Photoelectrochemical regeneration of all vanadium redox species for construction of a solar rechargeable flow cell

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ABSTRACT

Energy storage is pivotal for the continuous utilization of solar energy suffering from the intermittency issue. Herein, we demonstrate a solar rechargeable flow cell (SRFC) based on photoelectrochemical regeneration of vanadium redox species for in-situ solar energy harvest and storage. In this device, TiO_2 and MWCNT/acetylene black (MWCNT/AB) composite are served as the photoanode and the counter electrode, respectively, with all vanadium redox couples, VO_2^+/VO^{2+} and VO^{2+}/V^{3+}, as solar energy storage media. Benefitting from solar energy, the cell can be photocharged under a bias as low as 0.1 V, which is much lower than the discharge voltage of $\sim$0.5 V. Photocharged under the optimized condition, the cell delivers a discharge energy of 23.0 mWh/L with 67.4% input electric energy savings. This prototype work may inspire the rational design for cost-effective solar energy storage devices.

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1. Introduction

Due to the intermittent nature of sunlight, solar energy utilization via photovoltaic devices meets with insurmountable limitations in practical applications [1–5]. Converting solar-electricity into chemical energy stored in external electrochemical energy storage devices could address the above issue [6–9]. However, this approach suffers from the problems such as the complicated structure and substantial energy loss during the multistep energy conversion and storage process [10]. Therefore, it is highly desirable to develop a device with simplified processes for the direct capture and storage of solar energy.

Photoelectrochemical (PEC) synthesis of useful chemicals presents an alternative approach to storing solar energy in the form of chemical energy. If the reversible redox couples are applied as active species in the PEC conversion reactions, the products may be utilized on demand in a rechargeable battery. In this regard, preliminary efforts have been devoted to combining photoelectrolysis cells with energy storage devices. For instance, early researchers introduced a dye sensitized solar cell (DSSC) into an energy storage device for simultaneous solar energy harvest and storage [11–13]. However, the devices encounter challenges such as large internal resistance of brittle ceramic separators with low conductivity and high cost of noble metal platinum. Up to now, intensive efforts have been directed for improving the performance of the integrated devices [14–16]. Recently, our group reported an efficient solar rechargeable flow cell (SRFC) based on a dual-silicon PEC cell and a water-soluble quinone/bromine redox flow battery (RFB), achieving an overall solar energy conversion efficiency of 3.2% for the complete photocharge/discharge cycle [14]. Thus, PEC regeneration of electroactive species to directly charge all-aqueous SRFCs represents an ideal approach for in-situ solar energy conversion and storage.

Vanadium redox flow battery (VRB) has been considered as a promising candidate for large-scale energy storage because of its advantages like the long cycle life, the decoupling of power and energy, and the facility of electrolyte regeneration when the cross contamination occurs [17]. The standard redox potential of the couple VO_2^+/VO^{2+} is 1.000 V vs. RHE, which is about 0.23 V more negative compared to that of the water oxidation reaction $(2H_2O{\rightarrow}4H^+ + O_2 + e^-$ 1.229 V vs. RHE) and is helpful for reducing the influence of oxygen evolution reaction (OER). Furthermore, it is indicated that PEC oxidation of VO^{2+} has been realized on the surface of common semiconductors [18–20]. In view of these matters, the vanadium redox couples could be potential electroactive species for a SRFC.

Herein, we report a SRFC system based on all vanadium redox couples, in which TiO_2 and MWCNT/acetylene black (MWCNT/AB) composite with a large hydrogen evolution reaction (HER) overpotential are served as the photoelectrode and the counter electrode, respectively. The redox couples VO_2^+/VO^{2+} and VO^{2+}/V^{3+}

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(0.334 V vs. RHE), thermodynamically more favorable than water splitting reactions, are employed as the active species in anolyte and catholyte, respectively. The anode and cathode compartments are separated by a Nafion 117 membrane to conduct the protons and prevent the contamination of the redox couples. Upon illumination, the cell can be photocharged under an ultralow bias of 0.1 V, which is much lower than discharge voltage of $\sim$0.5 V. Photocharged under the optimized condition, the cell delivers a discharge energy of 23.0 mWh/L, 67.4% of which is contributed by solar energy. The feasibility of this new configuration of the SRFC paves the way for in-situ solar energy conversion and storage.

2. Experimental

2.1. Fabrication of photoelectrodes and counter electrodes

The TiO$_2$ photoelectrodes were prepared by employing a hydrothermal method [21]. In a typical synthesis, 15 mL concentrated HCl and 15 mL deionized water were mixed and stirred for 5 min, and then 0.4 mL titanium butoxide was dropped into the mixture under magnetic stirring. After stirring for another 10 min, the solution and a clean FTO glass substrate were transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 3 h. After the heating period, the autoclave was cooled to room temperature under a slow stream of tap water. The substrate was thoroughly rinsed with deionized water, dried in air, and finally treated in air at 450 °C for 1 h. In order to define the active area of photoelectrode ($\sim$3 cm^2), the substrate edges and the metal contact region were sealed with nonconductive epoxy resin.

Counter electrodes were prepared as follows. The pristine MWCNT was treated by refluxing in mixed acid (H$_2$SO$_4$:HNO$_3$ = 3:1 in volume) at 70 °C for 8 h [22,23]. Afterward, the treated sample was filtered, washed extensively with deionized water to pH 7, and dried at 60 °C. The modified MWCNT was mixed with acetylene black and polyvinylidene difluoride (8:1:1 in weight) in N-methyl-2-pyrrolidinone. Finally, the mixture was coated onto a graphite plate and dried at 60 °C before use. The working area of counter electrodes (MWCNT/AB) was $\sim$3 cm^2.

