup>439–441</sup> Additionally, electron transfer kinetics have been elucidated for systems comprised of dyes anchored to semiconducting quantum dots.<sup>442–445</sup>

Because of their potential applications in solar cells,<sup>1,123,446,447</sup> nanostructured electronic arrays,<sup>448,449</sup> and optoelectronic displays,<sup>450–453</sup> systems utilizing electron transfer between quantum dot donors and metal oxide acceptors have quickly become a prominent topic. However, fewer fundamental studies regarding the mechanistic nature of electron transfer between these two inorganic species have been reported than their dye-sensitized counterparts.<sup>276,288,454–459</sup> Robel et al. demonstrated an increase in electron transfer rate from CdSe quantum dots to TiO<sub>2</sub> nanoparticles with increasing electronic driving force (or decreasing quantum dot size) reporting electron transfer rate constants ranging from  $10^7$  to  $10^{10} \text{ s}^{-1}$ .<sup>459</sup>

In addition to electron transfer reactions between sensitizers and nanostructured substrates, proper function of a liquid-junction solar cell also requires electron transfer from the electrolyte to the sensitizer as well as from the counter electrode to the electrolyte. Further, electron transfer reactions from the metal oxide transport layer to the electrolyte, as well as those from the sensitizer to the electrolyte, can result in loss of device performance.<sup>151,283,460–465</sup> Given the importance of electron transfer reactions involving solar cell electrolytes, the rates of such have been widely studied using a variety of techniques.<sup>40,466–470</sup>

A major advantage of nanostructured solar cells is their large surface to volume ratios, which allows for increased loading

of sensitizers and the potential of an increased number of current-producing electron transfer chemical reactions. However, the large surface area present in nanostructured devices also means an increased likelihood of electron transfer from the working electrode to the electrolyte (electron scavenging), a reaction which limits photocurrent generation. Therefore, much attention is paid to the process by which electrons pass through the electron transport layer (typically a nanostructured metal oxide film) en route to extraction as photocurrent within the photoanode. The following section addresses this transport process, how it is characterized, and recent advances in the suppression of electron scavenging reactions.

## 4. Electron Transport in Metal Oxide Films

### 4.1. Mechanism of Photoinduced Carrier Transport

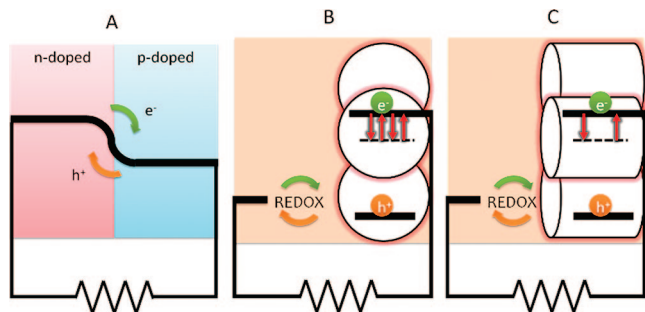
After transferring to the metal oxide layer, electrons must transport through the film and reach a conductive junction in order to produce photocurrent. Along this journey, electrons may also participate in other processes which ultimately result in a reduction of device performance, such as back transfer to the sensitizer, scavenging by the electrolyte or some other species around the electrolyte, or recombining with a hole. The faster an electron can be conducted through the transport layer, the higher the probability of collection at the photoanode. Therefore, much work has been performed on the transport mechanisms of charge carriers through metal oxide films.

Electron transport is explained classically by the Nernst–Planck equation:<sup>471–476</sup>

$$J_e = C_e v - D_e \nabla C_e - \frac{nF}{RT} D_e C_e \nabla \varphi \quad (11)$$

where the three terms on the right-hand-side of the equation represent convection, diffusion, and electrostatic transport,





**Figure 14.** Schemes of electron and hole pathways in a (A) p–n junction, (B) nanoparticulate metal oxide liquid-junction solar cell, and (C) one-dimensional metal oxide liquid-junction solar cell.

respectively.  $C_e$  is the concentration of electrons,  $v$  is the flow velocity of the system,  $D_e$  is the diffusion constant of an electron,  $n$  is the number of charges, which in the case of an electron is  $-1$ ,  $F$  is Faraday's constant, and  $\varphi$  is the electric potential. Although used primarily for charged species in an electric field, the concepts can still be applied to electrons within a photovoltaic cell, with some corrections. Because the metal oxide transport layers in solar cells are stationary, the convection term is dropped. In single-crystal systems, band bending drives the charge transport,<sup>477–479</sup> as illustrated in Figure 14A. As described in section 1, band bending is a result of the equilibration of Fermi levels across an interface caused by the buildup of a space charge layer.<sup>479,480</sup> In systems such as doped silicon, electrons are forced by the bent Fermi level at the interface to move in a certain direction, helping to separate them from their corresponding holes. Electric fields in these systems are so large, especially in thin film configurations, that the diffusion term of the Nernst–Planck equation becomes negligible.<sup>481–483</sup> Many of the commercial solar PV systems are based on this principle, including virtually all silicon cells, bulk heterojunctions, and CdTe thin films.

