Doping for Speed: Colloidal Nanoparticles for Thin-Film Optoelectronics

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ABSTRACT Solution-processable semiconductor materials ranging from conjugated polymers and small organic molecules to colloidal inorganic nanoparticles are being studied for applications in both low-cost solar cells and photodetectors. High-quality thin films of many inorganic semiconductors can be prepared by techniques such as chemical vapor deposition, molecular beam epitaxy, and atomic layer deposition. In contrast, preparing device-quality films of inorganic materials from colloidal solutions can be more difficult due to the challenge of achieving well-defined doping, controlled trap densities, and reproducible surface chemistry. Nevertheless, solution deposition using colloidal precursors is an attractive goal because of the potential for low-cost, large-area processing. In recent years, a great deal of effort has focused on the colloidal synthesis of wide-band-gap metal oxides such as TiO_2, visible-absorbing II—VI compounds such as CdSe, and small-band-gap materials such as PbSe. Much of the work on visible- and IR-absorbing photodetectors has been done on materials containing metals such as Cd and Pb. A new paper in this issue demonstrates photoconductive detectors made from Cu-containing In_2S_3 nanoplates. The incorporation of Cu into the In_2S_3 nanoplates leads to a significant decrease in the lifetime of the photoexcited carriers, resulting in significantly faster response times for the photodetectors processed from colloidal solution.

The study of physical phenomena such as quantum confinement and other finite-size effects has driven much of the fundamental research on semiconductor nanoparticles.[1−3] However, their large surface-area-to-volume ratios also confer other unique properties upon nanoparticles—not the least of which is their ability to be dispersed as colloidal suspensions. Currently, solution-processed nanomaterials are widely studied for potential applications in thin-film optoelectronic devices, and significant progress in the past decade in both the chemical synthesis and fundamental physics of materials such as semiconductor nanoparticles has led to increased performance of both photovoltaic[4−7] and photodetector[8−12] devices based on colloidal materials.

Although both photovoltaics (solar cells) and photodetectors convert an optical signal into an electrical current, they ultimately play different technological roles. A solar cell must generate power, while a photodetector can consume power (and can exhibit signal gain due to an external bias). In this issue, Sargent and co-workers demonstrate improved performance of a visible photodetector made from solution-processed colloidal In_2S_3 nanoplates.[13] These improvements stemmed from new insights into both the physics and the chemical synthesis of the material; in this case, it was the identification and subsequent elimination of charge trapping in lattice vacancies by the addition of Cu dopants. The material studied in this work, Cu-doped In_2S_3, is also noteworthy as it contains neither Cd nor Pb. This is a departure from much of the work being done on visible-light and infrared-absorbing colloids such as CdSe, PbS, and PbSe and is a step toward the use of "greener" colloidal materials for visible optoelectronics. We explore some of the recent work that has been done on both photovoltaics and photodetectors made from colloidal nanoparticles in order to provide context for this work.

Solar Cells. While a photodetector can operate with an applied bias, solar cells must generate power and, therefore, must produce both a photovoltage and a photocurrent. They are thus commonly characterized not only by their external quantum efficiency (EQE, electrons collected per incident photon) but also by their power conversion efficiency (PCE, electrical power produced divided by incident optical power). Figure 1A shows a schematic of a typical vertical structure photodiode, with the photoactive materials sandwiched between a transparent conducting bottom contact and a metal top contact.

Nanoparticle-based films of TiO_2 and ZnO have been widely studied as high-surface-area electrodes for dye-sensitized solar cells ("Grätzel cells"),[14,15] including those that use quantum dots as dyes.[5] However, utilizing colloidal nanoparticles as the active light-absorbing layer in solid-state cells has received less attention.

