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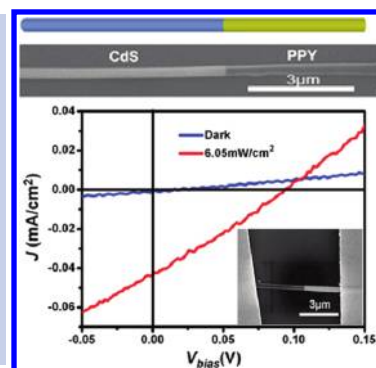
Assembled Organic/Inorganic p–n Junction Interface and Photovoltaic Cell on a Single Nanowire

Yanbing Guo,^{†,‡} Yajie Zhang,^{†,‡} Huibiao Liu,[†] Siu-Wai Lai,[§] Yuliang Li,^{*,†} Yongjun Li,[†] Wenping Hu,[†] Shu Wang,[†] Chi-Ming Che,[§] and Daoben Zhu[†]

[†]CAS Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China, [‡]Graduate School of Chinese Academy of Sciences, Beijing 100190, People's Republic of China, and [§]Department of Chemistry and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China

ABSTRACT We have utilized a single organic/inorganic p–n junction nanowire composed of the inorganic semiconductor cadmium sulfide (CdS) and a conducting polymer polypyrrole (PPY) to successfully convert light energy into electricity. The organic/inorganic semiconductor nanowire exhibits a power conversion efficiency of 0.018% under an illumination intensity of 6.05 mW/cm². The fundamental studies operated here will be helpful to understand photoinduced energy/charge transport in an organic/inorganic interface and might be also serve as promising building blocks for nanoscale power sources for developing nanoscale solar power conversion systems.

SECTION Nanoparticles and Nanostructures



The shortage of fossil fuels and rapidly growing environmental pollution problems have caused the quest for the development of new, clean, and renewable energy for the future sustainability of our society. A solar cell is one of the attractive candidates,^{1–5} but the vast majority of commercial solar cell modules are based on crystalline Si. In recent years, there has been growing interest in developing organic/inorganic hybrid thin film solar cells,⁶ which are inexpensive, easily solution-processed, highly stable, and of high carrier transport efficiency. Up to now, the organic/inorganic hybrid thin film solar cells exhibited power conversion efficiency of up to 1.5–1.7%.⁷

A single nanowire solar cell device is not only useful to understand the mechanism of large-area nanowire-array-based solar cells, but it also provides a new nanoscale test bed to accomplish nanoscale optical electrical integration.⁸ Recently, the photovoltaic properties of a single silicon coaxial p–i–n nanowire and axial p–i–n nanowire devices have been reported.^{8–10} These photovoltaic devices can serve as robust power sources to drive functional nanoelectronic sensors and logic gates.

Up to now, there has been no report on the photovoltaic effect in a single axial organic/inorganic p–n junction nanowire. Herein is described the findings on the investigation of an assembled interface in the organic/inorganic p–n junction nanowire and the corresponding photovoltaic properties. This new photovoltaic element could provide a new nanoscale criterion for the investigation of photoinduced energy/charge transport in organic/inorganic interfaces, which might serve as electric power in a nanoscale circuit. An organic/inorganic p–n junction nanowire from polypyrrole (PPY) and cadmium sulfide (CdS) was synthesized by an electrochemical method

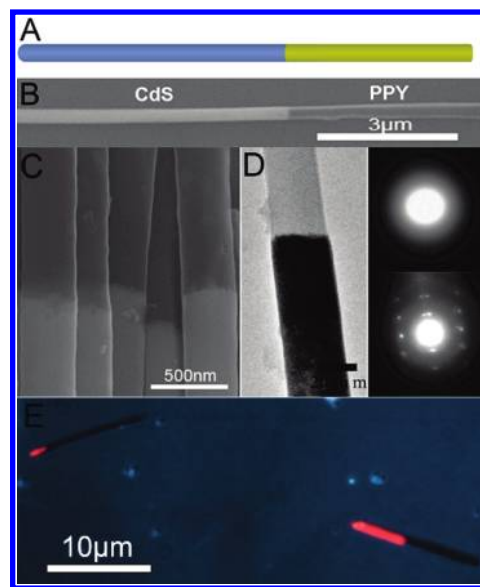


Figure 1. Scheme and structural characterization of an organic/inorganic p–n junction nanowire. (A) Schematic diagram for an axially modulated organic/inorganic p–n junction nanowire. (B) SEM image of a typical single CdS–PPY p–n junction nanowire. (C) Side-view SEM image of CdS–PPY nanowires. (D) TEM image of a single CdS–PPY nanowire and selective-area electron diffraction pattern (SAED) taken from two different segments in the nanowire. (E) Fluorescent microscopy image of CdS–PPY nanowires.