In nanoparticulate systems, like dye or quantum dot sensitized solar cells, band bending no longer plays a role in electron transport.<sup>88,484–486</sup> In bulk systems, space charge layers are typically on the order of micrometers, and with nanoparticles several orders of magnitude smaller than the space charge layer, there is little if any electrostatic driving force.<sup>88,484,485,487</sup> Even if space charge layers were on the order of the nanoparticle radii, it has been shown that the electrolyte in contact with the porous film would deplete any space charge layer by scavenging excess charges.<sup>88,485,487,488</sup> In such cases, diffusion becomes the key method of transport. In some models, a slight gradient in Fermi levels between metal oxide nanoparticles is used as a slight directionality force. However, several groups have shown that if the characteristic diffusion length ( $L_n$ ) is larger than the film thickness, the performance of the cell improves greatly,<sup>489–491</sup> which suggests that diffusion is the only significant mechanism for carrier movement.

The modern description of electron transport through nanoparticulate films, called the multiple trapping model, is well established.<sup>491–501</sup> This model states that photogenerated electrons will become trapped, subsequently detrap, and move to a neighboring trap state on their eventual transport path toward a conductive sink (Figure 14B). Nonlinear intensity dependencies show that traps can become filled with carriers by increasing incident power density, allowing other electrons to flow freely in the conduction band of the

nanoparticle film, a phenomenon which further validates the multiple trapping model.<sup>488,498,501–508</sup>

## 4.2. Characterization of Diffusion Length

Diffusion length is defined as  $L_n = (D_0\tau_0)^{1/2}$ , where  $D_0$  is the diffusion constant of a free electron in the film and  $\tau_0$  is the characteristic lifetime of a free electron within that film.<sup>490,509–511</sup> These intrinsic terms can be extracted using experimental techniques such as intensity modulation with intensity modulated photocurrent spectroscopy (IMPS), time-resolved photocurrent response, or open circuit decay.<sup>462,484,488,493,505,512,513</sup> However, the properties of free electrons cannot be directly measured due to traps in the system which cause seemingly slower mobilities than true free electrons.<sup>504,514,515</sup> Instead, effective constants are measured. In some cases, it has been shown that the effective diffusion coefficients can be several orders of magnitude less than a free electron in bulk TiO<sub>2</sub> crystals, a discrepancy primarily due to the trapping events.<sup>504</sup> To relate the free electron constants to effective constants,  $D_n$  and  $\tau_n$ , Bisquert and Vkhrenko<sup>514</sup> developed a model for dye sensitized solar cells which relates both constants to the changes in population of the occupied traps,  $n_L$ , and changes to the electron population in the conduction band,  $n_C$ .

$$\tau_n = \left( \frac{\partial n_L}{\partial n_C} \right) \tau_0 \quad (12)$$

$$D_n = \left( \frac{\partial n_C}{\partial n_L} \right) D_0 \quad (13)$$

When combined to calculate the diffusion length, the two population rate terms cancel and the same diffusion length is determined. From this analysis, it was also shown that there is no theoretical Fermi level dependence on the diffusion length, which is also observed experimentally using steady state experiments, like IPCE, although both constants exhibits this dependence and have been shown to almost entirely cancel each other's effects.<sup>488,504,512,514</sup>

Because there is no inherent directionality in electron transport, and as stated above, the small gradient in Fermi levels is negligible, diffusion through traditional nanoparticulate films is an inefficient mechanism for driving electrons to a conductive contact for photocurrent extraction. This mechanism creates a random walk process in which only a fraction of the excited charges are collected, especially with quantum dot sensitizers.<sup>489,510,516–519</sup> In terms of device performance, dye sensitized solar cells reached a plateau of  $\sim 11\%$  by the mid-1990s, with a portion of the losses coming from back-transfer to the electrolyte from the TiO<sub>2</sub> layer, essentially due to poor transport.<sup>5,520,521</sup> Groups then started to work with advanced nanoarchitectures with the aim of increasing electron diffusion lengths and improving cell efficiencies.<sup>273,522–529</sup>

## 4.3. One-Dimensional (1-D) Transport Architectures

By replacing nanoparticulate films with 1-D architectures, charges are allowed to move only in one dimension instead of randomly in three. Several groups have shown that the directed movement markedly improves cell currents and reduces losses by increasing the residence lifetime of charge

carriers, typically measured with intensity modulated photovoltage spectroscopy (IMVS) or open circuit photovoltage decay (OCVD).<sup>490,530</sup>

One key to the 1-D architecture's improvement is the increased diffusion length.<sup>531</sup> Caused by a combination of larger crystal sizes, better contact between particles, and fewer trap sites, residence lifetimes of electrons were found by Frank et al. to be more than an order of magnitude longer than a similar nanoparticle film.<sup>532</sup> Figure 14C demonstrates the lower trap population in 1-D films. Our group has also achieved a 20% improvement in photocurrent by using TiO<sub>2</sub> nanotubular in place of nanoparticulate film.<sup>310</sup> Other laboratories have shown similar improvements in cell power conversion efficiencies.<sup>532,533</sup> IPCE measurements have especially shown how photocurrents generated in 1-D architectures improve cell performance.<sup>310,490,533</sup> Although 1-D architectures also change how the film absorbs light,<sup>243,244,529,532,534</sup> the primary mechanism for improvement is the increased residence lifetime.