In an early study, Wang and Herron reported photosensitization of conductive polymers by CdS quantum dots in 1992,[16] and a few years later, Greenham *et al.* demonstrated photovoltaics based on bulk heterojunction blends of CdSe nanoparticles with the conjugated polymer poly(2-methoxy,5-(2′-ethyl)hexyloxy-*p*-phenylenevinylene) (MEH-PPV).[17] In these cells, light is absorbed by both the conjugated polymer and the CdSe nanoparticles, creating excitons, which are then dissociated at the interface between the materials.[18] This dissociation is driven by the differing electron affinities of the polymer and the CdSe nanoparticles, with

See the accompanying Article by Tang *et al.* on p 331.

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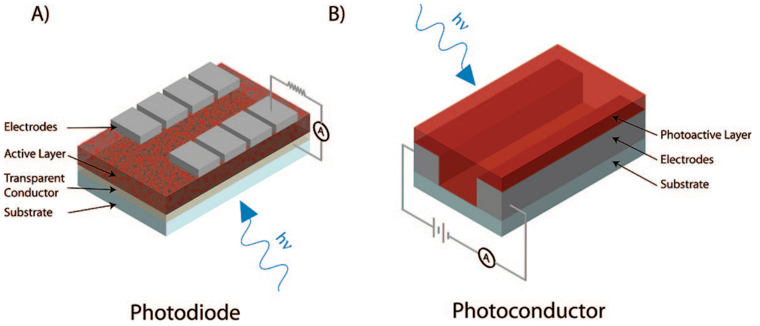

Figure 1. Schematic representation of (A) a photodiode typical of the photovoltaics discussed in the text with a bulk heterojunction active layer and (B) a photoconductor used for photodetection.

the CdSe acting as the electron acceptor. The EQE of these early devices peaked at ~12% at high CdSe nanoparticle loadings, corresponding to a PCE of less than 1%. Over the years, replacing the MEH-PPV polymer with poly-3-hexylthiophene (P3HT) and the continued expansion of CdSe syntheses to new shapes of nanoparticles (from spheres, to rods,[19,20] to tetrapods,[21] and to multibranched starbursts;[22] Figure 2) has led to PCEs of nearly 2% for bulk heterojunction blends of colloidal nanoparticles and conjugated polymers, with EQEs approaching 60% over much of the visible region of the spectrum. Although a PCE of 2% may be insufficient for commercial devices, the EQEs of 60% are quite respectable. Overall device performance could be improved by absorbing a broader range of the solar spectrum (current CdSe/polymer blends absorb mostly visible light) or by selecting material combinations that would provide larger photovoltages.

Another class of CdSe-based devices is the all-inorganic, solution-processed CdSe/CdTe solar cell.[24] The Alivisatos group showed that a bilayer heterojunction-type device could be fabricated from solution-processed CdSe and CdTe nanorods. Their best devices had peak EQEs over 60% and PCEs of roughly 3%.

Colloidal syntheses of a wide range of semiconductor nanoparticles also enable the selection of band gaps ranging through the visible and into the infrared region. For a given class of material, the band gap can also frequently be tailored by controlling the size of the nanoparticle.[1] In theory, this material and size tunability could enable the solution processing of devices that can utilize a large portion of the solar spectrum, or precisely engineered multijunction devices. Presently, however, bulk heterojunction blends containing IR band gap nanoparticles such as PbS and PbSe have not been found to be nearly as efficient as those containing nanoparticles with visible band gaps such as CdSe. The best reported power conversion efficiencies of bulk heterojunctions using PbS and PbSe are on the order of a few tenths of a percent;[25−27] the reason for this remains an open question, though evidence points to the differences in surface chemistry or band alignments between CdSe and PbSe cells (unpublished results).

The low efficiencies of bulk-heterojunction-type photodiodes containing IR band gap nanomaterials have prompted exploration of different device geometries including Schottky diodes.[28−30] In a Schottky diode, the equilibration of the Fermi levels at the metal−semiconductor contact and the concomitant formation of a depletion zone in the semiconductor layer creates an electric field at the interface that can drive the separation and collection of photogenerated electrons and holes across the depletion layer.

