

Nanocrystal/Polymer Composite Photovoltaic Devices

W. Huynh, L. Manna, and A. P. Alivisatos
Department of Chemistry, University of California
Berkeley, California

Abstract

Unlike conventional solar cells, novel polymeric photovoltaic devices have flexibility, large area processibility and potential low costs. We have constructed devices consisting of a composite of CdSe nanocrystals and poly(3-hexylthiophene). The resulting monochromatic power conversion efficiency is 0.7 %. Since the efficiency in these devices is limited by poor electron transport, we seek to improve the mobility of electrons in the CdSe with nanorods in place of nanocrystals. Devices fabricated with small aspect ratio CdSe nanorods and poly(3-hexylthiophene) have enhanced conversion efficiencies up to 2 %. To further increase device efficiencies, soluble nanorods of CdSe were synthesized with aspect ratios reaching 20:1 by controlling the kinetics of nanocrystal growth in lyothermal solutions.

Introduction

Thin film electronic devices with polymeric active components have been intensely studied because of the possibility of constructing large area, flexible devices with simple processing.^{1,2} The first photovoltaic devices fabricated from single layer, thin films of semiconducting polymer were inefficient³ due to poor separation and collection of the generated electron-hole pairs (excitons). It was subsequently recognized that enhanced charge separation occurs at an interface between two materials with disparate electron affinities, allowing for transport of the carriers in separate materials with a lower probability of recombination. Substances introduced into the polymer to create heterojunctions for improved device performance include, C_{60} ,⁴ small organic molecules,⁵ and other conjugated polymers.^{6,7} In this paper we report the fabrication and characterization of nanocrystal/polymer composite photovoltaic devices as well as the synthesis of nanorods of CdSe and their incorporation in photovoltaic devices.

CdSe Nanocrystals

Colloidal crystals consisting of hundreds to thousands of atoms can be synthesized in a variety of inorganic semiconducting materials such as CdSe, InP and CdTe. In

this size regime of several nanometers, between molecular and bulk, the particles exhibit many interesting size dependent properties, such as band gap, charging energy, and melting point. The characteristic high surface-to-volume ratio of these nanoparticles provides for a very large interfacial area for the separation of charges in heterojunction photovoltaic devices. Semiconducting particles within the quantum confinement regime have an exciton radius that exceeds the physical radius. As a result, the absorption is tunable with size and extinction coefficient is higher than that of the bulk. Similar to polymers, nanocrystals behave as chemical reagents, being soluble in a variety of organic solvents. Easily processed, flexible and large area devices can be fabricated simply through spin casting.

CdSe Nanoparticle/Poly(3-hexylthiophene) Devices

Spherical Nanocrystals

Photovoltaic cells were fabricated by spin casting a chloroform solution of pyridine passivated 5 nm diameter CdSe nanocrystals and poly(3-hexylthiophene) (P3HT) onto an indium-tin oxide (ITO) coated glass substrate and evaporating aluminum top contacts. Films were of thickness typically between 50 to 100 nm.⁸ From the current-voltage response of 90 % wt. CdSe in P3HT (Fig 1), a quantum efficiency of 5 %, a open circuit voltage of 0.57 V and a fill factor of 0.51 can be calculated. The resulting power conversion efficiency is 0.7 %.

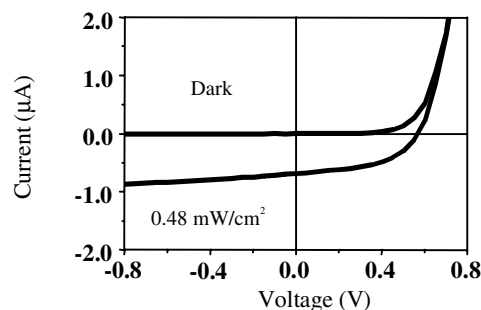


Figure 1. Current-voltage response of 90% wt. 5 nm CdSe in P3HT device under dark and illumination.

As compared with previous nanocrystal/polymer composite photovoltaic devices constructed from CdSe and the polymer MEH-PPV(poly(2-methoxy,5-(2'-ethyl-hexyloxy)-*p* phenylenevinylene), the devices reported here show a factor of three improvement in power conversion. This is mainly attributed to the higher fill factor and open circuit voltage. We can explain this in the context of reduced recombination rates due to a higher hole mobility in P3HT which is of the order 10^{-2} cm²/(sV) as compared with MEH PPV which is of the order 10^{-4} . Observation of TEM images of films of the polar CdSe and the non-polar P3HT indicate that there is microphase separation such that CdSe nanocrystals form a percolation path through the polymer (Fig. 2). Light is absorbed both in the polymer and nanocrystal. The generated exciton is dissociated at the organic/inorganic interface due to the built-in field resulting from the difference in electron affinity and ionization potential of the components. As a consequence of the blend geometry and the band structure of the components, electrons are transported within the nanocrystal aggregates while the holes reside within the polymer. The quantum efficiency increases with the concentration of CdSe, reaching a maximum at 90 % by weight. From photoluminescence quenching studies of CdSe in MEH-PPV, it is known that the charge separation is very efficient, greater than 90 %. Thus it is transport of the generated carriers which limits the efficiency of the photovoltaic. Estimates of the mobilities of the carriers indicate that electron transport is very poor (less than 10^{-4} cm²/(sV)). Measurements of the intensity dependence of the external quantum efficiency show an almost linear relation. This is consistent with a model of recombination at a fixed number of sites corresponding to "dead-ends" in the nanocrystal network. Since the mobility of electrons is so low, they cannot diffuse quickly enough out of the terminations in the network before recombination occurs. It is thus desirable to both increase the mobility of the electrons as well as reduce the possible traps in the network of particles.

