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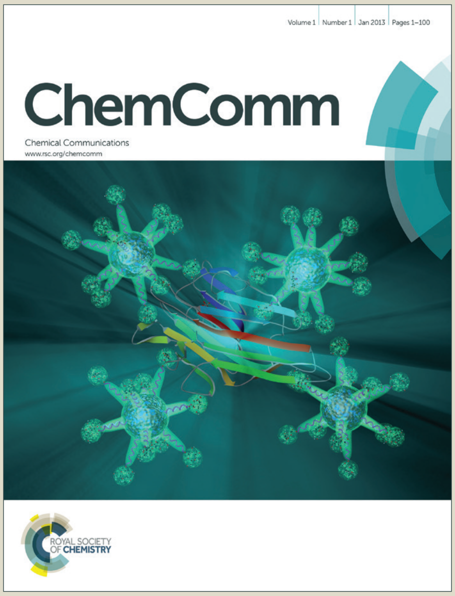

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Sulfur Copolymer Nanowires with Enhanced Visible-Light Photoresponse

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Sulfur copolymer nanowires have been reported for the first time as highly stable visible-light-active photocatalyst for photoelectrochemical water splitting depending on their size and sulfur content. The as-prepared sulfur copolymer nanowires can serve as sulfur source and templates to create metal sulfide/copolymer heterocatalysts.

Photocatalytic water splitting offers a clean and environmental friendly process to create clean and renewable hydrogen.[1] One of the most fundamental challenges in hydrogen production is the development of cheap and efficient visible-light-driven catalysts with photochemical and photoelectrochemical (PEC) activity for hydrogen evolution reaction (HER).[2] In the past two decades, intensive attention has been focused on compound semiconductor as photocatalysts.[3] Recently, elemental semiconductors such as silicon, selenium, red phosphorus, and boron are considered to be a promising class of photocatalysts and photoelectrocatalyst for solar energy conversion.[4] Among these elemental materials, silicon has been found to be a highly efficient photoelectrocatalyst for water splitting hydrogen evolution.[5] These intriguing photoelectrochemical applications of silicon are driven scientists to look for a new alternative to silicon. Now, sulfur has been attracting increasing attention due to its high electrochemical capacities as well as its abundance and environmental friendliness. Recently, α-sulfur was first reported by Cheng and coworkers as the visible light active elemental catalysts for photoelectrochemical water splitting and photodegradation of Rhodamine B, indicating new opportunities of sulfur as efficient photoelectrocatalysts for HER.[6] However, sulfur as catalyst is still in the bulk powder form.

Compared to bulk counterparts, nanoscale catalysts show the improved activities towards photocatalytic and photoelectrochemical HER owning to the size-related increase of surface area and active centers as well as the quick migration of photogenerated carriers to semiconductor surface.[7] For instance, silicon nanowires demonstrates the higher photoelectrochemical performance over solid film.[8] Thus, nanosized sulfur is expected to exhibit enhanced PEC activity than bulk sulfur. But, for sulfur, it is difficult to directly prepare its nanoscale shape due to the limited processability. And thermal ring-opening polymerization of elemental sulfur can lead to the formation of polymeric sulfur with poor mechanical properties. Copolymerization strategies have been utilized to develop the advantages of elemental sulfur by combination with other comonomers. Recently, Pyun and coworkers have reported a facile method to prepare high sulfur content copolymer with tunable thermomechanical properties and comparable electrochemical properties to elemental sulfur.[9] In addition, the doping of g-C_3N_4 with S species is effective to lower bandgap and improve photocatalytic activity of carbon materials.[10] Therefore, the nanoscale sulfur copolymer with high sulfur content may be highly active for HER.

Herein, we reported the fabrication of the poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB)) copolymer nanowires using anodic aluminum oxide (AAO) membranes as templates, and demonstrated for the first time that the sulfur copolymer nanowires were visible-light active for photoelectrocatalytic HER through water splitting with preservation of the photochemical properties of elemental sulfur. In addition, the photochemical behavior of the sulfur copolymer nanowires was highly dependent on the sulfur content and size of the copolymer nanowires with high resistance to photocorrosion. Furthermore, the copolymer nanowires were used as sulfur source and templates for fabricating metal sulfide/copolymer hybrid nanowires with potentially improved photoactivities.

The procedure for the synthesis of sulfur copolymer nanowires is displayed in Figure 1a. The bulk sulfur copolymers were synthesized by a reported copolymerized method named inverse vulcanization by Pyun and coworkers (see ESI† for details)[9]. Then, AAO membranes were used as templates for the preparation of copolymer nanowires with 80 wt%, 70 wt% and 50 wt% sulfur content, respectively (see ESI† for details). Typical scanning electron microscopy (SEM) images (Figure 1 b,c) clearly show that the nanowires are synthesized successfully in high yields with a length of about 10 μm and a diameter of ~200 nm when AAO membranes with a pore of ca. 200 nm was used. The electron energy loss spectroscopy (EELS) elemental mapping images (Figure 1 d, e) indicate the uniform distribution of S and C in the as-prepared sulfur copolymer nanowires. These results demonstrate that the sulfur copolymer nanowires can be synthesized successfully by introducing DIB into elemental sulfur through copolymerization, also confirm the successful manipulation of elemental sulfur into processable polymeric materials.