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In such Schottky contact devices, post-deposition ligand treatments have been critical to improving the electronic coupling between the nanoparticles in the films to facilitate carrier transport.[30,31] With proper ligand exchange, the performance of Schottky diode devices using IR nanoparticles has been much better than that of bulk heterojunction blends, with photovoltaic power conversion efficiency as high as 1.1% for PbSe Schottky diodes under airmass (AM) 1.5 illumination and with EQEs as high as 20% across the NIR,[30] and slightly better performance for similar diodes made from PbS.[32] Careful treatment of these films with bidentate ligands that simultaneously passivate surface traps and bridge the nanoparticles in the films had led to carrier mobilities in the range of 10^{-3} cm^2 V^{-1} s^{-1} and depletion regions reported to be on the order of ~10^2 nm. The thick active layers are important to allow absorption of a significant fraction of the incident light, while the high mobilities allow collection of many of the photogenerated carriers, with the combination leading to the improvements in reported efficiencies.

Photodetectors. In parallel with their use in photovoltaic cells, increasing amounts of research have been directed at using colloidal semiconductor nanoparticles as active absorbers in photodetectors.[9−12] Because the purpose of a photodetector is to transduce an optical signal into an electrical one rather than to generate power, PCE is no longer a relevant figure of merit, but EQE can still be used as a measure of sensitivity. However, to compare devices of different sizes and geometries, sensitivity is sometimes reported as normalized, or specific, detectivity (D^*) in units of Jones ($\text{cm} \times \sqrt{\text{Hz}}/\text{W}$).

The unit Jones is defined as the inverse of the noise equivalent power after it has been normalized for the active area of the device. Common photodetectors have detectivities in the range of 10^{10} to 10^{13} Jones.[33] In addition, photodetectors with end uses in photographic and video applications require fast response times. Fast response time, which is the rise (fall) time of the electrical signal when the optical signal is turned on (off), is important if a photodetector is to be used for digital imaging in order to support fast frame rates.

Since photodetectors can operate under an applied bias, they can exhibit gain (the collection of multiple electrons per photon). One way to generate gain is if defects in the material lead to carrier trapping and persistent photoconductivity.[33,34] In that case, photogenerated carriers with recombination lifetimes longer than the time it takes to travel through the device can essentially be collected more than once, leading to gain.[33] Of course, long-lived photocarriers are also detrimental to fast device response times. Thus, when using trapping-based mechanisms to generate gain in photodetectors, one needs to strike a balance between higher gains (and thus higher sensitivities) and faster response times. The long-term stability of the trap distribution also becomes a topic of technological importance, lest the device properties evolve over time.

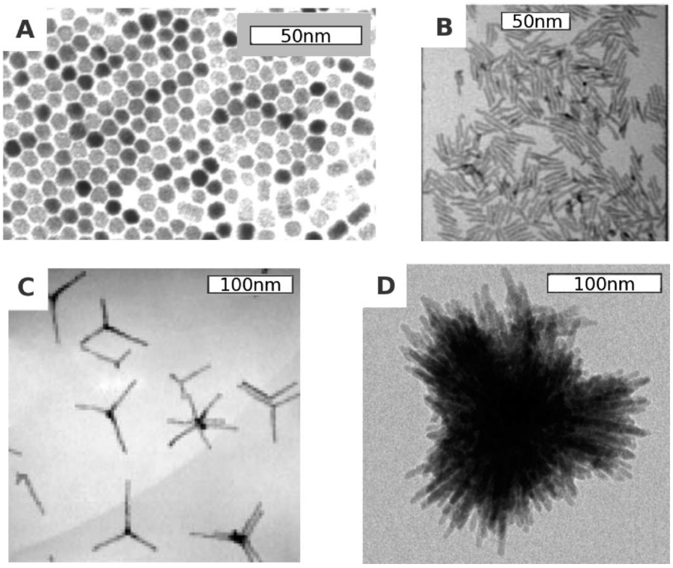

Figure 2. Transmission electron micrographs of (A) quantum dot, (B) rod, (C) tetrapod, and (D) hyperbranched nanostructures of CdSe. Panels A and B were reproduced with permission from ref 23, copyright 2000 Macmillan Publishers Ltd. Panel C was reproduced with permission from ref 21, copyright 2005 Materials Research Society. Panel D was reproduced from ref 22, copyright 2007 American Chemical Society.

