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Subcontractor Report

Hybrid Nanorod-Polymer Solar Cell

Final Report
19 July 1999–19 September 2002

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NREL Technical Monitor: R. Matson

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Abstract

With the support of this grant, we successfully demonstrated that semiconductor nanorods can be used to fabricate readily processed and efficient hybrid solar cells together with polymers. By controlling nanorod length, we changed the distance over which electrons are transported directly through the thin film device. Tuning the band gap by altering the nanorod radius enabled us to optimize the overlap between the absorption spectrum of the cell and the solar emission spectrum. A photovoltaic device consisting of 7 nanometer by 60 nanometer CdSe nanorods and the conjugated polymer poly-3(hexylthiophene) was assembled from solution with an external quantum efficiency of over 54 % and a monochromatic power conversion efficiency of 6.9 % under 0.1 mW/cm^2 illumination at 515 nm. Under A.M. 1.5 Global solar conditions, we obtained a power conversion efficiency of 1.7 %.

Key publications supported by this grant:

(1) W. U. Huynh, X. G. Peng, and A. P. Alivisatos, "CdSe Nanocrystal Rods/poly(3-hexylthiophene) Composite Photovoltaic Devices," Adv. Func. Mat., **11**, 923, (1999).

(2) W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, "Hybrid Nanorod-Polymer Solar Cells," Science, **295**, 2425 (2002).

(3) W. U. Huynh, J. J. Dittmer, W. Libby, G. L. Whiting, and A.P. Alivisatos, “Controlling the Morphology of Nanocrystal-polymer Composites for Solar Cells,” Adv. Func. Mat. **13**, No. 1, 73-79 (January 2003).

(4) W. U. Huynh, J. J. Dittmer, N. Teclemariam, D. Milliron, A. P. Alivisatos, and K. W. J. Barnham, “Charge Transport in Hybrid Nanorod-Polymer Composite Photovoltaic Cells,” Phys. Rev. B., **6711**, No. 11, 5326 (March 2003).

The widespread expansion in the use of inorganic solar cells remains limited due to the high costs imposed by fabrication procedures involving elevated temperature (400-1400 ºC), high vacuum and numerous lithographic steps. Solution processible polymers have been investigated as a low-cost alternative and solar power efficiencies of up to 2.5% have been reported *(1).* Nonetheless conventional inorganic solar cells routinely exhibit solar power conversion efficiencies of 10 % and can reach up to 30 % for the most advanced, but also the most expensive models *(2)*. The main factor for the superior efficiency of inorganic over organic devices lies in the high intrinsic carrier mobilities that exist in inorganic semiconductors. Higher carrier mobilities mean that charges are transported to the electrodes more quickly, which reduces current losses via recombination. For many conjugated polymers, electron mobilities are extremely low, typically below 10^{-4} $cm^2V^{-1}s^{-1}$, due to the presence of ubiquitous electron traps such as oxygen *(3)*. Therefore, polymer photovoltaic (PV) devices rely on the introduction of another material for electron transport, which also provides the interface for charge transfer. Compounds such as small conjugated molecules have therefore been blended with polymers at a concentration that enables the formation of percolation pathways for electron transport *(1, 4-6)*. The efficiency of these devices is limited by inefficient hopping charge transport *(7)* and electron transport is further hindered by the presence of structural traps in the form of incomplete pathways in the percolation network *(6).*

One way to overcome these charge transport limitations is to combine polymers with inorganic semiconductors. Charge transfer is favored between high electron affinity inorganic semiconductors and relatively low ionization potential organic molecules and polymers *(8, 9)*. Charge transfer rates can be remarkably fast in the case of organics that are chemically bound to high density of states nanocrystalline and bulk inorganic semiconductors *(10)*. Because of the nanoscale nature of light absorption and photocurrent generation in solar energy conversion, the advent of methods for controlling inorganic materials on the nanometer scale opens new opportunities for the development of future generation solar cells. We have therefore used colloidal semiconducting nanorods as the inorganic phase in the construction of these solar cells via solution phase nano-assembly. By varying the radius of the rods, the quantum size effect can be used to control the band gap; furthermore, quantum confinement leads to an enhancement of the absorption coefficient as compared to the bulk such that devices can be made thinner *(11).* One-dimensional nanorods are preferable to quantum dots or sintered nanocrystals in solar energy conversion, since they naturally provide a directed path for electrical transport. The length of the nanorods can be adjusted to the device thickness required for optimal absorption of incident light.