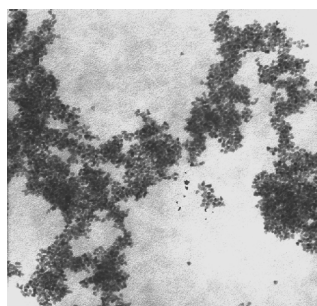


Figure 2. Low resolution TEM of 60% by wt. CdSe nanoparticles in P3HT.

Nanorods

Oriented elongated CdSe nanocrystals have the advantage of reducing the number of interparticle hopping incidences for the electron. It is also known that elongated

rods pack more efficiently than spherical particles due to increased contact area for van der Waals interactions. However, the challenge is to increase the nanocrystal domain just to the threshold of the exciton diffusion length within CdSe. Above this, excitons generated by CdSe absorption will recombine before they can diffuse to a CdSe/polymer interface and undergo dissociation.

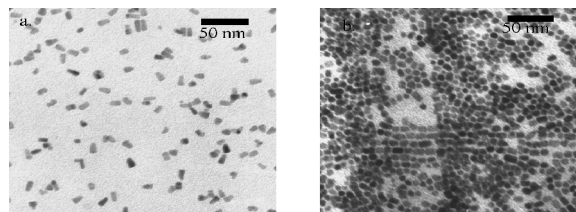


Figure 3. a) Transmission electron micrograph of 8×13 nm CdSe nanocrystal rods. b) TEM of chains of 5×8 nm CdSe particles stacked along the *c*-axis.

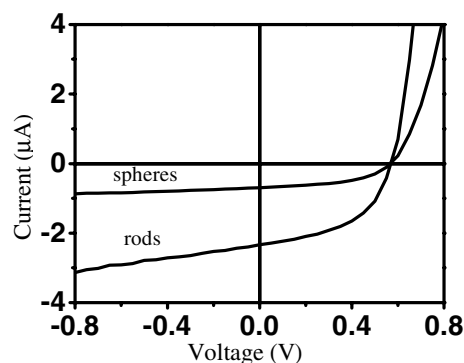


Figure 4. Current-voltage response of 80 % wt. 8×13 nm CdSe in P3HT device under dark and illumination.

Elongated rod-shaped CdSe nanocrystals were synthesized (Fig. 3a) and incorporated into the P3HT polymer. From TEM images, it can be seen that rods have a tendency to organize along their long axes, possibly forming a directed pathway for electron transport.(Fig. 3b). Films of 80 % by weight 8×13 nm CdSe rods in P3HT were used in photovoltaic devices and we observe an increase in quantum efficiency by a factor of three to 16 % (Fig. 4). By comparing TEM images produced from various concentrations of CdSe spheres in P3HT with that of rods in P3HT it can be concluded that the domains formed by the rods are significantly higher, almost an order of magnitude. The reduction of the amount of interparticle transport in addition to the enhanced nanoparticle aggregation most likely account for the improvement in quantum efficiency. The fill factor and open circuit voltage are essentially unchanged from devices made of spherical nanocrystals. An overall power conversion efficiency of 1.9 % at 514 nm is obtained for the nanorod devices. This is comparable to the most efficient of the recent polymer composite devices reported.

Device Photoresponse

The most efficient nanorod device, with a thickness of 100 nm converts 36 % of sunlight to electrical energy. External quantum efficiencies given do not account for the transmission of radiation due to the low optical density of the thin films. Such a 100 nm thick film has a maximum optical density of 0.7, corresponding to an absorption of 80 % of the incident light. Devices of higher film thickness display an antibatic photoresponse, in which the maximum quantum efficiency is red-shifted with respect to the maximum absorption (Fig. 5). Maximal absorption also corresponds to the minimal penetration depth for the incident radiation, with the majority of the carriers generated near the ITO surface. Electrons which have been created near the ITO electrode must traverse the entire thickness of the device to be collected at the aluminum electrode under short circuit. Since electron transport is poor, recombination will occur on the most part before the electrons reach the aluminum electrode. Consequently, light which is absorbed near the aluminum surface yields the highest quantum efficiency. To further enhance the device performance, it is necessary to provide an effective pathway for the transport of electrons throughout the entire thickness of the film.