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through an anodic aluminum oxide (AAO) template.¹¹ Further characterization and analysis of photovoltaic properties were conducted on the single p–n junction nanowire.

Examination by scanning electron microscopy (SEM) revealed that the as-grown CdS–PPY of large-area axial p–n junction nanowires has smooth surfaces with a uniform diameter (Figure 1B). The lengths of the CdS–PPY nanowires are consistent with the growth rates of CdS nanowires under similar conditions as those in the control experiment. The length of CdS and PPY segment in the p–n junction nanowire could be adjusted by monitoring each of the synthetic processes. Figure 1C depicts the side-view image of CdS–PPY nanowires, from which the two different segments can be easily distinguished and the contact interface can be clearly visualized. All of the nanowires were found to have similar

diameters of around 200–400 nm, which could be correlated to the hole diameter of the AAO template. The CdS–PPY axial nanowires could be effectively synthesized in large quantity via the method used here. The transmission electron microscopy (TEM) image and selective-area electron diffraction pattern (SAED) of different segments in the nanowire (Figure 1D) provide more structural information; the bright part is amorphous PPY, and the dark part is crystalline CdS.

Figure 1E shows the fluorescent image of two strands of CdS–PPY nanowire having different lengths. The dark part corresponds to PPY, while the red fluorescence part is CdS for its surface-trap emission ranging from 570 to 670 nm.

The growing processes of the CdS–PPY p–n junction nanowire have been investigated. Figure 2A shows the TEM image of a CdS nanowire absorbed with pyrrole molecules (left), the TEM image of a CdS–PPY p–n junction in which PPY polymerized only for a few minutes (middle), and the image of a CdS–PPY p–n junction in which PPY polymerized for 30 min (right). According to these experimental results, we suggested that the growth of CdS–PPY p–n junction nanowires occurred in three different stages, (i) CdS crystals were deposited into the AAO template and partly filled in the holes; (ii) the electrolyte was changed into pyrrole solution and pyrrole molecules were absorbed on the surface of the CdS crystal by the interaction of $-\text{NH}$ with Cd^{2+} ion; and (iii) pyrrole molecules absorbed on the surface of CdS crystals were polymerized under the applied bias of +0.85 V (vs SCE). At approximately the same time, ClO_4^- ions were aggregated into the PPY segment. We believe that the interactions among Cd^{2+} , $-\text{NH}$, and ClO_4^- lead to the formation of distinct interface, which would not be disrupted even under ultrasonic waves. Figure 2B depicts the models of the CdS top surface in different growing stages. HRTEM images shown in Figure 2C clearly demonstrate the surface of the CdS crystal and the interface of the CdS–PPY p–n junction. Similarly, we can easily distinguish the amorphous PPY and crystalline CdS in the CdS–PPY p–n junction. We can also observe the boundary surface between CdS and PPY, which can be attributed to the complex interaction among Cd^{2+} , $-\text{NH}$, and ClO_4^- ions. Moreover, such a CdS–PPY interface plays an important role in the single nanowire photovoltaic cell.

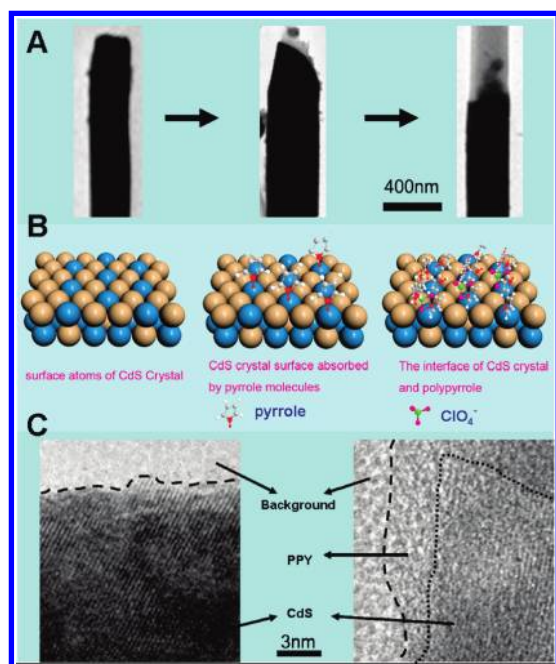


Figure 2. (A) TEM images of a CdS–PPY p–n junction nanowire in different growing stages. (B) Models of the CdS surface in different growing stages. (C) HRTEM image of the CdS crystal and CdS–PPY interface.