We have recently established that both diameter and length of colloidal semiconductor nanorods of CdSe can be systematically varied to aspect ratios above 20 and lengths greater than 100 nanometer (nm), following a solution phase synthesis at temperatures below 300 °C *(12, 13).* In the present work CdSe nanorods were combined with the conjugated polymer poly-3(hexylthiophene) (P3HT) (Fig. 1A) to create charge transfer junctions with high interfacial area. From the schematic energy level diagram for CdSe nanocrystals and P3HT, it can be seen that CdSe is electron-accepting and P3HT is hole-accepting (Fig. 1B). CdSe is used as the electron transport material, while P3HT is an effective hole transport material in its regioregular form, demonstrating the highest field effect hole mobilities observed in polymers so far (reaching up to 0.1 $cm^2V^{-1}s^{-1}$ *(14)*).

The mechanical properties of P3HT allow for the room-temperature solution-casting of uniform, flexible thin films. However, dispersing the inorganic nanorods at high density within P3HT to facilitate charge transfer is a challenge because the complex surface chemistry of the nanocrystals can limit its solubility in the polymer. In Fig. 2, nanocrystals of diameter 7 nm and various lengths of up to 60 nm are shown. As nanocrystals increase in aspect ratio from spherical to rod-like, they move from the molecular regime closer to the realm of a one-dimensional wire and they become less readily soluble. Although we can control microphase separation and aggregation for low-aspect ratio CdSe nanocrystals dispersed in polymers (Fig. 3A), the performance of the resulting PV device is limited by inefficient hopping electron transport *(15)*. In order to accommodate high aspect ratio nanorods, we developed a solvent mixture consisting of a good solvent and ligand for CdSe nanorods and a good solvent for the polymer. Nanorods were co-dissolved with P3HT in a mixture of pyridine and chloroform and spin-cast to create a uniform film consisting of dispersed nanorods in polymer (Fig. 3B) *(16)*. We now show that by controlling the aspect ratio of CdSe nanorods dispersed in P3HT, we can tailor the length scale and direction of electron transport through a thin film PV.

We fabricated an efficient inorganic-organic hybrid solar cell by spin-casting a solution of 90 % by weight CdSe nanorods in P3HT onto an indium tin oxide glass substrate coated with poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) with aluminum as the top contact (Fig. 1C). With CdSe nanorods 7 nm by 60 nm, a power conversion efficiency of 6.9 % was obtained under 0.1 mW/cm^2 illumination at 515 nm inside an inert atmosphere of flowing argon. For plastic PV devices, this monochromatic power conversion efficiency is one of the highest reported *(1)*. At this intensity, the open circuit voltage is 0.5 V, the photovoltage at the maximum power point is 0.4 V and the fill factor is 0.6 (Fig. 4B). When our devices were tested in simulated sunlight (under A.M. 1.5 Global solar conditions and flowing argon *(18)*) a power conversion efficiency of 1.7 %, open circuit voltage of 0.7 V, photovoltage at maximum power point of 0.45 V and fill factor of 0.4 were obtained (Fig. 4C) *(17)*. The maximum open circuit voltage is determined by the difference between the work functions of the electrodes, PEDOT:PSS and aluminum, as well as the difference between lowest unoccupied energy level in the CdSe nanorod and the highest occupied energy level in P3HT. This difference is close to what we obtained at solar intensity.

Because CdSe and P3HT have complementary absorption spectra in the visible, these nanorod-polymer blend devices have a very broad photocurrent spectrum extending from 300 to 720 nm (Fig. 4A). Unlike other electron acceptors such as C_{60} in organic blend devices, and sintered TiO_2 in dye-sensitized solar cells, CdSe nanorods absorb a significant part of the solar spectrum *(1, 19)*. Furthermore, the absorption spectrum of the hybrid devices presented here can be tuned by altering the diameter of the nanorods in order to optimize the overlap with the solar emission spectrum (Fig. 4D). The onset of absorption for 60 nm long nanorods with 3 nm radius is at a wavelength of 650 nm, while the onset for those with 7 nm radius is at 720 nm. Because P3HT shows no absorption beyond 650 nm, we can tune the onset of the photocurrent action spectrum from 650 to 720 nm by increasing the diameter of the nanorods while maintaining the length constant. The characteristics of these two devices, such as open circuit voltage and fill factor, are comparable. This further suggests that nanorod length, not diameter determines device performance. Moreover, band gap tuning in nanorods enables the realization of high efficiency device architectures, such as tandem solar cells in which the different band gaps can be obtained by modifying only one chemical compound.

