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Light-Controlled Organic/Inorganic P-N Junction Nanowires

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Low dimension organic/inorganic hybrids of nanostructures are materials that combine functional organic molecules and inorganic molecules to produce a new class organic/inorganic solid materials which have distinct properties that were not observed in the individual component on nanosize and their bulk materials.¹ This may include either new or improved chemical and physical properties that can be exploited for fabricating novel nanoscale devices.^{2–8}

It is known that the P–N junctions are of great importance both in modern electronic applications and in understanding other semiconductor devices.⁹ Recently, some research has focused on P–N junctions possessing electrical and photoelectrical properties in the nanoscale.^{10–13} Nevertheless, there has been no report on the light-controlled diode on a single organic/inorganic semiconductor hybrid nanowire. We report herein the fabrication of the organic/ inorganic semiconductor P–N junction nanowire and the remarkable performance on light-controlled diode within a single hybrid P–N junction nanowire.

We used ordered porous AAO templates and chose the p-type organic semiconductor of PPY (polypyrrole) and n-type inorganic semiconductor of CdS to prepare heterojunction nanowires (the detailed synthesis procedure is in the Supporting Information). The morphology and size of the CdS-PPY heterojunction nanowires are shown in the scanning electron microscope (SEM) images. Figure 1A shows the side view of a large area of CdS-PPY heterojunction nanowires at lower magnification. The large amount of nanowires indicated the high filling density of the membrane. These nanowires are well-defined, with a smooth surface and with diameters of 200-400 nm. Figure 1B depicts a single nanowire of CdS-PPY with a clear interface between organic and inorganic materials. We directly demonstrated the end-to-end structure of an as-prepared nanowire by element mapping (Figure 1C), which shows the dispersion of C element (green) and Cd element (red). The EDS results (Figure S2) collected from the two different parts of the hybrid nanowires clearly display the detailed chemical components, which indicated that the hybrid nanowire was indeed composed of CdS and PPY. The segmented structure of the CdS-PPY hybrid nanowire can also be confirmed by an optical image (Figure 1D) and a fluorescence image (Figure 1E). According to the fluorescent property of CdS, the red part within the single CdS-PPY nanowire is attributed to CdS, for its surface-trap emission ranged from 570 to 670 nm under the excitation of a 405 nm laser. The dark part corresponds to PPY because PPY does not exhibit any fluorescence emission under excitation. All of the above data are consistent with the asymmetric structure within the single nanowire.

Further structure information and characterization of the CdS–PPY nanowires were performed by transmission electron microscopy (TEM), as shown in Figure 2. Figure 2A depicts a typical image of the single CdS–PPY heterojunction nanowire with a diameter



Figure 1. SEM images of CdS–PPY heterojunction nanowires: (A) side view image of CdS–PPY nanowires inside the AAO template; (B) typical image of a single CdS–PPY nanowire; (C) element mapping of a single CdS–PPY nanowire; (E) fluorescent image of a single CdS–PPY nanowire excited by a 405 nm laser.

of 250 nm, which agrees with the SEM images well. We can clearly observe the organic/inorganic junction formed by inorganic semiconductor CdS and organic semiconducting polymer PPY from Figure 2A. Figure 2B displays the interface of an independent hybrid nanorod under a higher magnification. A HRTEM image (Figure 2C) reveals the exact interface structure of the CdS-PPY, indicating the single-crystalline CdS attached firmly with amorphous PPY. The two-dimensional lattice part (left part of the dashed line) is CdS, and the amorphous part (right part of the dashed line) is PPY. The clear lattice-fringe observations in the HRTEM image are indicative of good crystallinity. The lattice spacing around 0.34 nm observed in this image agrees well with interplanar distance of the (002) direction parallel in the hexagonal wurtzite phase of CdS, which also indicates [100] as the main growth direction for the component part of CdS. The crystallinity of the wurtzite structure CdS can also be proved by XRD (Figure S3).

The electrical properties of P–N junctions within the organic/ inorganic hybrid nanowires were also probed by the current (I) versus bias voltage (V) measurements (Figure 3). The devices were fabricated as described previously.¹⁴ (For detailed preparation, see Supporting Information.) Typical I-V properties of individual CdS nanowires and individual PPY nanowires in the dark and under



Figure 2. TEM images of CdS-PPY heterojunction nanowire: (A) typical image of a single CdS-PPY heterojunction nanowire; (B) interface of CdS-PPY heterojunction nanowire under a higher magnification; (C) HRTEM image of the interface of CdS-PPY heterojunction nanowire.



Figure 3. Typical current-voltage (I-V) curves for a single CdS-PPY heterojunction nanowire under light illumination with different intensities at room temperature. Inset: SEM image and EDS line analysis of the measured nanodevice.

illumination were measured (Figure S5). The I-V curve of an individual CdS nanowire shows that the CdS nanowires are highly insulating in the dark with the resistivity of $1.055 \times 10^7 \,\Omega \cdot cm$, and the photoresponse was detected along with the increase of white-light illumination power. The typical I-V curve of the PPY nanowire (Figure S5B) exhibits that the PPY nanowire served as a semiconductor with a resistivity of 65.2 $\Omega \cdot \text{cm}$. The *I*-*V* property of the CdS-PPY heterojunction nanowire shown in Figure S5C is similar to the individual CdS nanowire and does not exhibit any diode effect. However, we observed the unique phenomenon of

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light-controlled diode on the single nanowire. Figure 3 shows the typical I-V curves under illumination of different light intensity, and as expected, the CdS-PPY heterojunction nanowire acts as a diode and exhibits rectifying property at room temperature. With the forward bias, current increases as the increment of applied bias. In reverse bias, the current transporting through the junction nanowire is close to zero. With the increase of illumination intensity, the conductivity of the CdS-PPY heterojunction nanowire increased. With an applied bias of 5.0 V, the rectification ratio of the diode increased from 8.0 to 13 along with the enhancement of light intensity from 1.12 to 5.76 mW/cm². The rectification ratio of the diode at 10.0 V is the same as the ratio at 5.0 V (about 13), under 5.76 mW/cm² illuminations. The SEM image and EDS line analysis (inset in Figure 3) display the complete morphology and exact interface structure of the CdS-PPY heterojunction nanowire device that was used in the current-voltage experiment. It is seen that the two different blocks within the nanowire were connected to the Au electrode.

In summary, we designed and fabricated a new organic/inorganic semiconductor P-N junction nanowire by facile template method. Such a prepared hybrid semiconductor P-N junction nanowire shows a strong photodependent rectifying effect, and the conducting property of the organic/inorganic P-N junction nanowire can be tuned by changing the intensities of incident light. It is believed that the novel concept and interesting photoelectrical properties we developed here will have great influence in both the basic research field of nanoscience and the device application field of nanotechnology.

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Supporting Information Available: Experimental details of preparing CdS-PPY P-N junction nanowire; EDS; XRD and the CLSM images of the CdS-PPY nanowire; typical I-V curves of individual CdS, individual PPY nanowire; energy level diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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