Supporting Information

Sulfur Copolymer Nanowires with Enhanced Visible-Light Photoresponse

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1. Experimental Details

1.1 Chemicals: All chemicals are analytical grade and used as received without further purification.

1.2 Synthesis of poly(sulfur-random-(1,3-diisopropenylbenzene)) (Poly(S-r-DIB)): The Poly(S-r-DIB) was synthesized using the reported method.[1] In a typical synthesis procedure, sulfur powder was added into a 25 mL glass vial equipped with a magnetic stir bar, and heated to 185 °C in a thermostated oil bath until a clear orange colored molten phase was formed. 1,3- Diisopropenylbenzene (DIB) was then directly added to the molten sulfur medium via syringe. The resulting mixture was stirred at 185 °C for 10 minutes, and then the product was allowed to cool to room temperature. S_8 (4.0 g, 15.65 mmol), DIB (1.0 g, 6.32 mmol); S_8 (3.50 g, 13.7 mmol), DIB (1.50 g, 9.48 mmol) and S_8 (2.50 g, 9.69 mmol), DIB (2.50g, 15.8 mmol) were carried out for the preparation of poly(S-r-DIB) with 20-wt% DIB, 30-wt% DIB and 50-wt% DIB, respectively. The transparent red color of the as-prepared copolymers become much deeper as the DIB content increased from 30 wt% to 50 wt% (see Figure S1). NMR spectroscopy was conducted for structure characterization of the copolymers with 50 wt% DIB content which was completely soluble in $CDCl_3$ (see Figure S2-3). The prepared poly(S-r-DIB) copolymers were proved to be chemically stable and without any color change over a period of several months under ambient conditions.

1.3 Synthesis of sulfur copolymer nanowires: Anodic aluminum oxide (AAO) membranes were used as templates for the preparation of sulfur copolymer nanowires. Sulfur copolymer nanowires with different sizes and various DIB contents were acquired depending on the AAO membrane and sulfur copolymer we used. NaOH solution was applied to remove the AAO membrane.

1.4 Synthesis of CdS-poly(S-r-DIB) nanowires: The as-prepared sulfur copolymer nanowires can serve as sulfur source and templates to grow metal sulfides on their surface and generate heterogeneous metal sulfide/sulfur copolymer nanowires. Here, CdS nanoparticles are selected as the model system to demonstrate its template role in creating heterogeneous nanowires (see Figure S8) Typically, a given amount of $CdCl_2$ and sulfur copolymer nanowires were uniformly dispersed in ethylene glycol solvent, and then maintained at 80 °C in a thermostated oil bath until a bright yellow was appeared. The yellow samples were collected and washed several times with water and ethanol respectively, and then dried at 60 °C for 5h. Typical SEM and TEM images (Figure S9a,b,c) illustrate that nanoparticles with diameter about 10 nm are uniformly distributed on the surface of the sulfur copolymer nanowires. High-resolution TEM (HRTEM) image (Figure S9d) reveals that CdS nanoparticles with lattice spacing of ca. 0.34 nm germinate on the surface of sulfur copolymer nanowires. The composition and distribution of the as-prepared CdS-poly(S-r-DIB) nanowires are further confirmed by point-scan EDX (Figure S9e, O and Cu result from the impurities of copper grid.) and line-scan STEM elemental distributions (Figure S9f).

1.4 Photolectrochemical measurements: Photoelectrochemical measurements were carried out in a standard three-compartment quartz cell consisting of a working electrode, a Pt foil counter electrode, and a saturated calomel reference electrode (SCE) performed using an electrochemical workstation (CHI 660D, CH Instruments, Austin, TX) under repeated on/off cycles of visible light illumination ($\lambda > 420$ nm) in the presence of 0.2 M Na_2SO_4 aqueous solution as electrolyte. A 300 W Xe lamp

(AULTT, CEL-HXF300) equipped with an UV cutoff filter ($\lambda > 420$ nm,) served as light source. An indium-tin oxide glass (ITO) decorated with catalyst samples were used as the working electrode. For a typical procedure for fabricating the working electrode, 2 mg of catalysts were dispersed in 1.096 mL of 1:1 v/v water/ethanol containing Nafion solution (20 μL, 5 wt%), then the mixture was ultrasonicated to generate a homogeneous ink. Then 80 μL of the catalyst ink (containing 0.145 mg of catalyst) was spreaded on an ITO glass (loading amount: ~ 0.13 mg/cm^2). In addition, α-S crystals were deposited on a ITO transparent conductive glass substrate by electrophoretic deposition due to its poor hydrophilicity according to the reported method[2]. Electrophoretic deposition was also applied to prepare poly(S-r-DIB) nanowire photoanode for stability test (see Figure S6-7). The electrochemical impedance spectroscopy (EIS) measurements were carried out in the same configuration at $\eta = 0.6$ V from 1000 kHz - 0.02 Hz with an AC voltage of 5 mV.