We can understand the origin of the high efficiency of nanorod-polymer devices by studying the dependence of charge transport on nanorod length. The external quantum efficiency (EQE), which is the percentage of electrons collected per incident photon (with no correction for reflection losses), can be used as a measure of the efficiency of charge transport given that the following quantities are comparable for a set of devices: (i) incident light intensity, (ii) fraction of light absorbed, (iii) charge collection efficiency at the electrodes, which is mainly given by the choice of electrodes, and (iv) the charge transfer efficiency, as determined from photoluminescence quenching. These four conditions are met for the devices for which EQE data are presented in Fig. 4A. We can therefore conclude that as the aspect ratio of the nanorods increases from 1 to 10, the charge transport has to improve significantly to yield an EQE enhancement by a factor of approximately 3. In networks consisting of shorter nanoparticles, electron transport is dominated by hopping and in those consisting of longer particles, band conduction is prevalent. In a cross section of the blend film (Fig 3D), most nanorods were oriented partly in the direction of the electric field and thus the direction of electron transport. Because the thickness of the nanorod-polymer film is approximately 200 nm, a 60 nm long nanorod can penetrate through a significant portion of the device while a 30 nm and a 7 nm long particle are progressively less effective (Fig 3C). The best device, which contained 7 nm by 60 nm nanorods, performed with a maximum EQE of 55 % under 0.1 mW/cm^2 illumination at 485 nm (Fig. 4A), and this value has been remarkably reproducible *(20)*.

In order for plastic nanorod devices to achieve typical power conversion efficiencies of conventional inorganic solar cells, it is necessary to reduce charge recombination, which decreases the EQE and the fill factor at solar light intensities. An increase in carrier mobilities would realize this by decreasing the carrier concentration within the device. Further enhancement of carrier mobilities can be accomplished by improving the nanocrystal/polymer interface to remove nanorod surface traps, aligning the nanorods perpendicular to the substrate and further increasing their length.

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16. We used between 5 and 15 % pyridine in chloroform. The optimal amount of pyridine is determined by the number of non-passivated Cd surface sites on the nanorods. An excess of pyridine, however, is to be avoided, as this mediates the precipitation of P3HT, which is insoluble in pyridine. Replacing chloroform with this solvent mixture leads to an increase in energy conversion efficiency of more than 50 %.
17. The fill factor (FF) is defined as $FF = \frac{\{I \cdot V\}_{\max}}{I_{SC} \cdot V_{OC}}$. The power conversion efficiency is $\eta = \frac{FF \cdot I_{SC} \cdot V_{OC}}{Light\ Intensity}$. The power conversion efficiency can be calculated both under monochromatic and white light, such as solar, illumination.
18. The sun simulator essentially consists of a 75 W Xenon source and a set of Oriel A.M. 0 and A.M. 1.5 filters. The temperature was maintained at 25 ºC, verified by an *in situ* thermocouple, by flowing argon past the device during measurements. The spectral overlap and intensity integral between the A.M. 1.5 Global standard (ASTM E892 Global, 1000 W/m^2 (IEC 904-3)) and our sun simulator were optimized for the wavelength region in which the active layer shows absorption. The error in the simulation with regards to the obtained photocurrent is approximately 10 %.
19. B. O'Regan, M. Grätzel, *Nature* **353**, 737 (1991).
20. The results reported represent the median of five sets of devices made on separate occasions from three different synthetic batches of CdSe totaling 57 individual solar cells. The maximum external quantum efficiency of each of these 57 devices are all within 10 % relative to the median with the highest obtained efficiency at 59 %, all under ~ 0.1 mW/cm^2 monochromatic illumination. Individual devices have been characterized repeatedly over the time scale of several months and showed no significant change between measurements.

