Supporting Information

Photo-assisted Rechargeable Battery: Synergy, Compatibility and Stability of TiO_2/dye/Cu_2S Bifunctional Composite Electrode

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Experiments

Materials

FTO conductive glasses are purchased from Zhuhai Kaivo Optoelec-tronic Technology Co., Ltd. N719 was purchased from Kunshan Sunlaite Co., Ltd. Pt counter electrodes are purchased from Dalian seven colors solar energy technology Co., Ltd. Acetone, ethanol, ethylene glycol and methanol were purchased from Beijing Chemical Works. CuCl and thiourea were purchased from Shanghai Chemicals. Polyvinylpyrrolidone (PVP), PVDF, $Cd(CH_3COO)_2{\cdot}2H_2O$, Na_2S and NMP were supplied by Aladdin. LiTFSI was obtained from DodoChem Reagent, Suzhou, China. All chemicals were used directly without further purification.

Preparation of electrode materials

The p25 paste is prepared according to previous work.[1] Briefly, the paste is prepared by mixing ethye cellulose (0.4 g), α-terpinol (3.2 g), and P25 (0.8 g) in ethanol (8.5 ml), followed by stirring.

To synthesis Cu_2S, a mixed solution including 20 mL alcohol, 20 mL ethylene glycol, 0.25 g CuCl, 0.3 g PVP, and 0.3 g thiourea are prepared and transferred into

an autoclave for heating 12 h at 150 °C. After centrifuging and washing, the product is dried and grinded for later use.

Preparation of bifunctional compatible electrodes

The Cu_2S based bifunctional electrode for photoelectric conversion and energy storage is made of three steps. Firstly, the mesoporous TiO_2 film is prepared by spin-coating of as-prepared TiO_2 paste on the FTO substrate, followed by drying and sintering at 450℃. Secondly, the TiO_2 film was soaked in N719 included solution for 24 h to prepare dye-sensitized photoanode. Finally, the Cu_2S paste (8:1:1 of Cu_2S, PVDF and carbon black in NMP) is deposited on the surface of photoanode by doctor blade method, and followed by drying.

To compare, two reference bifunctional compatible electrodes are fabricated, which are based on photoanode of CdS quantum dot (QD) sensitized solar cells. CdS QDs deposited on the mesoporous TiO_2 film are prepared by successive ion layer absorption and reaction (SILAR) method: the TiO_2 photoanode was alternately dipped into $Cd(CH_3CO_2)_2$ and Na_2S for 30s/dip for 8 cycles and rinsed with methyl alcohol. Two kinds of methods are used to prepare copper sulfide on CdS sensitized TiO_2 photoanode: (1) The Cu_2S paste mentioned above is pasted on the surface of CdS sensitized TiO_2 photoanode by doctor blade method. (2) The Cu_xS was made by SILAR method grown directly on the surface of photoanode according to in-situ grown copper sulfide method.[2] Typically, the photoanode was alternately dipped into

0.06 M $CuSO_4$ and 0.09 M Na_2S aqueous solution for 30s/dip and rinsed between every dips.

Electrochemical measurements

The photo-response of integrated device was measured by recording the changing of voltage during light (50s) and dark (50s). It was scanned at the rate of 0.1mV/s with no additional voltage. The galvanostatic charge and discharge were tested at 0.1mA from 1.6 - 3.2V. For the process of photo-response charging, the light source was turned off when the device was charged to 3V. Cyclic voltammetry was measured from 1.5 to 3.4V at a scan rate of 0.5 mV/s in dark. These measurements were recorded by electrochemical workstation. The other galvanostatic charge and discharge with and without illumination were measured by LAND. For comparison to the integrated device, the galvanostatic charge and discharge of alone Cu_2S as cathode (lithium ion battery) was tested at 0.15 and 0.3C (1 C=337 mA g-1). The photo-assisted charge and discharge of integrated device were measured at 0.3C. The range of voltage was set from 1.6 to 3.2V.