Recently, Peter and co-workers showed that with a 20  $\mu\text{m}$  TiO<sub>2</sub> nanotube film nonideality factors must be taken into account to calculate the electron residence lifetime constant.<sup>490</sup> They found that, at short circuit conditions, the Fermi level is displaced from the operating Fermi level for an applied potential, and a shift of 0.15 eV was needed to accurately determine the diffusion length of 100  $\mu\text{m}$ . This length is five times the thickness of the film and demonstrates how 1-D architectures allow for higher collection efficiency over corresponding nanoparticle films, which typically have diffusion lengths three times the cell thickness.

One-dimensional architectures like TiO<sub>2</sub> nanotubes, nanorods, or VLS nanowires are typically synthesized on a substrate in such a manner as to maintain uniform, parallel orientation of the 1-D axis normal to the substrate. Uniform orientation provides directionality in a system and allows for the possibility of each 1-D pillar to have contact with the substrate, minimizing grain boundary crossings for charge carriers.<sup>529,535,536</sup> Although both arguments for uniformity have the benefit of improving cell performance, several studies have shown that randomly oriented 1-D networks still provide exceptional enhancement with uniform networks only demonstrating a slight improvement over random networks. The primary mechanism for enhancement is the improved diffusion length (stemming from the lifetime), which allows charge carriers to move through the metal oxide films more efficiently.<sup>276,533,537,538</sup>

#### 4.4. Electrolyte Interactions

The key feature that distinguishes the liquid-junction solar cell from all others is the liquid electrolyte used to shuttle charge from the counter electrode to the working electrode. How the electrolyte interacts with both electrodes, in both desired and undesired manners, is of great importance to the performance of these cells.<sup>11,286,539–542</sup>

Dissolved in the electrolyte are redox couples which are used to react at the surfaces of the counter and working electrodes. The difference in potential between the redox potential in the electrolyte and the TiO<sub>2</sub> conduction band is what determines the maximum open circuit voltage. In a TiO<sub>2</sub> based system, the redox couple is oxidized at the working electrode surface and reduced at the counter electrode. Reacted species must diffuse across the liquid layer and react with the second electrode to complete the circuit of the cell. This process can be slow if the electrodes are greatly

separated. The sandwich cell design (which has been gaining popularity in recent years) limits the time required for electrolyte species to diffuse between electrodes. However, a stronger technique is to dissolve both species of a redox couple into the electrolyte such that there is always an excess of reactants to reduce or oxidize at the surface of the counter or working electrode, causing reaction rates to be the limiting step rather than diffusion.

Not all redox couples are compatible with all sensitizers. Electrochemically, the redox potential of the couple must be more negative than the HOMO of a dye sensitizer, or the valence band of the quantum dot sensitizer, so an electron can be donated to the excited species. Aside from this restriction the primary motivation in choosing a redox couple is its chemistry with the working and counter electrodes. Despite many searches, ruthenium-based dyes have shown no better electron transfer than with an iodide/tri-iodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) couple.<sup>543–545</sup> The reaction rate is even faster than with other couples which have larger electrochemical driving forces. In the quantum dot sensitized cell, the optimal redox couple has been found to be sulfide/polysulfide (S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup>).<sup>546,547</sup>

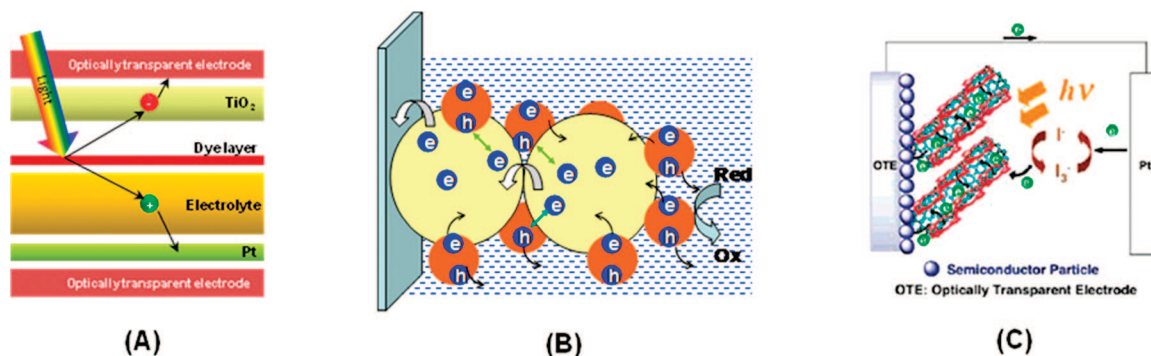
Chemistry also plays an important role in the degradation of films. For example, if an iodide couple is used with CdSe quantum dots, the film starts to degrade quickly upon illumination.<sup>354</sup> A redox couple must be stable with the working and counter electrodes over a long lifetime to be adequate. The S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup> couple is very stable with metal-chalcogenide semiconductors because the sulfide can react on the surface of the quantum dot, making a thin barrier layer. However, sulfides react very strongly with platinum which can cause poisoning of the surface, reducing activity.<sup>548,549</sup>