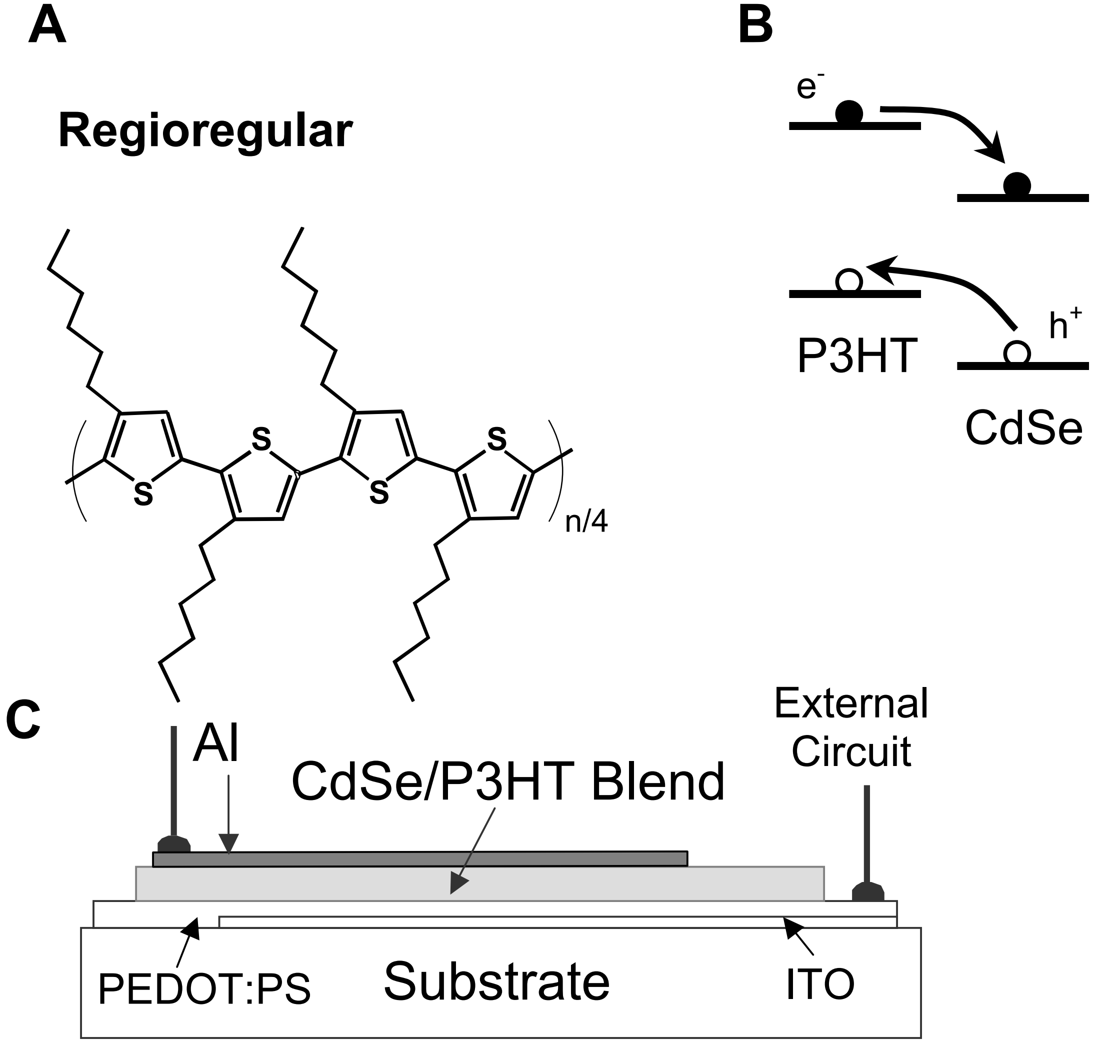

Figure 1. (A) The structure of regioregular P3HT. (B) The schematic energy level diagram for CdSe nanorods and P3HT showing the charge transfer of electrons to CdSe and holes to P3HT. (C) The device structure consists of a film ~ 200 nm in thickness sandwiched between an aluminum electrode and a transparent conducting electrode of PEDOT:PSS (Bayer AG), which was deposited on an indium tin oxide glass substrate. The active area of the device is 3 mm^2. This film was spin-cast from a solution of 90 % by weight CdSe nanorods in P3HT in a pyridine/chloroform solvent mixture.