> In theory, the material and size tunability of colloids could enable the solution processing of devices that can utilize a large portion of the solar spectrum, or precisely engineered multijunction devices.

The photodiodes discussed in the solar cells section above can also act as photodetectors since they produce photocurrent when illuminated. Familiar materials from the photovoltaic world appear frequently as the photoactive layer, with reports utilizing CdSe[12] for visible or PbSe[8,35] and PbS[10,36,37] for infrared detection. For the most part, these devices have exhibited low EQEs (below 20%) even under applied bias. Two reports worth noting blended either PbS[36] or CdTe[38] into polymer photodiodes and achieved gains of 1.4 and 800 (that is, EQEs of 140 and 8000%) under bias, but response times were not reported.

Photoconductors are another class of photodetectors incorporating solution-processed colloidal materials. These devices consist of a photoactive material (which can be cast from solution) spanning two planar contacts (Figure 1B). Illumination of the photoactive layer generates charge carriers, increasing the conductance of the material.

Several groups have recently reported examples of nanoparticle-based photoconductors with this geometry.[39−41] For instance, the Sargent group studied the use of PbS in IR photodetectors, both in polymer blends[10] and as nanocrystalline solids.[11] The authors reported a detectivity of 10^{13} Jones for the nanocrystalline solids, which compares favorably with the performance of many other IR photodetectors. Once again, colloidal surface traps played an important role, and the authors showed they could adjust the gain and response time by manipulating the surface ligand chemistry.[42] Strongly confined PbS nanocrystals have also been reported as visible wavelength photodetectors with similarly high performance.[9]

In this issue, the Sargent group has looked beyond Cd- and Pb-containing materials and explored In_2S_3 nanoparticles as the photoactive layer in photoconductive photodetectors.[13] They show that visible photodetectors with detectivities of 2.8×10^{11} Jones can be made from colloidal In_2S_3 nanoplates. Furthermore, they demonstrate the ability to tailor the response time and gain by controlling the incorporation of Cu into the material. They explain this effect as the result of Cu doping reducing trapping in the In_2S_3 nanoparticles,

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which in turn leads to shorter carrier lifetimes and thus faster device response. In the films they studied, Cu doping into In_2S_3 shortened the photoresponse time from several seconds to 100 ms. They showed that the gain decreases with increasing Cu doping, from 500 (observed in the undoped films) to 40 electrons per incident photon at the highest doping levels. Though the faster response times came at the price of gain, filling charge carrier traps likely also increased the carrier mobility. Thus, the time constant is reduced by several orders of magnitude while maintaining an appreciable gain. Although the reported detectivities and response times fall short of those of commercially available visible range photodetectors, they are encouraging as a first report of a solution-processed device. Futhermore, this work provides a device demonstration of another visible-absorbing material, and a very welcome one, as it contains neither Pb nor Cd.

CONCLUSION AND OUTLOOK

A systematic understanding of the chemistry of colloidal materials has the potential to lead to significant improvements in their performance in technological applications such as solar cells and photodetectors. Materials such as TiO_2, ZnO, and CdSe will continue to play a major role in both basic science and new technologies, but the periodic table offers a far richer variety than has been systematically explored to date. As demonstrated in this issue by Sargent and co-workers, opportunities abound for groups to explore new materials as well as to revisit colloidal formulations of semiconductors that have received less recent attention. The effects of doping, surface states, ligand binding, stability, size, and shape control will remain important topics for any colloidal material being considered for optoelectronics applications. These will provide motivation for studies of the fundamental chemistry and physics of future solution-processed nanomaterials, as well as opportunities to tailor the properties of materials for specific device applications.

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