Characterization

Morphologies and structures were analyzed by XRD (D-MAX II A X-ray diffractometer) and SEM (S4800, Hitachi). Power conversion efficiency (PCE) is characterized by AM 1.5 solar simulator (Zolix), and the active area of photoanodes and bifunctional compatible electrodes were 0.36 cm^2. The integrated battery was texted with electrochemical workstation (CHI660e, Shanghai, China) and LAND

(LAND-CT2001A, Wuhan, China) with or without light, and the light source is 150 W Xe lamp (LSP-X150, Zolix).

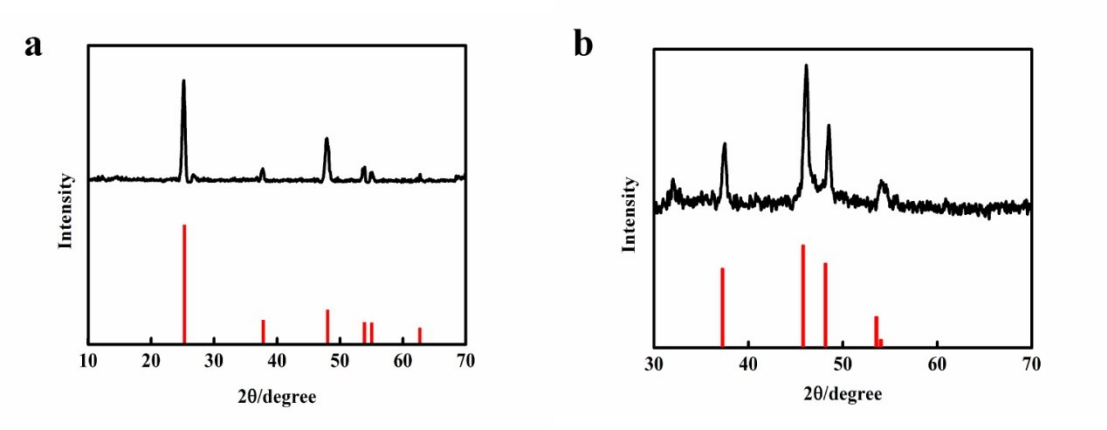

Figure S1. Characterization of materials. The XRD patterns of a) TiO_2 and b) Cu_2S of the composite electrode.