2.2. Physical and PEC characterization

The morphology of the TiO$_2$ was examined using a scanning electron microscopy (SEM, Quanta 200FEG).

The photoresponse measurement of the photoelectrode was performed using a three-electrode configuration with the TiO$_2$, saturated calomel electrode (SCE), and MWCNT/AB as working, reference and counter electrode, respectively. The electrolyte used was 0.05 M VOSO$_4$ + 0.1 M H$_2$SO$_4$ solution in all cases unless otherwise specified. Linear sweep voltammetry was recorded by a CHI 760D electrochemical workstation (Shanghai Chenhua Instruments, China) with a scanning rate of 50 mV/s. To simulate solar irradiation, the light source was a Xe lamp (300 W, PLS-SXE 300C) and the intensity was 100 mW/cm^2. For all PEC measurements reported herein, photoelectrode was illuminated from the backside side and ultrahigh purity Ar was bubbled to remove the dissolved oxygen from the solution. The MS plot was measured on a PARSTAT 2273 electrochemical workstation (Princeton Applied 20 Research) in 0.05 M VOSO$_4$ + 0.1 M H$_2$SO$_4$ electrolyte (pH 0.71).

2.3. Solar rechargeable flow cell tests

The photocharge process of the SRFC was carried out in a homemade two-electrode photo-reactor. The TiO$_2$ photoelectrode and MWCNT/AB composite were employed as working electrode and counter electrode, respectively. Both of the initial anolyte and catholyte were 3.8 mL 0.05 M VOSO$_4$ + 0.1 M H$_2$SO$_4$ solutions,
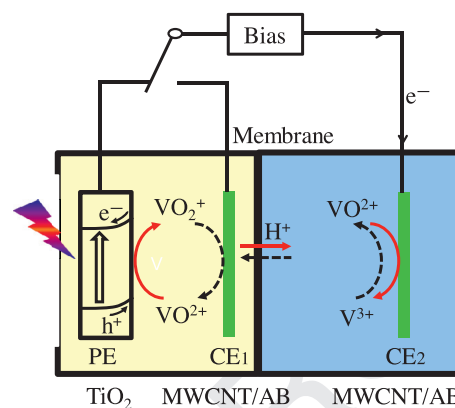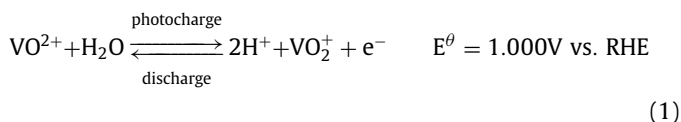

Fig. 1. Schematic diagram of the solar rechargeable flow cell.

which were continuously bubbled with ultrahigh purity Ar during the tests. I–t tests under different biases were measured by a CHI 760D electrochemical workstation under 100 mW/cm^2 irradiation with a 300 W xenon lamp. All measurements reported herein were run with the backside illumination. After irradiation, the concentrations of VO^{2+} in both anolyte and catholyte were analyzed with UV–visible (UV–vis) spectrophotometer. The cell was galvanostatically discharged at a current of 0.1 mA on Neware battery testing system, while two pieces of graphite plate with MWCNT/AB were used as positive and negative electrodes, respectively. The lower limit of discharge voltage was 0.01 V.

By comparison, control experiments were conducted as follows. PEC water splitting reactions were also measured with the backside illumination, replacing the 0.05 M VOSO$_4$ + 0.1 M H$_2$SO$_4$ electrolytes with blank H$_2$SO$_4$ solutions. Afterward, the discharge of the cell was evaluated in the same way. Electrolysis experiments were carried out without illumination, replacing the photoelectrode with the counter electrode.

3. Results and discussion

Fig. 1 illustrates the configuration and working principle of the SRFC that employs VO$_2^+$/VO^{2+} and VO^{2+}/V^{3+} as the electroactive species. The anode compartment is fitted with TiO$_2$ (nanorod arrays in morphology, Fig. S1) as photoanode (PE) during photocharge and MWCNT/AB as positive electrode (CE$_1$) during discharge. The cathode compartment contains MWCNT/AB (CE$_2$) working as counter electrode during photocharge and negative electrode during discharge. During photocharge process, the PE and CE$_2$ are connected, while the CE$_1$ is open-circuit. Once illuminated, PE will absorb the photons of $h\nu > E_g$. Subsequently, electrons will jump from the valance band to the conduction band. Driven by the electric field existing in the space charge region, the minority carriers (h$^+$) sweep toward the surface to participate in the oxidation reaction of VO^{2+}; while the majority carriers (e$^-$) migrate to the counter electrode via the external circuit to take part in the reduction reaction of VO^{2+}. In this regard, the photogenerated electrons and holes are separately stored in the redox couples. During the discharge process, the CE$_1$ and CE$_2$ are short-circuited and the discharge reactions of the battery take place at the surface of counter electrodes. Cell reactions involved in the above-described process could be written as follows:

$$VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{photocharge}}{\rightleftharpoons}} 2H^+ + VO_2^+ + e^- \qquad E^\theta = 1.000V \text{ vs. RHE}$$

(1)