Several promising new electrolytes have been developed for liquid-junction solar cells. For quantum dots, cobalt-based electrolytes have proved to be a step forward to improve performance.<sup>550,551</sup> Developed for reducing overpotentials in fuel cells, the cobalt electrolyte also has been shown to improve the fill factor of the cell. Dye sensitized solar cells have been developed over the years to have very good fill factors, but because of the limitation in redox couple, the open circuit potentials had been limited to  $\sim 0.6$  V, with some notable exceptions.<sup>552</sup> The limitation with redox couples is the main reason for the stagnant improvements of dye cells over the past decade. Recently, there is some new hope with cobalt complexes and nitroxide radicals boosting efficiencies beyond the iodide's capability.<sup>543</sup>

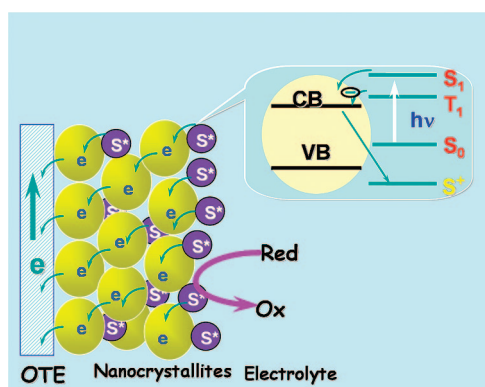
Electron transfer from the counter electrode to the redox couple is an extremely important step that seems to not receive its due attention. It has been shown by the Zaban group that the typical iodide couple is much more active at the platinum than the sulfide couple.<sup>354</sup> By covering the quantum dots with a thin layer of TiO<sub>2</sub>, degradation was eliminated and a drastic increase in performance was observed. To develop higher performing quantum dot solar cells, the interaction of the redox couple with the counter electrode needs to be understood in much greater detail.

#### 5. Recent Trends in Liquid-Junction Solar Cells

New strategies are being developed which aim to utilize the recent advances in nanoscience for the benefit of nanostructured photovoltaics.<sup>553</sup> In this section, we briefly review recent developments in liquid-junction solar cells which utilize each of three different nanoarchitectures, as illustrated in Figure 15: dye sensitization of semiconductor



**Figure 15.** Strategies to utilize nanostructures in photoelectrochemical solar cells: (A) dye-sensitized solar cell, (B) quantum dot sensitized solar cell, and (C) carbon nanostructure based solar cells. Adapted from refs 5, 290, 706. Copyright 2009, 2006, and 2006, respectively, American Chemical Society.



**Figure 16.** Principle of the dye sensitized solar cell. The scheme shows charge injection from excited sensitizer ( $S^*$ ) into semiconductor nanoparticles.

nanostructures (15A), quantum dot solar cells (15B), and carbon nanostructure based solar cells (15C).

## 5.1. Dye Sensitized Solar Cells

The same photosensitization reactions which had been the principle behind silver halide photography were adopted to sensitize large bandgap semiconductors in photoelectrochemical cells.<sup>197,554–564</sup> The initial photosensitization studies employed adsorption or covalent linkage of dyes on single-crystal electrodes. Because of the low surface area of the electrode, the observed photocurrent under visible light irradiation was small. However, the design of nanostructured oxide semiconductors (mainly  $\text{TiO}_2$ ) revolutionized the operation of dye sensitized solar cell (DSSC). The high porosity of mesoscopic semiconductor films employed in these cells enables the incorporation of sensitizing dyes in large concentrations.

Nanostructured  $\text{TiO}_2$  films modified with a ruthenium complex have been shown to exhibit power conversion efficiencies in the range of 11%, which is comparable to that of amorphous silicon-based photovoltaic cells.<sup>212,356,565–567</sup> Bignozzi et al. have presented a supramolecular approach for designing photosensitizers.<sup>568</sup> By optimizing the design of light harvesting dye molecules (sensitizers), it should be possible to suppress interfacial charge recombination and improve the cross section for light absorption.

The principle behind dye sensitized cell operation is illustrated in Figure 16. When the electrode is illuminated with visible light, sensitizer molecules absorb light and inject electrons into neighboring semiconductor particles. This design has been used with  $\text{SnO}_2$ ,<sup>87</sup>  $\text{ZnO}$ ,<sup>569</sup> and  $\text{TiO}_2$ <sup>380,395,397,570–572</sup>

particles as the basis for electron transport layers. Electrons are then collected at the conducting glass surface to generate anodic photocurrent. The redox couple (e.g.,  $\text{I}^-/\text{I}_3^-$ ) present in the electrolyte quickly regenerates the sensitizer.<sup>573</sup> The quenching of the excited sensitizer by the redox couple can be readily suppressed by the use of  $\text{C}_{60}$  clusters, which act as a relay to shuttle electrons across the interface.<sup>574</sup> The charge injection between excited sensitizer and the semiconductor film can be readily modulated by applying external bias.<sup>575–577</sup> Ru(II) bisbipyridyl complex modified  $\text{TiO}_2$  nanostructured films exhibit IPCE values of nearly 90% under optimized light harvesting conditions.<sup>212</sup> By choosing an appropriate sensitizer, it is possible to tune the photoresponse of these nanostructured semiconductor films. For example, sensitizing dyes such as chlorophyll analogues,<sup>110,399,578,579</sup> squaraines,<sup>580,581</sup> rhodamines,<sup>582</sup> and oxazines<sup>583</sup> can extend the photoresponse of metal oxide films to the near-infrared region. Recently, excited state interaction between Ru(II) polypyridyl complex and CdSe has been investigated for the hole transfer process.<sup>584</sup>