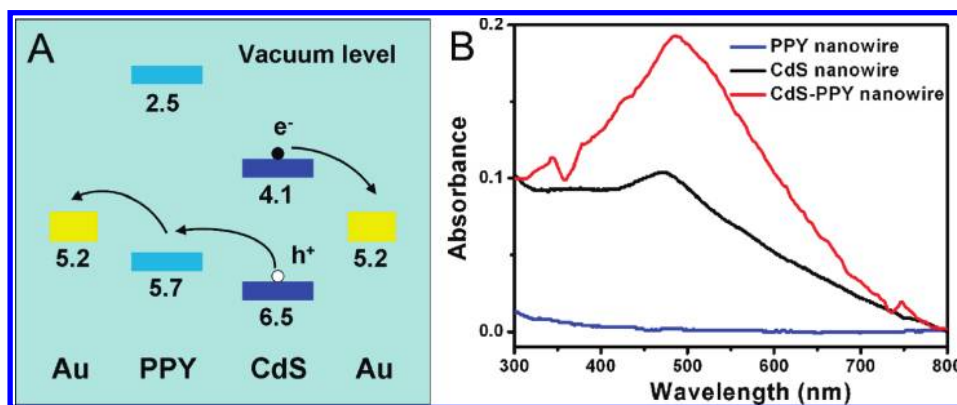


Figure 3. (A) Energy level diagram of a CdS–PPY nanowire. (B) UV–vis absorption spectra of CdS–PPY p–n junction nanowires, an individual CdS nanowire, and an individual PPY nanowire dispersed in ethanol.

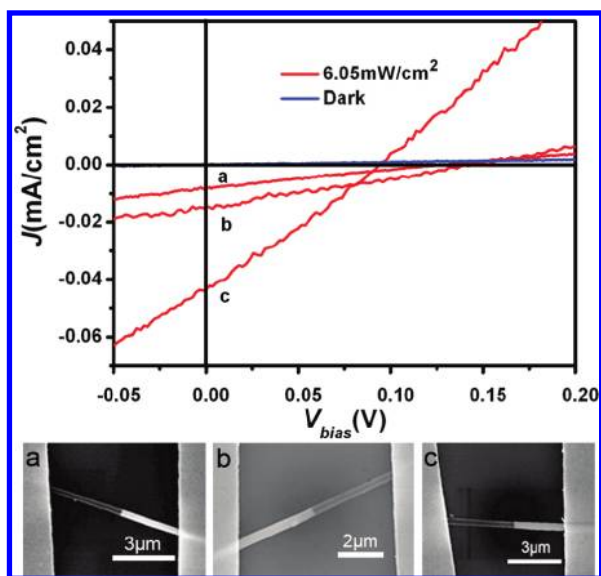


Figure 4. Dark/light current density versus applied voltage bias (J - V) data of typical single CdS-PPY nanowire solar cells with device lengths of 7.428 (a), 6.922 (b), and 6.597 μm (c). The (a, b, c) below are SEM images of each device.

To examine the application of the CdS-PPY p-n junction nanowire in the field of nanoscale solar cells, the energy level diagram of the CdS-PPY nanowire device (Figure 3A) was analyzed. Due to the different electron affinities of CdS and PPY,¹² excitons generated by the incident light reach the hybrid interface from the CdS side and effectively dissociate at the interface of CdS-PPY.¹³ The electrons and holes generated in this process could also transport through CdS and PPY, respectively. Thus, a photocurrent could be generated in the CdS-PPY p-n junction nanowire, which would be an effective energy source for a nanoscale circuit. Figure 3B shows the UV-vis absorption spectrum of the CdS-PPY nanowires dispersed in ethanol. CdS-PPY nanowires exhibit a large absorption peak at wavelengths ranging from 700 to 300 nm, which almost covers the entire visible light scale. The wide light absorption range will be helpful to improve the solar energy power conversion efficiency. The photovoltaic properties of the axial CdS-PPY nanowire diodes having different lengths were characterized under 6.05 mW/cm^2 white light illumination (Figure 4). SEM images of typical CdS-PPY

nanowire solar cell devices with different lengths are shown and labeled as (a), (b) and (c). Power generation is observed in the single nanowire device with the highest photocurrent density of 0.043 mA/cm^2 (Figure 4c). The projected active area was calculated by using the entire length between the two Au electrode contacts in the device for the depletion widths, and the minority carrier diffusion lengths could be ignored. The use of the projected area to estimate the apparent current density is consistent with the methodology used with other nanostructured photovoltaic devices.⁸⁻¹⁰ The open circuit voltage of this device is about 0.094 V. The maximum open circuit voltage acquired in this kind of single nanowire (Figure 4a) devices could be 0.15 V per nanowire. The fill factor, FF, for the device is 26.5%, giving a power output per nanowire of 22.34 fW.

