Photoenergy Storage

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Integrating a Photocatalyst into a Hybrid Lithium–Sulfur Battery for Direct Storage of Solar Energy**

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Abstract: *Direct capture and storage of abundant but intermittent solar energy in electrical energy-storage devices such as rechargeable lithium batteries is of great importance, and could provide a promising solution to the challenges of energy shortage and environment pollution. Here we report a new prototype of a solar-driven chargeable lithium–sulfur (Li-S) battery, in which the capture and storage of solar energy was realized by oxidizing S^{2-} ions to polysulfide ions in aqueous solution with a Pt-modified CdS photocatalyst. The battery can deliver a specific capacity of 792 $mAh\,g^{-1}$ during 2 h photocharging process with a discharge potential of around 2.53 V versus Li^+/Li. A specific capacity of 199 $mAh\,g^{-1}$, reaching the level of conventional lithium-ion batteries, can be achieved within 10 min photocharging. Moreover, the charging process of the battery can proceed under natural sunlight irradiation.*

Solar energy as the largest renewable energy source is regarded as a most promising candidate for addressing the challenges of fossil fuel shortage and environment pollution issues facing current society.[1] The prerequisite of enabling continuous utilization of solar energy is the effective storage and dispatching on demand to the end users in view of the intermittency and low-energy density of solar light. Storage of solar energy in electrochemical devices such as rechargeable lithium batteries provides an attractive approach of reaching this purpose. Currently, the dominant route of storing solar energy in the form of electrical energy involves the conversion of solar energy to electricity in photovoltaic cells and subsequent storage of electricity in electrochemical energy-storage devices such as supercapacitors and lithium batteries. To simplify the storage process of solar energy in the form of electricity, some early attempts have focused on the direct integration of photovoltaic cell and capacitor/battery into one device with the dual function of conversion and storage of solar energy to electricity.[2] However, up to now, electrical energy-storage devices hybridized with photovoltaic cells exhibit low storage capacity,[2] which is inadequate for large-scale solar-energy storage and long-term operation. Moreover, the use of embedded photovoltaic cells greatly increases the cost and also causes additional reliability issues. Consequently, the direct and massive storage of solar energy in electric energy-storage devices without using photovoltaic cells is highly desirable yet remains a challenge.

Here, in contrast to the past designing of using photovoltaic cells to realize solar-energy conversion in the device containing energy-storage component, we for the first time introduce Pt/CdS photocatalyst in an aqueous polysulfide cathode to realize the conversion and storage of solar energy in the Li-S battery, whose theoretical specific capacity is three to five times higher than that of conventional lithium-ion batteries.[3] During the photocharging process, the S^{2-} ions produced in the discharging process are oxidized to polysulfide ions by photoexcited holes from the photocatalyst. The designed cathode of the Li-S battery delivers a specific discharge capacity of 792 $mAh\,g^{-1}$ after 2 h light irradiation. Moreover, hydrogen as an ideal clean fuel with the largest heating value (120 $MJ\,Kg^{-1}$),[4] is simultaneously produced through the reduction of protons induced by the photoexcited electrons from the photocatalyst. The most remarkable feature of this device is the simultaneous realization of both electrochemical storage and chemical fuel conversion of solar energy in one device.

The two-electrode solar-energy-storage device consists of a lithium anode with organic electrolyte, a $Li_{1.35}Ti_{1.75}Al_{0.25}P_{2.7}Si_{0.3}O_{12}$ (LATP) glass ceramic separator and an aqueous Li_2S_n ($1 \leq n \leq 4$) alkalic cathode containing Pt/CdS photocatalysts (Scheme 1 a). The aqueous dissoluble polysulfide electrode not only has higher reaction activity than the solid electrode,[5] but also reduces the heating effect during long-term light irradiation. The discharging process is the same as that of a common aqueous Li-S battery (reaction 1; Scheme 1 b). However, the charging process is achieved by solar-driven photocatalytic oxidation of the discharge product S^{2-} ions back to polysulfide ions using Pt/CdS photocatalysts (reaction 2). Meanwhile, the photoexcited electrons, freed from the Coulomb attraction of the holes, are transferred to the Pt nanoparticles loaded on CdS. These electrons will reduce protons to release hydrogen, which can be collected by designing an open system at the aqueous cathode part. By doing this, the stringent safety requirements