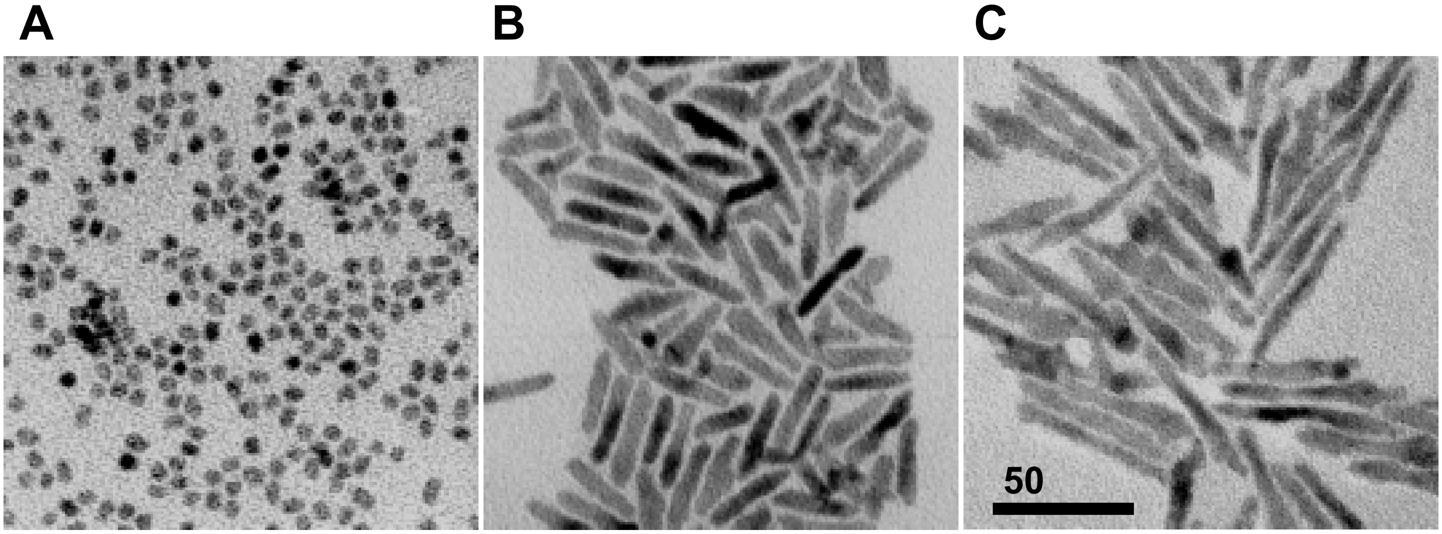

Figure 2. Cadmium selenide nanocrystals were synthesized with aspect ratios ranging from 1 to 10. The samples, shown by transmission electron micrographs (TEMs) at the same scale, have dimensions (A) 7 nm by 7 nm, (B) 7 nm by 30 nm and (C) 7 nm by 60 nm.