1.5 Characterizations. The scanning electron microscopy (SEM) images was taken with a Hitachi S-4800 scanning electron microscope (SEM, 5 kV). Transmission electron microscopy (TEM), point-scan EDX spectrum, line-scan STEM elemental distribution and Electron energy loss spectroscopy (EELS) elemental distribution images were obtained with FEI Tecnai G2F20 system equipped with GIF 863 Tridiem (Gatan). Specimens for TEM was prepared via dropcasting a droplet of ethanol suspension onto a copper gridand allowed to dry in air. Diffuse reflectance UV–Vis spectra were measured on a Shimadzu UV-2550 instrument in wavelengths of 190–800 nm by using $BaSO_4$ as a reference. Poly(S-r-DIB) copolymer with 50-wt% DIB soluble in $CDCl_3$ was used for structural characterization via ^{1}H NMR and ^{13}C NMR. ^{1}H, ^{13}C were recorded on Varian Mercury Plus 400 instruments at 400 MHz (1H NMR), 100 MHz (13C NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively.

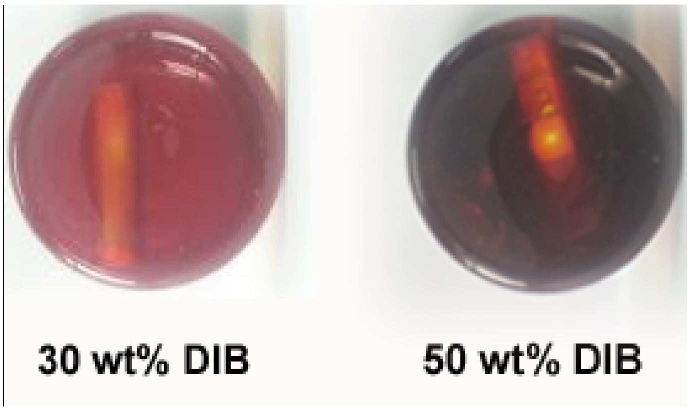

Figure S1 (a) Digital images of poly(S-r-DIB) with 30-wt% DIB and 50-wt% DIB, respectively. The transparent red colour of the as-prepared copolymers got into much deeper as the DIB content increased from 30 wt% to 50 wt%

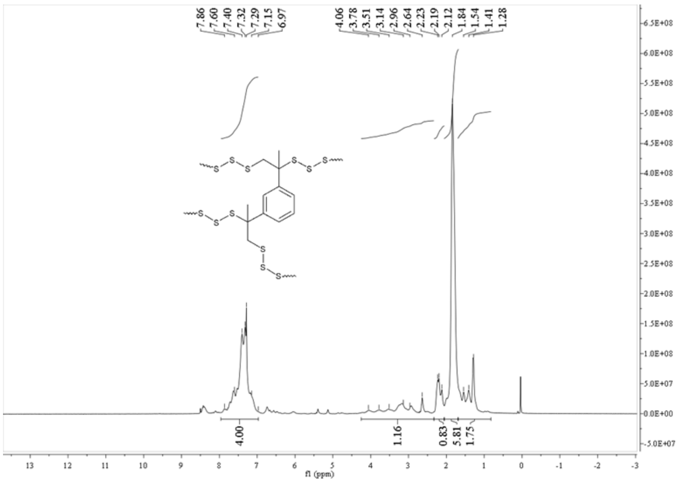

Figure S2 (a) ^{1}H NMR spectrum of poly(S-r-DIB) copolymer (50 wt% DIB) in $CDCl_3$. It demonstrates the presence of aromatic peaks at δ = 6.97– 7.86 ppm and methyl at δ = 1.28 – 2.64 ppm. In addition, resonances at δ = 2.96 – 4.06 ppm are correspond to methylene which were bonded to sulfur copolymer units.