The charge injection from excited sensitizers into semiconductor nanoparticles is an ultrafast process occurring on the time scale of femtoseconds to nanoseconds.<sup>387,397,406,408,424,571,585–593</sup> Electron transfer kinetics in dye-sensitized  $\text{SnO}_2$  and  $\text{TiO}_2$  systems have been evaluated in terms of Marcus theory.<sup>594,595</sup> Hupp and co-workers<sup>596</sup> have successfully applied this theory to probe the recombination of conduction band electrons from  $\text{SnO}_2$  to an oxidized sensitizer. Other researchers have also employed this model to investigate charge recombination kinetics.<sup>421,597</sup>

Both experimental and theoretical evaluations of dye sensitized cells have been carried out, and the efficiency limiting factors have been identified.<sup>598,599</sup> Recently, interest has been shown in developing ordered arrays of  $\text{TiO}_2$  nanotubes either by electrochemical etching of Ti foil in a fluoride medium or depositing  $\text{TiO}_2$  rods on a conducting surface.<sup>526,600–605</sup> Using this strategy, nanotube<sup>606</sup> and nanowire<sup>528</sup> based dye sensitized solar cells have been reported. Cells in which the traditional nanoparticle film is replaced by a dense array of oriented, crystalline nanowires ensures the rapid collection of carriers generated throughout the device.<sup>528,607</sup>

Over the past decade, a number of research groups have worked toward fine-tuning the performance of electrode structure, including the pretreatment of  $\text{TiO}_2$  surface, sensitizer modification, regenerative redox couples, and various electrolytes. Despite this large body of work, the maximum attainable efficiency has remained in the range of 11–12%. A detailed discussion on various aspects of dye-sensitized



solar cell is beyond the scope of the present review. Recent review articles provide more details on such dye-sensitized solar cells (DSSC) and their application in constructing solar panels.<sup>5,491,497,608–612</sup> Industrial interest in testing these systems for commercial solar panels is a bright spot in the realization of the potential of nanostructured photoelectrochemical devices.

## 5.2. Quantum Dot Sensitized Solar Cells

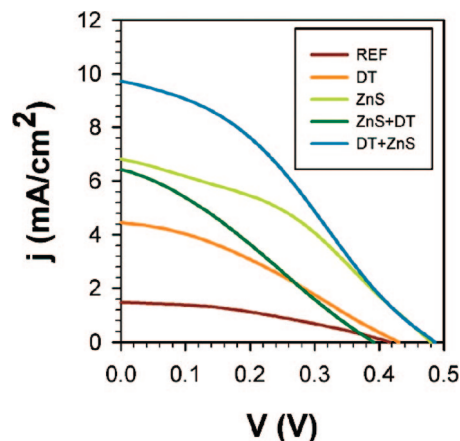
Inorganic materials such as CdS and CdSe have been shown to work well as sensitizers for liquid-junction solar cells.<sup>123,613,614</sup> They have electronic and optical properties which allow charge separation and electron transfer to metal oxide semiconductors while absorbing the most intense regions of the solar spectrum. When the bulk of metal oxide solar research was made on single-crystal TiO<sub>2</sub>, CdS was the popular material employed for photosensitization.<sup>103,615</sup> In the advent of nanocrystalline TiO<sub>2</sub> films, dyes became the popular choice for sensitization and inorganic materials received markedly less attention.

In recent years, however, semiconducting nanocrystals as sensitizers have made a comeback thanks in large part to the development of facile quantum dot fabrications.<sup>444,584,616–629</sup> Semiconductor sensitizers have many advantages over their dye counterparts.<sup>117,123,151,465,613,630–634</sup> Unlike most dyes which have a narrow absorption band, semiconductors absorb photons with energies equal to or greater than the bandgap. This allows one sensitizer to single-handedly capture the entire solar spectrum.<sup>635</sup> With dyes, there are several molecules which can absorb most of the solar spectrum,<sup>212,636</sup> but for the most part semiconductors can harvest a wider range.

Other benefits quantum dots have over dyes are the amount of light absorbed and the tunability of the bandgap. Dyes are limited to one monolayer of coverage.<sup>637</sup> Usually this is overcome with higher surface area particles.<sup>638</sup> Unlike dyes, quantum dots can take advantage of the multiple trapping model and move charge through a film made of sensitizer, allowing for thinner metal oxide films.<sup>639–641</sup> As quantum dots become smaller, their bandgaps widen due to quantum confinement. As explained earlier, this has significant implications for electron transfer rates. Conceptual rainbow solar cells have been proposed which could potentially take advantage of this phenomenon. Through a sequential size controlled arrangement of quantum dots such that incident light interacts with larger bandgap quantum dots first, higher electron transfer rates can theoretically be obtained while still harvesting the entire solar spectrum.<sup>125</sup>

A special feature of quantum dot solar cells is the possibility of tapping hot electron transfer<sup>642–646</sup> and carrier multiplication processes.<sup>444,619,647,648</sup> When semiconductor nanocrystals absorb light with energy greater than the bandgap, so-called “hot” carriers are instantaneously generated. If an electron transfers to the metal oxide layer before “cooling,” it can theoretically generate higher open circuit potentials. The cooling time, however, is on time scales orders of magnitude faster than current electron transfer rates. To make hot electron transfer a reality in photovoltaics, a method must be developed to either slow the thermalization of quantum dots or increase electron transfer rates.