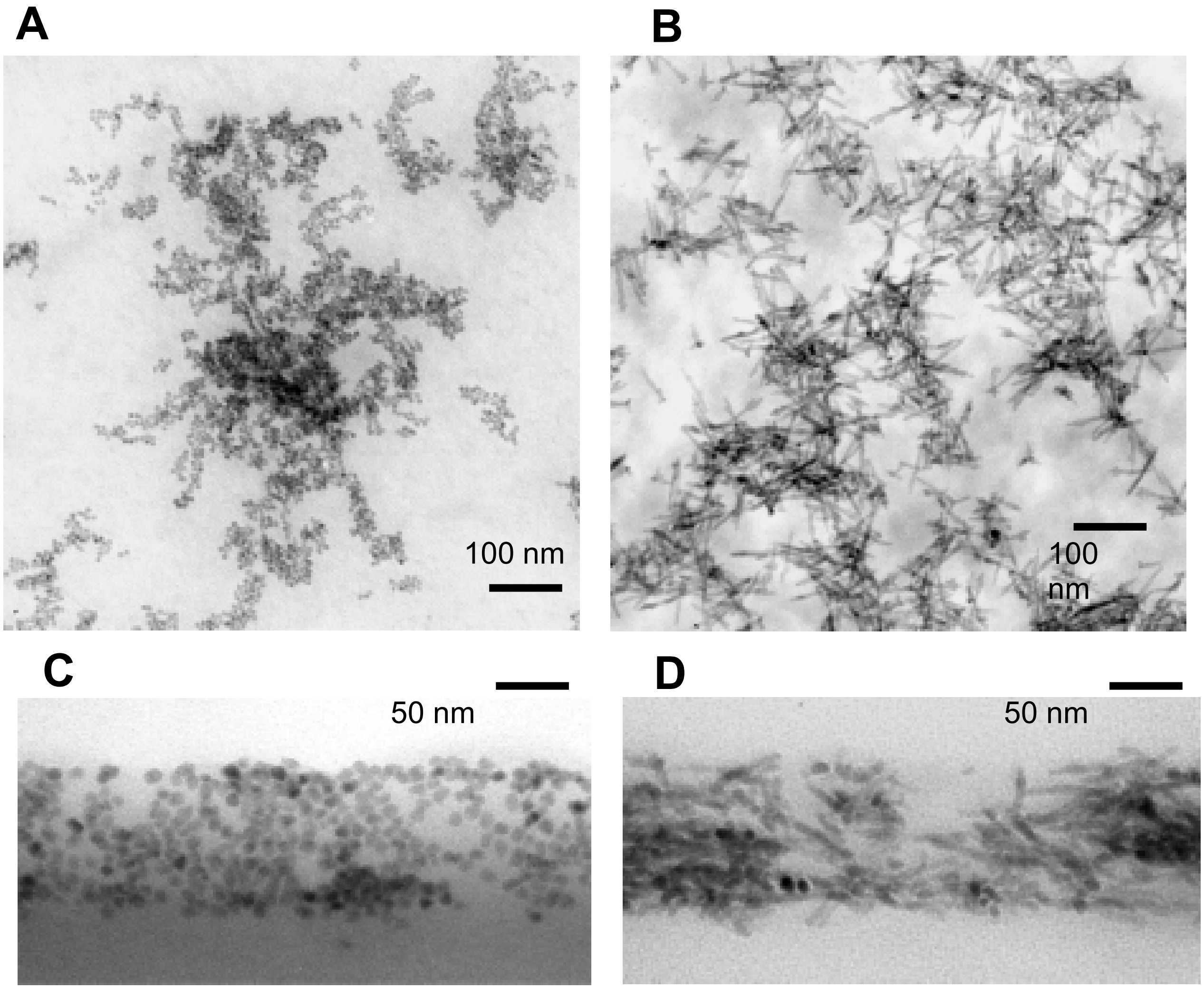

Figure. 3. Thin films of 20 % by weight (A) 7 nm by 7 nm (B) and 7 nm by 60 nm CdSe nanocrystals in P3HT were studied via transmission electron microscopy. In (C), a TEM of a cross section of a film with 60 % by weight 10 nm by 10 nm CdSe nanocrystals in P3HT reveals the distribution and organization of nanoparticles across the 110 nm thick film. A solution of CdSe in P3HT was spin cast onto a Polybed® epoxy substrate and we used an ultramicrotome to obtain ultrathin cross sections. In (D), a TEM of a cross section of a 100 nm thick film consisting of 40 % by weight 7 nm by 60 nm CdSe nanorods in P3HT reveals that most nanorods are partially aligned perpendicular to the substrate plane. The solutions were cast onto an Epon/Aradite epoxy substrate, embedded into epoxy, cured and sliced using an ultramicrotome. This extra support is required to microtome the nanorods, as the blend film has a tendency to tear as the rods get longer.