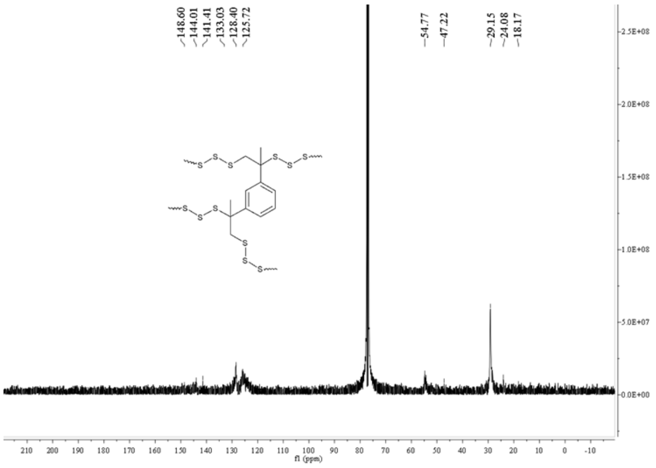

Figure S3 ^{13}C NMR spectra of poly(S-r-DIB) copolymer (50 wt% DIB) in $CDCl_3$. It further confirms the formation of copolymers. Typically, aromatic carbons were observed at δ = 125.72-148.60 ppm, methylene and quaternary carbons from DIB bonded to sulfur units were observed at δ = 47.22 ppm and δ = 54.77 ppm, respectively. Methyl carbons located in the region of δ = 18.17-29.15 due to the formation of different microstructures and compositional heterogeneity.

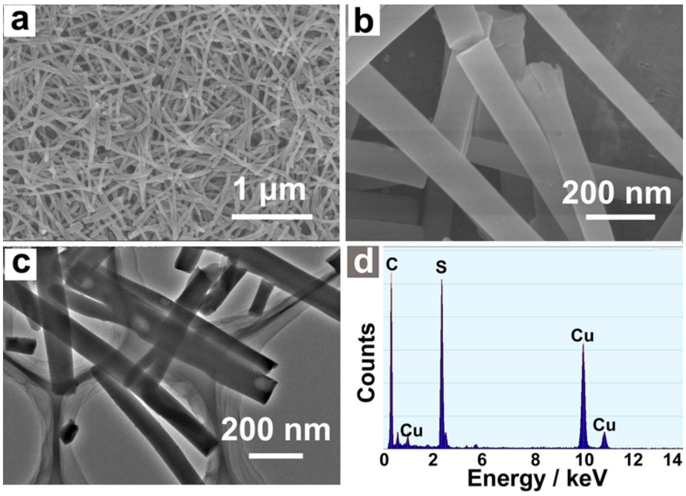

Fig. S4. (a,b) SEM images (c) TEM image and (d) point-scan EDX spectrum of the sulfur copolymer nanowires with a diameter of 100 nm and 30 wt% DIB content. The small size of the copolymer nanowires enable them to harvest much more visible light due to the high specific surface area. Furthermore, the flat band potential shifts to negative potential for about 0.1 V when the diameter of nanowires decrease from 200 nm (0.25 V vs SCE, pH=7) to 100 nm (0.15 V vs SCE, pH=7), which is also beneficial to the reduction of water. Thus, we speculate that the photoelectrochemical performance of the sulfur copolymer is size-dependent.

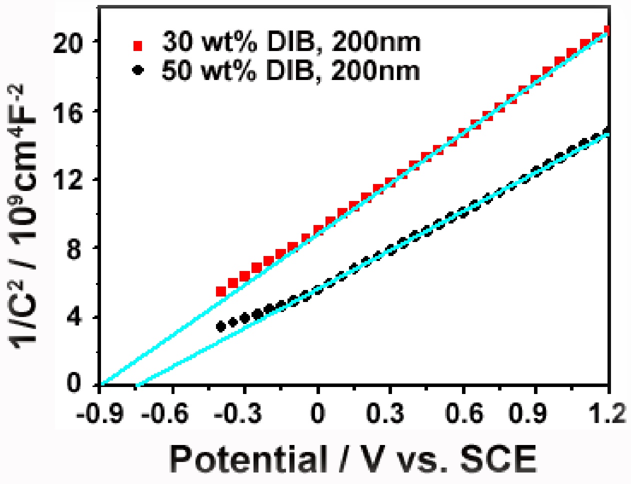

Figure S5 Mott-Schottky plots for the sulfur copolymer nanowires with 30 wt% DIB content and 50 wt% DIB content, respectively. It demonstrates that the flat band potential positive shifts from -0.9 V vs SCE to -0.75 V vs SCE when the DIB content increases from 30 wt% to 50wt%. The discrepancy between the flat band potential and the photocurrent of hydrogen generation onset may be due to the HER overpotential losses and voltage drops in the circuit[3], as well as the surface (interface) states at the electrode/electrolyte[4].