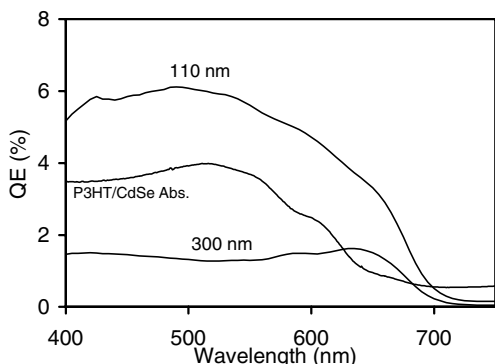


Figure 5. The action spectra of 80 % wt. CdSe nanorods in P3HT at various thicknesses. An absorption curve for the blend is included for comparison.

CdSe Nanorods

We seek to further improve these composite devices by incorporating wires to transport electrons rather than a network of discrete nanoparticles. Recently the kinetic control of CdSe nanocrystal growth has been used to vary the shapes of particles from a nearly spherical morphology to rod-like with aspect ratios as large as twenty to one⁹.

In a classical CdSe nanocrystal synthesis Cd and Se precursors in solution are rapidly injected into hot (340-360 °C), surfactant, usually tri-octyl phosphine oxide (TOPO). Nucleation occurs immediately, followed by growth. At the growth temperature, surfactant molecules adsorb and desorb rapidly from the nanocrystal surface, enabling the addition (as well as removal) of atoms from the crystallites, while

aggregation is suppressed by the presence, on average of one monolayer, of surfactant at the crystallite surface. The reaction can be stopped at any time with heat removal producing nanocrystals of a desired average size.

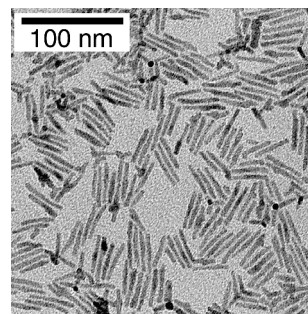


Figure 6. Low resolution TEM of CdSe nanorods.

A modification of this preparation leads to shape control of CdSe nanocrystals. According to this new protocol, Cd and Se precursors are injected into a binary surfactant mixture composed of TOPO and hexylphosphonic acid (HPA), with a well defined ratio of HPA/TOPO. Moreover, the amount of precursors injected is much higher than used in conventional CdSe nanocrystals synthesis. In this system the growth of CdSe nanocrystals is very fast and highly anisotropic, resulting in a rod-like shape where the long axis is the c-axis of the wurtzite crystal structure (Fig. 6). The aspect ratio of the rods increases quickly just after injection, while the short axis shows only a slow increase. This stage is considered to be strongly over-driven growth, since the monomer concentration is high after the initial injection. As the monomer concentration depletes during growth, the aspect ratio gradually decreases to nearly one (ordinary quantum dots), but the short axis grows significantly. This stage is considered to be thermodynamically controlled, since a near-equilibrium spherical morphology of the nanocrystals would minimize their surface area. The rod morphology can be maintained by additional (slow) injections, which replenish the monomer, resulting in longer quantum rods (up to 80 nanometers, Fig. 6). Nanorods synthesized with multiple injections also show high monodispersity of the short axis, as confirmed by optical absorption and emission spectra and low-resolution transmission electron microscopy.

Quantum rods of any desired size and aspect ratio can be systematically obtained by varying several parameters, like the reaction time, the amount of precursors injected, and the number of injections.

Conclusion

In this work we have demonstrated that rod-shaped CdSe nanocrystals blended with P3HT conducting polymer can be used to construct efficient photovoltaic devices. High aspect

rods have been synthesized to increase the efficiency of electron transport for future composite devices.

References

1. N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend and A. B. Holmes, *Nature*, **365**, 628-630 (1993).
2. P. K. H. Ho, D. S. Thomas, R. H. Friend and N. Tessler, *Science*, **285**, 233-236 (1999).
3. R. N. Marks, J. J. M. Halls, D. D. C. Bradley, R. H. Friend and A. B. Holmes, *Journal of Physics-Condensed Matter*, **6**, 1379-1394 (1994).
4. G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, **270**, 1789-1791 (1995).
5. R. A. J. Janssen, M. P. T. Christiaans, C. Hare, N. Martin, N. S. Sariciftci, A. J. Heeger and F. Wudl, *Journal of Chemical Physics*, **103**, 8840-8845 (1995).
6. J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, **376**, 498-500 (1995).
7. M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson and R. H. Friend, *Nature*, **395**, 257-260 (1998).
8. W. U. Huynh, X. G. Peng and A. P. Alivisatos, *Advanced Materials*, **11**, 923-927,886 (1999).
9. X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, **404**, 59-61 (2000).

Biography

Wendy Huynh is a senior graduate student at the University of California, Berkeley, working with Prof. Paul Alivisatos. Her current area of study is polymer/inorganic composite photovoltaic devices. She received her BSc. in physical chemistry from the University of Toronto in 1997. She has also published work with Prof. Geoffrey Ozin, on mesoporous materials and Prof. Martin Moskovits on the near-field spectroscopy of fractal silver colloids.