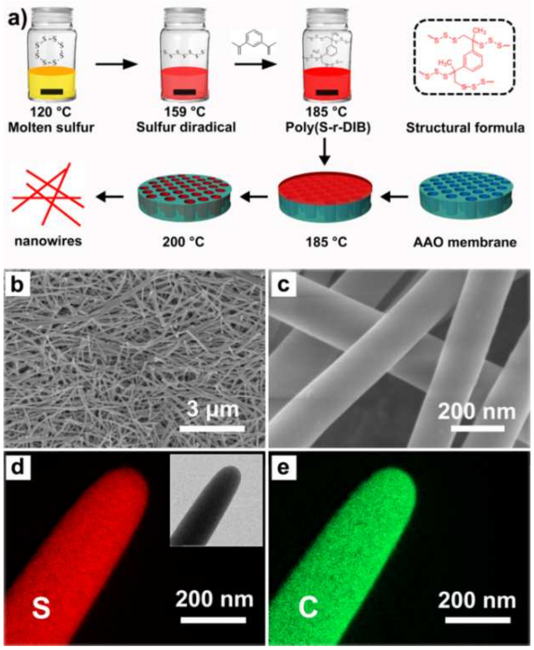

Figure 1. (a) Schematic representation of the synthesis of poly(S-r-DIB) copolymers and copolymer nanowires. (b,c) SEM images (d,e) EELS elemental mapping images of the sulfur copolymer nanowires fabricated by using AAO membranes as templates.

To improve the utilization of elemental sulfur, expand the chemical properties of sulfur copolymer, as well as develop the cheap and efficient photocatalyst, we investigate the photoelectrocatalytic hydrogen generation of the sulfur copolymer nanowires under visible light illumination. UV/Vis diffuse reflectance spectra (Figure 2a) shows that the spectrum of sulfur copolymer nanowires shifts to longer wavelengths with stronger absorption ability relative to the spectrum of α-sulfur crystal powder, indicating a decrease in the band gap of sulfur by incorporation into copolymer with DIB. As shown in Figure 2b, the photocurrent generated from sulfur copolymer nanowires increase remarkably with external bias voltage and reaches ~6.7 μA cm^{-2} at 0.8 V versus saturated calomel reference electrode (SCE), which corresponds to hydrogen evolution on Pt electrode. Meanwhile, the photocurrent is essentially negligible when the light turns off even at high potentials of 1.0 V vs. SCE, indicating the efficient generation and separation of the photo-induced charge carriers. However, the onset potentials of hydrogen generation on α-sulfur crystal powder and sulfur copolymer nanowires are 0.1 V and 0.25 V (vs SCE), respectively. These data mean that the apparent Fermi level or flat band potential of sulfur copolymer nanowires positively shift about 0.15 V relative to α-sulfur crystal powder.[11] On the one hand, We preliminarily think that the decrease of bandgap and the enhancement of photoelectrocatalytic activity of sulfur copolymer nanowires are associated with the fact that the conduction-band minimum (CBM) of sulfur is positively shifted by incorporation of DIB. On the other hand, the smaller size of the copolymer nanowires compared with bulk sulfur can enhance the visible light absorption capacity owing to the high specific surface area, and shorten the migration distance of photogenerated electrons and holes to reaction sites on the surface[12]. These results suggest that the manipulation of elemental sulfur into processable polymeric materials via copolymerization as photocatalyst can retain the photochemical activity of bulk α-sulfur.

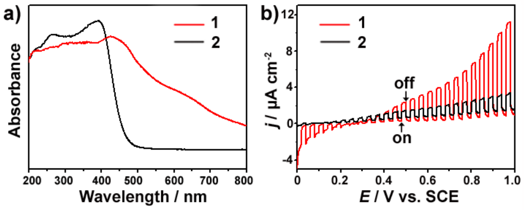

Figure 2. (a) UV/Vis diffuse reflectance spectra and (b) Photocurrent transients as a function of the applied potential for a photoanode sensitized with sulfur copolymer nanowires (1) and α-sulfur crystal powders (2) under repeated on/off cycles of visible-light illumination (λ> 420 nm) in 0.2 M Na_2SO_4, respectively.