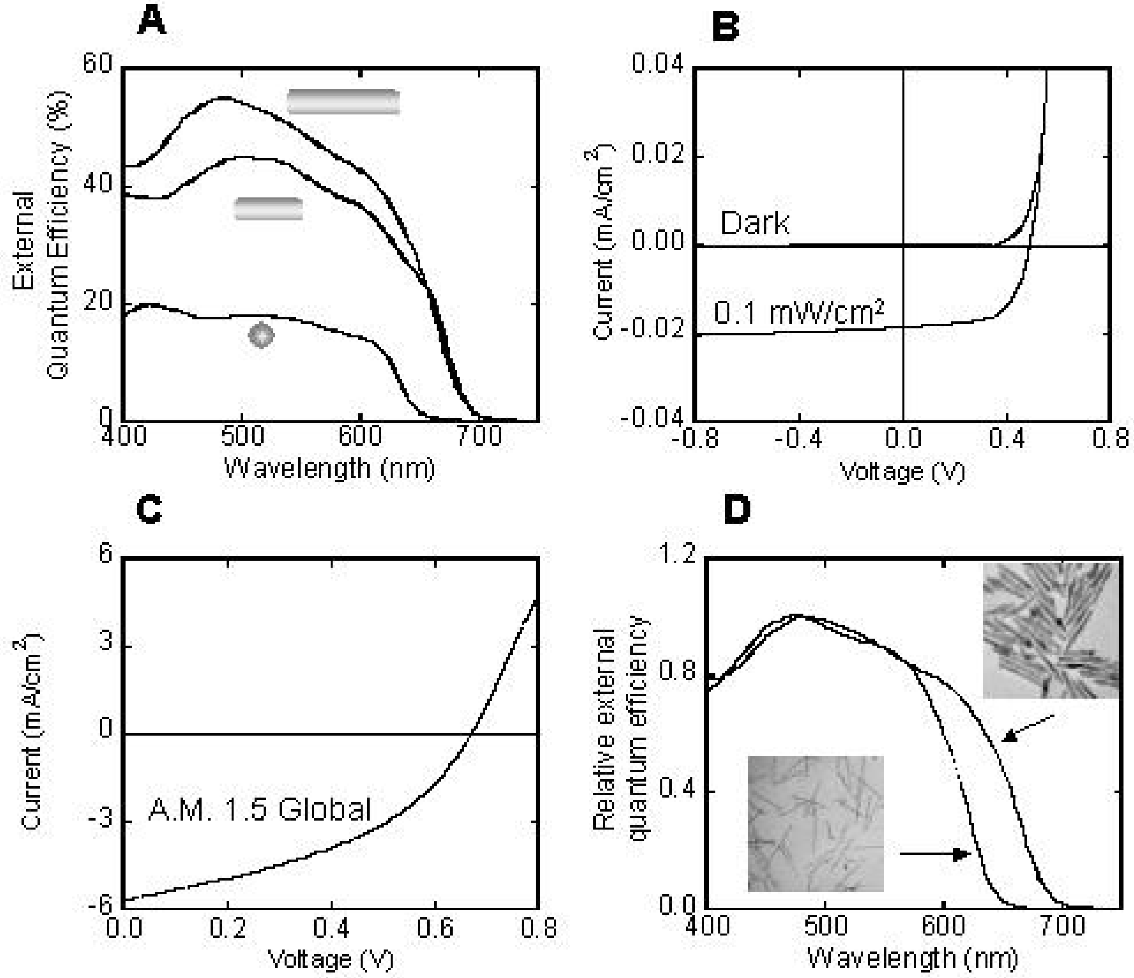

Figure 4. As the nanocrystal length is increased successively from 7 nm by 7 nm to 7nm by 30 nm and to 7 nm by 60 nm, the external quantum efficiency in (A) rises by almost a factor of 3 to 54 %, under illumination of 0.084 mW/cm^2 at 515 nm. (B) The corresponding current-voltage characteristics of the 7 nm by 60 nm nanorod device exhibit very high rectification ratios of 10^5 in the dark, a short circuit current of 0.019 mA/cm^2, fill factor of 0.62 and open circuit voltage of 0.52 V under the same illumination conditions. (C) Solar cell characteristics of this 7 nm by 60 nm CdSe nanorod device, measured with a simulated AM 1.5 Global light source, include a short circuit current of 5.7 mA/cm^2, fill factor of 0.42, open circuit voltage of 0.67 V to yield a solar power conversion efficiency of 1.7 %. (D) Tuning of the photocurrent spectrum is shown for 2 devices containing 60 nm long nanorods with diameters 7 nm and 3 nm at 90 % by weight concentration in P3HT.

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13. ABSTRACT *(Maximum 200 words):* With the support of this grant, we successfully demonstrated that semiconductor nanorods can be used to fabricate readily processed and efficient hybrid solar cells together with polymers. By controlling nanorod length, we changed the distance over which electrons are transported directly through the thin-film device. Tuning the bandgap by altering the nanorod radius enabled us to optimize the overlap between the absorption spectrum of the cell and the solar emission spectrum. A photovoltaic device consisting of 7-nm by 60-nm CdSe nanorods and the conjugated polymer poly-3(hexylthiophene) was assembled from solution with an external quantum efficiency of over 54% and a monochromatic power conversion efficiency of 6.9% under 0.1 mW/cm^2 illumination at 515 nm. Under AM 1.5 Global solar conditions, we obtained a power conversion efficiency of 1.7%.

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