In addition, we also estimate the power conversion efficiency, η , based on the same projected active area as that mentioned above. Most of the CdS-PPY axial p-n nanowire solar cell devices have an efficiency around 0.016% under an illumination intensity of 6.05 mW/cm^2 , and the maximum efficiency for the CdS-PPY axial p-n nanowire device is up to 0.018% under the same illumination intensity (6.05 mW/cm^2). The light source intensity that we used in the experiment is only 6.05 mW/cm^2 , about 17 times lower than AM 1.5G (100 mW/cm^2), and the light's irradiation is parallel to the CdS-PPY interface, leading to limit light effective absorption. These factors directly result in the lower power conversion efficiency of the CdS-PPY p-n nanowire solar cell, compared with that of a silicon single nanowire. However, there is still large room to improve the power conversion efficiency of CdS-PPY nanowire solar cells.

To prove that the photovoltaic properties were caused by the unique organic/inorganic p-n junction formed in the single nanowire, additional tests were conducted on individual CdS and individual PPY nanowires. Neither the results of the CdS nanowire (Figure 5A) nor those of the PPY nanowire (Figure 5B) exhibits power generation under the same illumination intensity, confirming that the photovoltaic properties were characteristic of a CdS-PPY nanowire.

In conclusion, we fabricated the single CdS-PPY axial p-n junction nanowire for photovoltaic devices, and we investigated the photophysical properties of such nanowire devices for the first time. The CdS-PPY nanowires exhibit a power conversion efficiency of 0.018% under an illumination

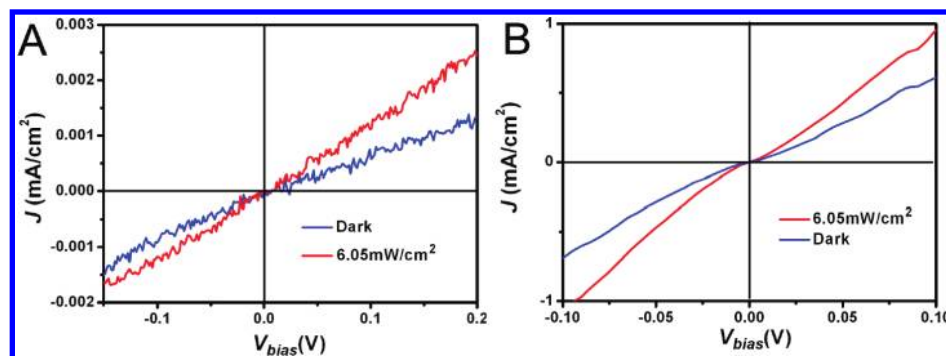


Figure 5. Dark/light current density versus applied voltage bias (J - V) data of an individual CdS nanowire device (A) and an individual PPY nanowire device (B).

intensity of 6.05 mW/cm^2 . The fundamental studies operated here will be definitely helpful to understand the work mechanism of organic/inorganic hybrid solar cells on the nano-scale, and this implies that such organic/inorganic p–n junction nanowires are promising building blocks for nano-scale power sources for developing nanoscale solar power conversion systems.

Experimental Method

Briefly, a layer of Pt was first evaporated on one side of the AAO template as a conducting layer, and the AAO template with a Pt layer was put into a homemade electrolytic cell as the working electrode. CdS nanowires were deposited into the AAO template at a current density of 2.5 mA/cm^2 in a DMSO solution. After washing with hot DMSO, acetone, and acetonitrile, the AAO template containing CdS nanowires was immersed into the pyrrole electrolyte for electropolymerization to afford PPY nanowire. Therefore, the CdS–PPY heterojunction nanowire-embedded AAO membrane was acquired.

SUPPORTING INFORMATION AVAILABLE Experimental details about the synthesis of CdS–PPY nanowires and the fabrication of devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: ylli@iccas.ac.cn.

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