To further explore the dependence of the photoelectroactivity of sulfur copolymer nanowires on their size and composition, we carry out the comparison experiments of sulfur copolymer nanowires with different sizes and sulfur contents. When the DIB content with 30 wt% is kept unchanged, the photocurrent of sulfur copolymer nanowires with a diameter of about 100 nm reach 12 μA cm^{-2} at 0.8 V vs. SCE, which is nearly 2 times higher than that of 200 nm (Figure 3a). Furthermore, the flat band potential shifts negative potential 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). These results indicate the size dependence of photoelectrocatalytic activity of sulfur copolymer due to the small size effect[12] (see Fig. S4, ESI†). In addition, the nanowires have an increased ability to absorb photons when the DIB contents increased from 20 wt% to 30 wt% (Figure 3c). However, the nanowires with DIB content about 50 wt% have a reduced ability to absorb photons than that of 30 wt%, suggesting that much more DIB content can cause blue shift in absorption spectrum (Figure 3c). Meanwhile, the flat band potential was found to positive shift from 0.14 V to 0.38 V (V vs SCE) when the DIB content increased from 20 wt% to 50 wt% (Figure 3b, ESI†, Figure. S5). In addition, copolymer nanowires with 30 wt% DIB show the highest photocurrent density compared with other contents (Figure 3b). Thus, 30 wt% DIB content is considered as the optimal composition of the sulfur copolymer nanowires for the highest PEC performance considering the photon absorption capacity, sulfur content and suitable flat band potential. It has been reported that the incorporation of the DIB contents ranging from 10-50 wt%, on the average, correspond to 44-10 S units per DIB unit of the copolymer.[9] Thus, we preliminarily think that sulfur is responsible for the visible light activity of the copolymer, and DIB has a direct effect on the energetics of the copolymer by adjusting the number of sulfur atoms in the ring unit. However, the origin of the synergistic effect mechanism of the sulfur and DIB is still needed for further investigation. In addition, the as-prepared sulfur copolymer nanowires exhibit high resistance to photocorrosion (see Figure S7, ESI†), and all of the short-circuit photocurrent response (Figure 3d) are prompt, steady, and reproducible, which also confirms the size and sulfur content dependence of the PEC activity.

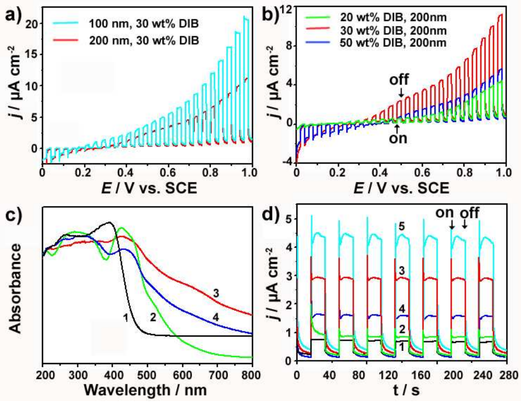

Figure 3 (a,b) Photocurrent transients as a function of the applied potential, (c) UV/Vis diffuse reflectance spectra, and (d) photocurrent-density response at an applied bias of 0.6 V versus SCE of sulfur copolymer nanowires with different diameters and DIB contents: (1) α-sulfur crystal powder; (2) 20% DIB, 200nm; (3) 30 wt% DIB, 200nm; (4) 50 wt% DIB, 200nm; (5) 30 wt% DIB, 100 nm

Furthermore, the 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 ESI† for details). This unique heterogeneous structure may be helpful to facilitate the separation of charge carriers and improve the corresponding photoelectrochemical activities.[13] Electrochemical impedance spectroscopy (EIS) confirms the enhanced charge transfer rate of semiconductor-electrolyte interface after in-situ growing CdS nanoparticles (see Figure S11, ESI†).[14] The coupling of metal sulfides and sulfur copolymers by in situ growth on the surface of sulfur copolymers opens up new opportunities of elemental sulfur as efficient photocatalysts.

In summary, we have demonstrated for the first time that sulfur copolymer nanowires can be used as visible-light-active photoelectrocatalysts for water splitting. These as-prepared sulfur copolymer nanowires exhibit improved PEC activity over bulk α-S powder, which may be associated with the high visible light absorption capacity and the narrower bandgap of the nanosized copolymer structures. The incorporation of DIB is found to have a direct effect on the energetics of the copolymer by adjusting the number of sulfur atoms in the ring unit and the flat band potential of the copolymer nanowires. In addition, the photoelectrochemical performance of the sulfur copolymer nanowries is determined by the sulfur content and size of the nanowries with high resistance to photocorrosion, making them promising inexpensive photoelectrocatalysts for HER. Furthermore, the sulfur copolymer nanowires are found to be utilized as sulfur source and templates for creating metal sulfide/copolymer heterocatalysts. Our work may open up interesting possibilities to develop low-cost efficient visible-light-responsive catalysts and optoelectronic devices by transforming bulk sulfur to easy-processable sulfur copolymers and metal sulfide/copolymer hybrid nanostructures.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures and additional characterization results. See DOI: 10.1039/c000000x/

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