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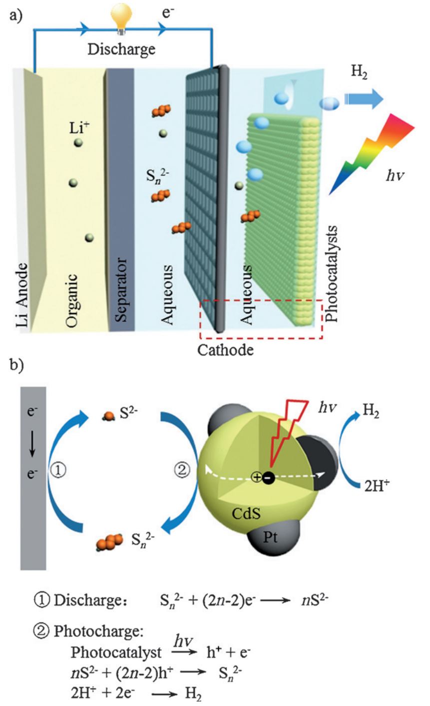

Scheme 1. a) The battery consists of a Li anode with organic electrolyte, a Li-ion conductive LATP glass ceramic separator, and an aqueous Li_2S_n ($1 \leq n \leq 4$) alkalic catholyte containing the Pt/CdS photocatalysts (coated on Ti mesh). b) The discharging process is the same as that of a common aqueous Li-S battery. However, the charging process is different, the discharge product S^{2-} ions are oxidized to polysulfide ions by photoexcited holes from the CdS photocatalyst driven by light irradiation. Meanwhile the photoexcited electron, freed from the Coulomb attraction of the hole, transfers to the Pt particle, where it then reduces protons to hydrogen.

of batteries can be well satisfied. CdS was chosen in our device based on the fact that sulfide electrolytes are generally used as efficient sacrificial agents to be oxidized by photoexcited holes of CdS to polysulfide ions for impeding electron–hole pair recombination in the photocatalytic water-splitting reaction.[6] Loading Pt nanoparticles on CdS as reducing co-catalyst can effectively lower the overpotential for the water reduction reaction.[7] The Pt/CdS is therefore an ideal photocatalyst candidate to induce the targeted oxidation of the discharge product S^{2-} ions to the charge products polysulfide ions by following the reaction $nS^{2-} + (2n-2)h^+ \rightarrow S_n^{2-}$ ($2 \leq n \leq 8$).

The high-resolution transmission electron microscopy (HRTEM) image in Figure 1a clearly shows two distinct types of lattice fringes, which are assigned to CdS and Pt. The average sizes of CdS and Pt nanoparticles obtained are around 8 and 4 nm, respectively. The fast-Fourier transform (FFT) pattern (inset in Figure 1a) indicates that Pt can be identified because of its characteristic (111) diffraction spots. The composite Pt/CdS was also analyzed by X-ray diffraction (XRD), as shown in Figure 1b. Three broadened diffraction peaks attributed to the (111), (220), and (311) planes of CdS consistently suggest the small crystal size of as-prepared CdS particles. No peak assigned to Pt could be identified due to the low content. The ultraviolet (UV)-visible absorption spectrum of Pt/CdS shows an absorption edge at about 540 nm (Figure 1c), which suggests that the photocatalyst can efficiently absorb visible light.