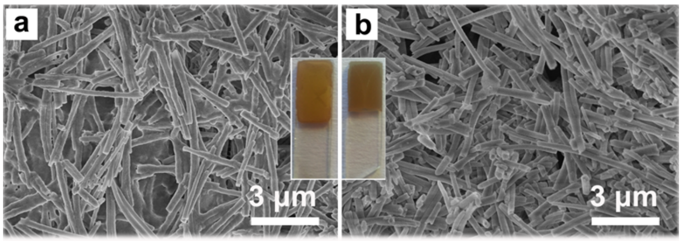

Figure S6 SEM images and Digital images of photoanode prepared with (a) drop casting and (b) electrophoresis method, respectively. It indicates that the crystals decorated on the ITO glasses by the two methods are identical in macroscopic and microscopic view. Therefore, it is reasonable to utilize electrophoresis method to prepare photoanode for the stability test.

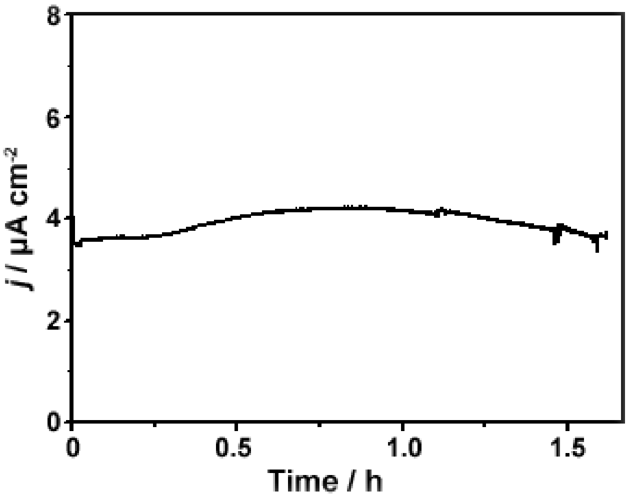

Figure S7 Photocurrent-time curve of photoanode decorated with poly(S-r-DIB) nanowires (30 wt% DIB) at a bias potential of 0.6 V vs SCE under visible light illumination ($\lambda > 420$ nm,). It shows that the as-prepared sulfur copolymer nanowires exhibit high resistance to photocorrosion.

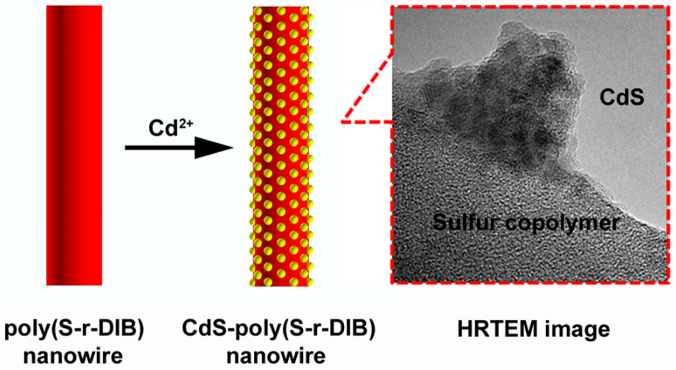

Figure S8 Schematic representation of the synthesis of CdS-poly(S-r-DIB) nanowires This unique heterogenous structure may be helpful to facilitate the separation of charge carriers and improve the corresponding photochemical activities.