Carrier multiplication is a second unique feature of semiconductor sensitizers.<sup>648–653</sup> It is essentially an inverse Auger process by which an electron excited by a photon greater than twice the bandgap energy thermalizes and excites



**Figure 17.** Current–voltage curves of various quantum dot solar cells with different coatings on the TiO<sub>2</sub>–CdSe structure. Coatings include combinations of a dipole treatment (DT) and zinc sulfide (ZnS) coatings on top of a reference (REF) device. From ref 632. Copyright 2010 American Chemical Society.

another electron in the process. There has been great debate over carrier multiplication, with several groups reporting evidence of its existence in many materials while others claim quantum dots such as CdSe and CdTe do not exhibit these properties.<sup>654</sup> Despite the debate, time scales are also the primary hindrance to the use of carrier multiplication in photovoltaic devices. A quantum dot with two or more excited carriers has an expedited recombination lifetime; therefore, an appropriate strategy needs to be developed to extract these carriers before recombination renders them unusable in photovoltaic applications.

Figure 17 shows typical *I*–*V* curves for CdSe sensitized cells.<sup>632</sup> In a two-electrode system, use of the S<sup>2−</sup>/S<sub>n</sub><sup>2−</sup> redox couple results in open circuit potentials similar to the I<sup>−</sup>/I<sub>3</sub><sup>−</sup> system (~0.6 V) due to the high pH of the electrolyte shifting the TiO<sub>2</sub> bands to more negative positions.<sup>660</sup> Compared to dye sensitized cells, semiconducting sensitizers have smaller fill factors and lower currents which have been attributed to the presence of trapping events. Power conversion efficiencies of quantum dot sensitized cells have also traditionally been much smaller than their dye counterparts. The maximum reported quantum dot solar cells efficiencies approach 4%,<sup>657</sup> while dye cells have maximum efficiencies above 11%. Despite all the advantages described above, the low efficiencies show that much work still needs to be done to boost performance. Table 1 compares typical values from characterized cells of different construction. The possible sources of losses in the quantum dot system were recently reported by Hodes.<sup>547</sup> Potential major losses came from the back transfer of electrons to the electrolyte and potentially backtransfer of electrons from the TiO<sub>2</sub> layer into trap states of quantum dots. This last explanation stems from looking at the major differences between dyes and semiconductors. With traps playing such key roles in the transport of carriers, they may also be the main limiting factor in the observed power conversion efficiencies.

New strategies are being implemented to improve the performance of quantum dot solar cells (Figure 18). To overcome the attack of iodine and further sensitize the QD response into the visible, Zaban and co-workers<sup>641</sup> have designed a strategy to employ a TiO<sub>2</sub> barrier layer over CdS and further sensitize it with a dye. These efforts are in line with earlier efforts to sensitize TiO<sub>2</sub> coated CdS nanostructured films with chlorophyll *a*<sup>110</sup> and Ru(II)bispyridyl deriva-

**Table 1. Compilation of Device Parameters Associated with Some of the Best Performing Quantum Dot Solar Cells of Several Construction Types: Colloidal Quantum Dot (CQD), Depleted Heterojunction (DH), Shottky Barrier, and Quantum Dot Sensitized Solar Cells (QD-SSC) (Adapted from ref 655; Copyright 2010, American Chemical Society)**

ref	quantum dot ( $E_g$ )	type	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	$\eta$ (%)
655	PbS (1.3 eV)	CQD-DH	0.51	16.2	58	5.1
655	PbS (1.1 eV)	CQD-DH	0.45	13.2	35	2.1
655	PbS (0.9 eV)	CQD-DH	0.38	11.3	21	0.9
656	PbS <sub>0.7</sub> Se <sub>0.3</sub>	CQD-Shottkey	0.45	15.0	50	3.3
657	PbS (1.3 eV)	CQD-Shottkey	0.51	14.0	51	3.6
658	PbS (1.6 eV)	QD-SSC	0.56	4.6	57	1.5
151	CdSe (2.0 eV)	QD-SSC	0.51	7.1	48	1.8
659	Sb <sub>2</sub> S <sub>3</sub>	QD-CQD	0.61	10.6	48	3.1

tive.<sup>118</sup> Zhang and co-workers,<sup>661</sup> on the other hand, employed two-sided conducting glass electrode to anchor CdS and CdSe on the opposite sides and thus harvest the light energy more efficiently. Metal nanoparticles with plasmon resonance are being considered to increase light absorption or improve charge separation.<sup>662–664</sup> Similarly, polymer–semiconductor nanocrystal-based assemblies offer new opportunities to tune the charge separation organic hybrid systems.<sup>665–672</sup> One-dimensional architectures of ZnO and TiO<sub>2</sub> have also been used to increase the lifetime of injected electrons.<sup>125,275,276,310,673,674</sup> Composite films of CdSe nanowire and quantum dots have shown synergistic effects in enhancing the photocurrent response in the red region of the visible spectrum.<sup>393</sup> These and other strategies<sup>675</sup> are currently being pursued by several groups to further improve the performance of quantum dot sensitized liquid-junction solar cells.