The device was first discharged to 2.3 V versus Li^+/Li at a rate of 0.1 mA cm^{-2} (Figure 1d, left), delivering a specific capacity of 1066 mAh g^{-1}. The S_4^{2-} ions are reduced to S^{2-} ions during the discharge process, as indicated by the clear color change of the electrolyte from yellow to transparent. The solar-energy-storage device is then irradiated by a 500 W Xe-lamp to realize the charging process. The electrolyte color reverted to the original yellow color after prolonged light irradiation (Figure 1d, middle), indicating that the S^{2-} ions are oxidized to polysulfide ions by photoexcited holes from the CdS photocatalyst. After 2 h irradiation, the device can deliver a specific discharge capacity of 792 mAh g^{-1} ($\approx 47.2\%$ of the theoretical specific capacity for conventional Li-S battery) at a rate of 0.1 mA cm^{-2} as shown in the second discharge curve (Figure 1d, right). Meanwhile, the photoexcited electrons reduce protons to release hydrogen and vigorous bubbles of hydrogen were observed on the surface of the Pt/CdS photocatalyst.

On the basis of the fact that the number of photoexcited electrons is equal to that of photoexcited holes, the rate of hydrogen evolution is estimated to be about 1.02 mmol g^{-1} h^{-1} according to the number of electrons stored in the device. To confirm and quantify the hydrogen generation observed in the

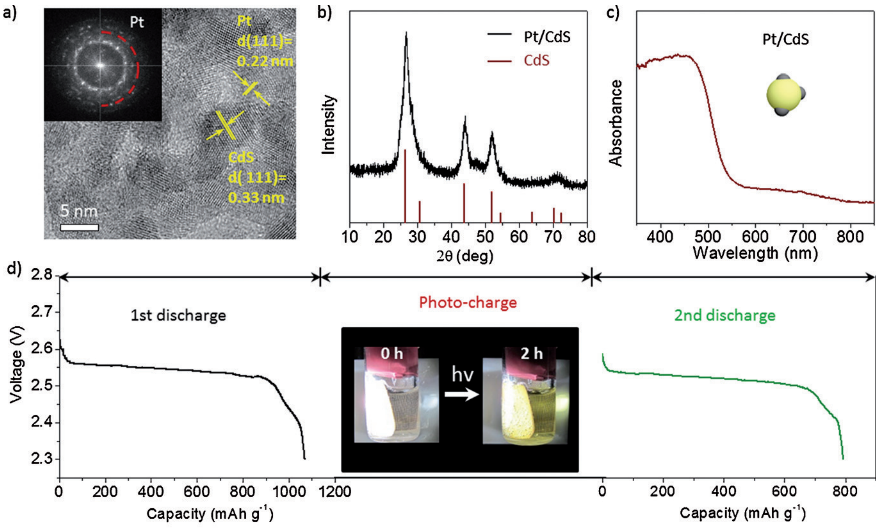

Figure 1. a) HRTEM image of Pt/CdS photocatalyst. The inset is the FFT of the HRTEM image. b) XRD pattern and c) UV-visible absorption spectrum of Pt/CdS photocatalyst. d) The initial discharge curve and discharge curve after 2 h photocharging of the Li-S battery. Middle picture showing the color change of the catholyte before (left) and after (right) 2 h irradiation.

developed solar-energy-storage device, a photocatalytic hydrogen-generation test from Pt/CdS photocatalyst in 0.01 M Li_2S aqueous solution under light irradiation was carried out. The produced gas was monitored and quantified by gas chromatography (GC). The corresponding hydrogen production rate is around 3.04 mmol $g^{-1}h^{-1}$ as presented in Figure S2. The discrepancy of the hydrogen evolution rate measured from the photocatalytic water splitting system and that calculated from the stored electrons in the Li-S battery could be attributed to the different reaction conditions in two situations. However, this result does provide clear evidence for the hydrogen production.