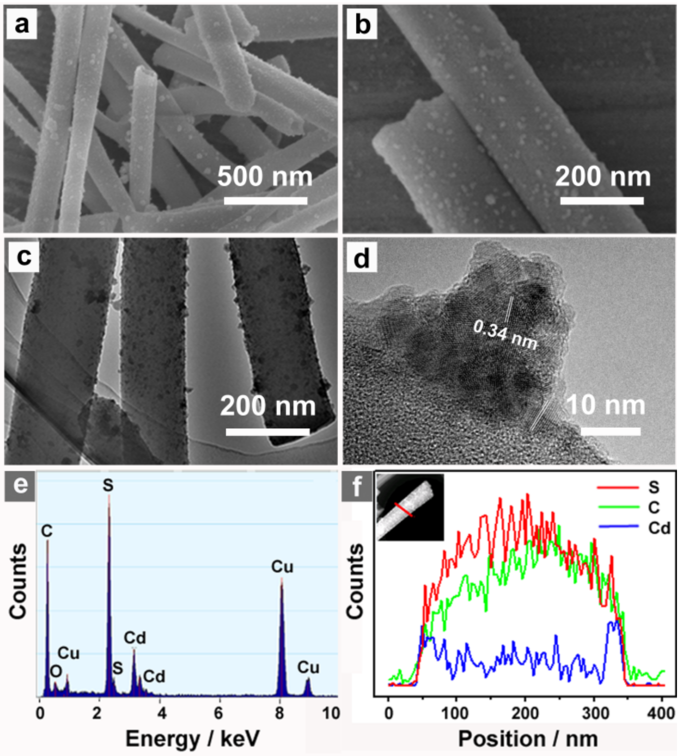

Figure S9 (a,b) SEM images, (c) TEM image, (d) HRTEM image, (e) point-scan EDX spectrum, and (f) line-scan STEM elemental distribution of the CdS-poly(S-r-DIB) nanowires.

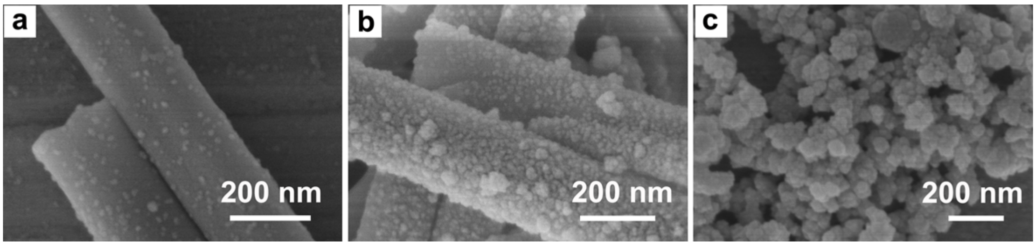

Figure S10 SEM images of CdS-poly(S-r-DIB) nanostructures with increase of Cd^{2+} density in the medium. The content of the CdS nanoparticles on the surface of the copolymer nanowires can be tuned by controlling the concentration of Cd^{2+} ions added (Fig. S10a,b). However, when excessive amounts of Cd^{2+} were used, the products were particle-like aggregates of CdS nanoparticles rather than CdS-poly(S-r-DIB) nanowires (Fig. S10c).

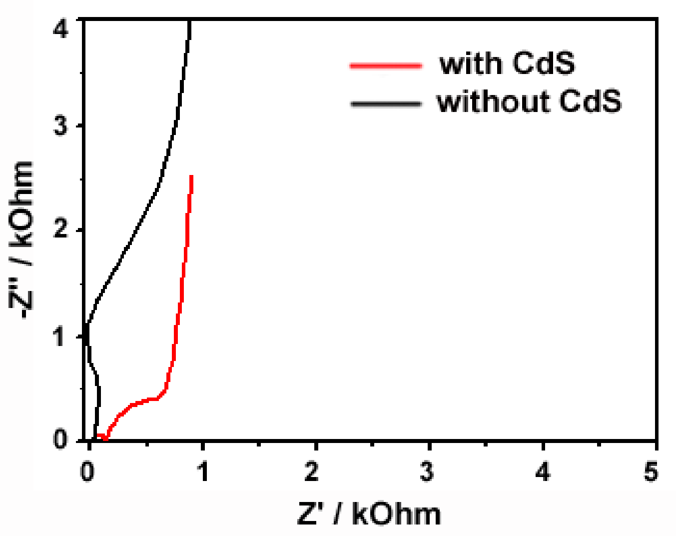

Figure S11 Electrochemical impedance spectroscopy (EIS) of sulfur copolymer nanowires with and without CdS nanoparticles performed in the same configuration at η = 0.6 V vs SCE from 1000 kHz - 0.02 Hz with an AC voltage of 5 mV. under visible light (λ > 420 nm) irradiation. The decrease of radius at low frequency indicates the enhanced interface charge transfer rate after in-situ growing CdS nanoparticles on the surface of sulfur copolymer nanowires.[5]

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