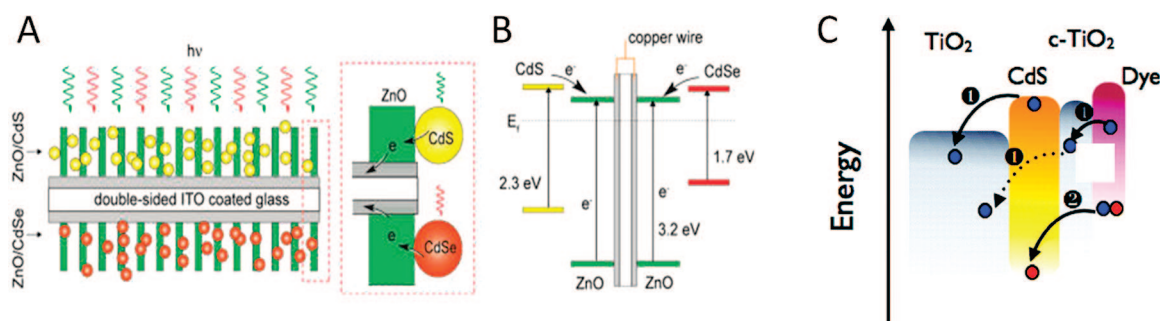
### 5.3. Carbon Nanostructure Based Photochemical Solar Cells

Fullerenes, graphene, and carbon nanotubes have played a major role in designing energy conversion devices.<sup>676–683</sup> These carbon nanostructures exhibit photochemical activity and participation in electron transfer process. Their ability to store and shuttle electrons has also been well established.<sup>684–686</sup> Fullerenes, and their derivatives, also exhibit rich photochemistry and act as electron acceptors in organic hybrid solar cells.<sup>574</sup> On the other hand, semiconducting carbon nanotubes undergo charge separation when subjected to bandgap excitation.<sup>687</sup> The exciton annihilation and charge separation processes have been characterized by transient absorption and emission measurements.<sup>688–691</sup> Fullerene cluster films are electrochemically active and exhibit electrocatalytic<sup>692,693</sup> and photoelectrochemical effects.<sup>687,694–696</sup> Single-walled carbon nanotube (SWCNT) films cast on optically transparent electrodes respond to visible light excitation.<sup>687</sup> These electrodes when used in a photoelectro-

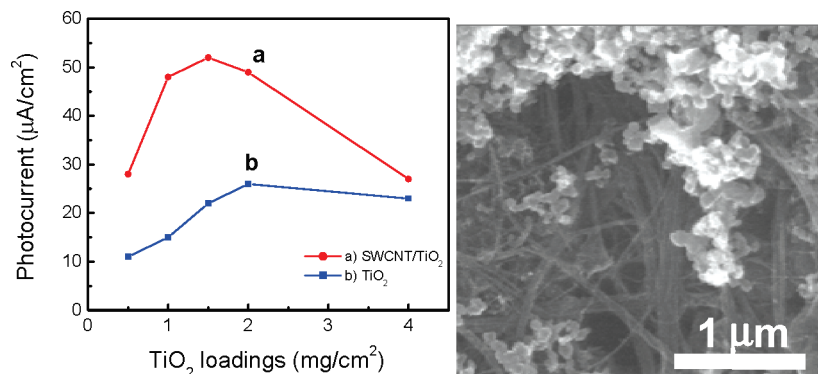
chemical cell containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> as a redox couple exhibit photocurrent generation. Another new class of carbon nanostructures is stacked-cup carbon nanotubes (SCCNT), which also exhibit excellent photoelectrochemical activity.<sup>696–698</sup> Photon harvesting properties of carbon nanotubes have been discussed in detail in recent review articles.<sup>699,700</sup>

Carbon nanostructures also serve the role of support to anchor electrocatalyst particles in fuel cells and storage batteries.<sup>693,701,702</sup> The same concept can be further extended to collect charges from semiconductor nanostructures. SWCNT architectures, when employed as conducting scaffolds in CdS, TiO<sub>2</sub>, or ZnO semiconductor-based photoelectrochemical cells can boost photoconversion efficiencies by a factor of 2.<sup>403,686,703</sup> It has been shown that by dispersing TiO<sub>2</sub> nanoparticles on single-wall carbon nanotube films, there was an improvement of photoinduced charge separation and transport of carriers to the collecting electrode surface (Figure 19). The interplay between the TiO<sub>2</sub> and SWCNT toward attaining charge equilibration is an important factor for improving photoelectrochemical performance of nanostructured semiconductor-based solar cells. Similar enhancement in photocurrent with 2-D carbon nanostructures viz., graphene architectures, has been demonstrated.<sup>704</sup> Figure 20 shows the photoelectrochemical behavior of graphene–TiO<sub>2</sub> composite films. Improved photoelectrochemical behavior of nanostructured TiO<sub>2</sub> films is seen as they collect electrons and transport them to the collecting electrode surface.