On the other hand, the device can also be electrochemically charged (Figure S1). The 1st discharge, 1st charge, and 2nd discharge capacity is 1073, 807, and 793 mAh g^{-1}, respectively. The electrochemical charging process takes 11 h, which is 5.5 times longer than the photocharging process. The discharge capacity after different irradiation time was further investigated. After the irradiation for 1 h, 30 min, and 20 min, the subsequent discharge capacities are 602, 407, and 317 mAh g^{-1} at the rate of 0.1 mA cm^{-2} (Figure 2a). A shorter light irradiation of 10 min can still deliver a specific capacity of 199 mAh g^{-1}, reaching the level of conventional lithium-ion batteries. As expected, the discharge capacity increases with increasing irradiation intensity (Figure S3). It is noted that the discharge capacity decreased with a prolonged irradiation time of 2 h (Figure 2b). For instance, a discharge capacity of 762 mAh g^{-1} was achieved after 3 h irradiation, which is slightly lower than that after 2 h of irradiation.

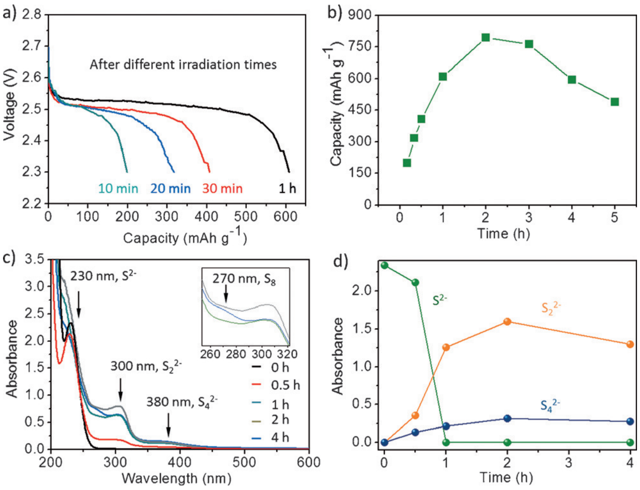

Figure 2. a) The discharge curves at different irradiation times. b) Specific discharge capacity versus irradiation time. c) UV-visible absorption spectra of catholyte at different irradiation times. d) Absorption intensity of S^{2-}, S_2^{2-}, and S_4^{2-} ions versus irradiation time. Intensities of S_2^{2-} and S_4^{2-} ions have doubled.

To understand the non-monotonic dependence of discharge capacity on irradiation time, the variations of polysulfide species in catholyte after different irradiation times were monitored by UV-visible absorption spectroscopy. As shown in Figure 2c, only one peak at 230 nm assigned to S^{2-} is observed before irradiation,[8] indicating complete discharge and no residue of high-order polysulfide ions. After 30 min irradiation, the peaks assigned to S_2^{2-} and S_4^{2-} species are identified in the spectra, suggesting that the S_2^{2-} and S_4^{2-} ions were simultaneously generated by photocatalytic oxidation of S^{2-} by Pt/CdS photocatalyst under light irradiation. The peaks of the S_2^{2-} and S_4^{2-} species become stronger with prolonged irradiation time, and the peak for the S^{2-} species becomes weaker and gradually disappears (Figure 2d). These results further verify the photocharging process. It is worth mentioning that the elemental sulfur (S_8) species with its characteristic peak at about 270 nm is identified after 4 h irradiation in Figure 2c,[9] which indicates that the S_2^{2-} and S_4^{2-} ions are further oxidized to S_8 with prolonged light irradiation by following the reaction $8\,S_n^{2-}\ (2 \leq n \leq 4) + 16n\,h^+ \rightarrow n\,S_8$. Therefore, the peaks of the S_2^{2-} and S_4^{2-} species become weaker after 2 h irradiation. The insoluble S_8 species is not able to acquire electrons from the current collector and consequently causes the capacity loss. The decreasing capacity with a prolonged irradiation could be attributed to the generation of solid-state S_8, which is a consequence of the overoxidation of S^{2-} ions by Pt/CdS photocatalyst. Therefore, overcharging should be avoided by controlling the irradiation time. The optimal light irradiation time for the photocharging is determined to be 2 h in the current study.

To evaluate the stability of this device, we studied the photocharging cycling performance (Figure 3a). After ten cycles (10 min photocharging and then discharging), the battery can still deliver a capacity of 185 mAh g^{-1}, exhibiting a 92.5 % capacity retention compared with the first discharge capacity (201 mAh g^{-1}). No detectable change of XRD

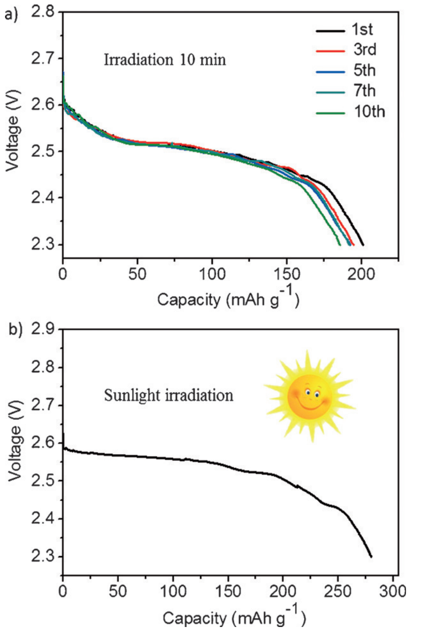

Figure 3. a) The discharge curves at a rate of 0.1 mA cm^{-2} after 10 min irradiation for ten cycles. b) The discharge curve at a rate of 0.1 mA cm^{-2} after 2 h natural sunlight irradiation. The sunlight irradiation started from 11:00 a.m. to 1:00 p.m. on September 2, 2014, National Institute of Advanced Industrial Science and Technology, Japan.

patterns was found after ten cycles of charge/discharge, suggesting the good stability of the photocatalyst (Figure S4). Concerning the practical application, the device was exposed to natural sunlight irradiation for the photocharging process. Excitingly, a capacity of 280 $\mathrm{mAh\,g^{-1}}$ was achieved after 2 h sunlight irradiation (Figure 3b).

Different from the previously reported photo-rechargeable battery, which is actually an integrated pack of a dye-sensitized solar cell and an electrochemical battery, the newly developed device in this work realized the direct storage of solar energy in a Li-S battery without using photovoltaic cells. It consists of a lithium anode, a LATP glass ceramic separator and an aqueous Li_2S_n ($1 \leq n \leq 4$) alkalic cathode containing Pt/CdS photocatalyst. Besides, hydrogen as an ideal clean energy carrier for a hydrogen/air fuel cell (Figure S5) can be produced and collected during the photocharging process. Accordingly, the massive electrochemical storage and chemical fuel conversion were simultaneously realized in a single device. This energy-storage system can be easily scaled up with a reasonably increased energy density by combining a flow-through-mode system.

In summary, we proposed a novel solar-energy-storage device, which enables fast capturing and storing solar energy in a Li-S battery without using photovoltaic cells, accompanied with hydrogen generation. The device delivered a discharge capacity of 199 $\mathrm{mAh\,g^{-1}}$ after 10 min photocharging, which is higher than that of most conventional cathode materials for lithium-ion batteries, such as $LiFePO_4$ ($\approx 170\ \mathrm{mAh\,g^{-1}}$), $LiCoO_2$ ($\approx 140\ \mathrm{mAh\,g^{-1}}$), and $LiMn_2O_4$ ($\approx 148\ \mathrm{mAh\,g^{-1}}$). It is worth pointing out that our device also allows photocharging under sunlight irradiation and delivers a discharge capacity of 280 $\mathrm{mAh\,g^{-1}}$ after 2 h sunlight irradiation. Meanwhile, the corresponding hydrogen generation rate during the photocharging is determined to be 1.02 $\mathrm{mmol\,g^{-1}\,h^{-1}}$. For the first time, we realize simultaneous electrochemical storage and hydrogen production by introducing a photocatalyst into a Li-S battery, thereby opening a new avenue for the direct and large-scale storage of solar energy.

Keywords: electrochemical storage · hydrogen · lithium-sulfur battery · photocatalysis · solar energy storage

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