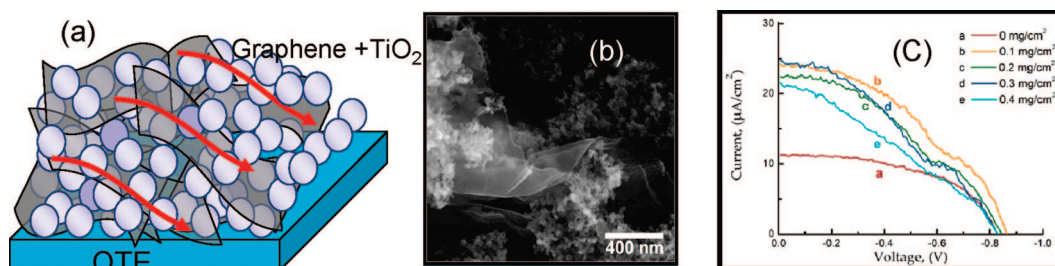
The ability of carbon nanostructures as conducting scaffolds to collect and transport charge carriers has been shown to improve the efficiency of dye sensitized<sup>400,705</sup> and quantum dot sensitized<sup>324,674</sup> solar cells. Although one observes a higher photocurrent, the lower lying conduction band of SWCNT causes the open circuit potential to decrease. The Fermi level equilibration between TiO<sub>2</sub> and SWCNT has been studied separately.<sup>684,685</sup> In another study, photoinduced charge separation between a porphyrin derivative and C<sub>60</sub>



**Figure 18.** Illustration of (A) the architecture and (B) the energy diagram of a double-sided CdS-ZnO-ZnO-CdSe NW arrayed photoanode. (C) The interfacial charge transfer processes in a hybrid nanostructure. Upon bandgap irradiation, electrons are injected directly (solid lines) from the QD into the TiO<sub>2</sub> films and from the dye to the amorphous TiO<sub>2</sub>, which is in contact with the TiO<sub>2</sub> film (dotted line). From refs 661, 641. Copyright 2010 American Chemical Society.



**Figure 19.** (left) Photocurrent response as a function of the amount of  $\text{TiO}_2$  deposited on carbon fiber electrode with and without SWCNT. (right) SEM image of SWCNT- $\text{TiO}_2$  composite. From ref 686. Copyright 2007 American Chemical Society.



**Figure 20.** Graphene- $\text{TiO}_2$  composite films. (a) Schematic diagram showing the electron transport, (b) SEM image, and (c)  $I$ - $V$  characteristics at different graphene oxide concentrations. From ref 704. Copyright 2010 American Chemical Society.

was manipulated by anchoring them both on carbon nanotubes.<sup>706,707</sup> Two-dimensional carbon nanostructure assisted charge separation in semiconductor assemblies has also been shown to improve the performance of photoelectrochemical cells<sup>708</sup> and efficiencies of photocatalytic processes.<sup>704,709–715</sup> More careful functionalization of carbon nanostructures and anchoring of light harvesting antenna molecules is required to utilize them in solar cells effectively.

## 6. Future Outlook: A Promise for a Better Tomorrow

Liquid-junction photoelectrochemical solar cells make use of the principles of photochemistry, electrochemistry, and semiconductor physical chemistry. The field of photoelectrochemistry has nurtured the development and design of next-generation solar cells. This field, which originated with single-crystal semiconductor electrochemistry in the 1960s, has now expanded to nanostructured semiconductor electrodes. Basic research at the semiconductor/electrolyte interface continues to draw the attention of scientists around the world. The recent technological advances in the commercialization of dye sensitized solar cells have provided a further boost to the development of photoelectrochemical solar cells.

Whereas attaining large surface area with nanostructured semiconductor films in photoelectrochemical cells is advantageous to increase the interaction with the redox electrolyte, they pose the challenge of collecting and transporting photogenerated charge carriers for photocurrent generation. Minimizing the loss of charge carriers at grain boundaries is an important issue to tackle. One-dimensional architectures (nanotubes and nanorods) hold the promise of improving charge collection and transport with greater efficiency. While quantum dot sensitized solar cells lag behind dye sensitized solar cells in terms of overall power conversion efficiency, many salient features offer opportunities for improvement.

Capturing hot electrons and/or multiple electrons with high energy excitation will be an arduous task for their utilization in solar cells. Efforts to tailor the nanoparticle interface with a suitable electron acceptor need to be pursued.

The realization of renewable energy as an important part of the energy mix has resulted in increased research activities worldwide. Efforts are being geared toward developing economically viable solar cells and solar fuel generation schemes. *Fossil fuel barons* often undermine the strengths of solar cell technology by arguing that solar energy conversion is interruptive or not reliable 24 hours of the day. However, such critiques fail to recognize that the fossil fuels we use with convenience today are the result of millions of years of stored solar energy in the form of denatured biological matter. A hybrid technology which integrates solar cells and energy storage devices can pave the way for meeting humanity's ever-growing demand for clean, renewable energy. The next decade will continue to see an increased growth in developing multicomponent nanostructured architectures with tailored functionalities.

## 7. Acknowledgments

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## 8. Supporting Information Available

A complementary list of all cited works which includes reference titles. This material is available free of charge via the Internet at <http://pubs.acs.org>.



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