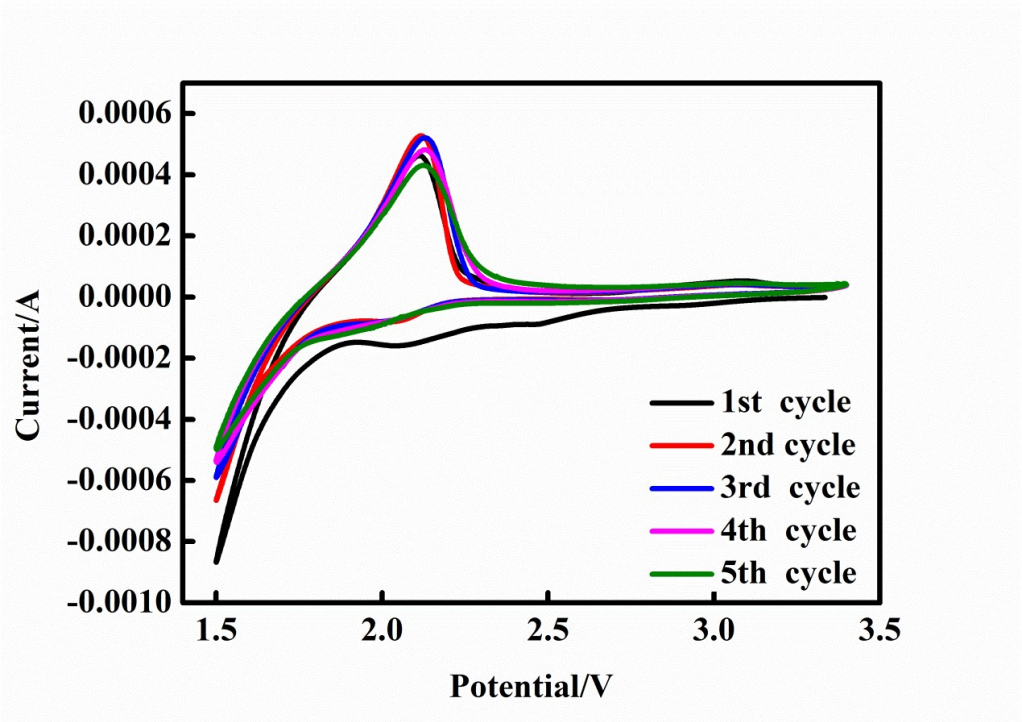

Figure S2. Electrochemical characterizations of of integrated battery. CV of integrated photo-assisted rechargeable battery at the scan rate of 0.5mV/s in dark.

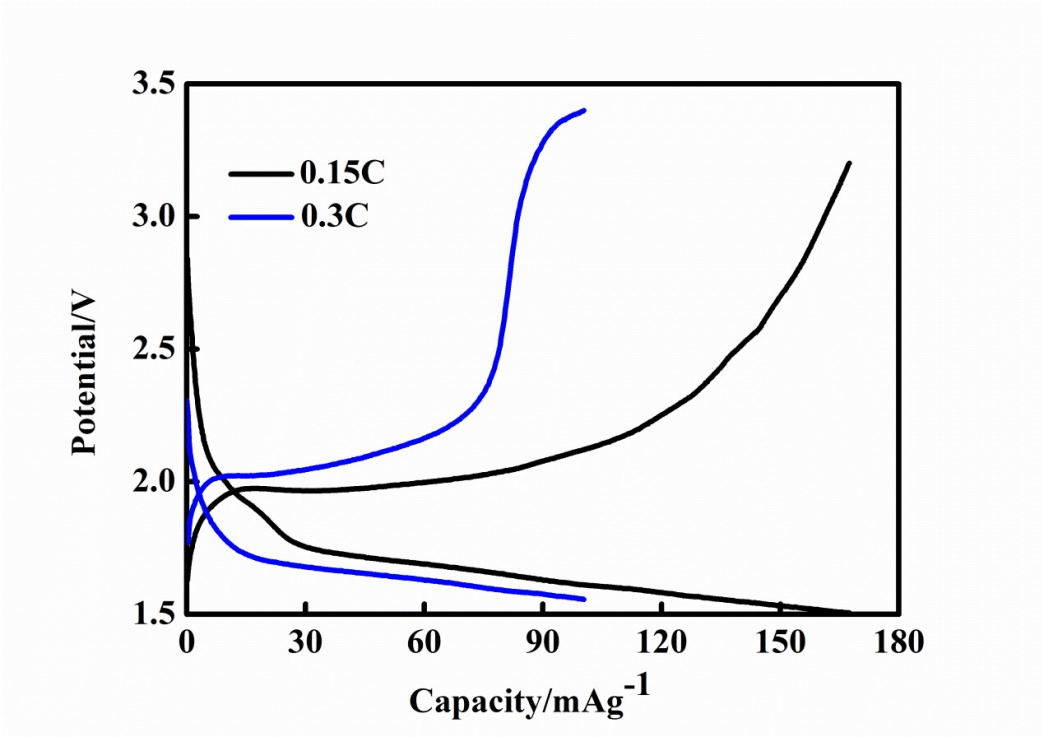

Figure S3. Galvanostatic charge/discharge curves at 0.15C and 0.3C for first cycle of lithium ion battery (FTO/Cu_2S/LiTFSI electrolyte/metallic Li) in dark.

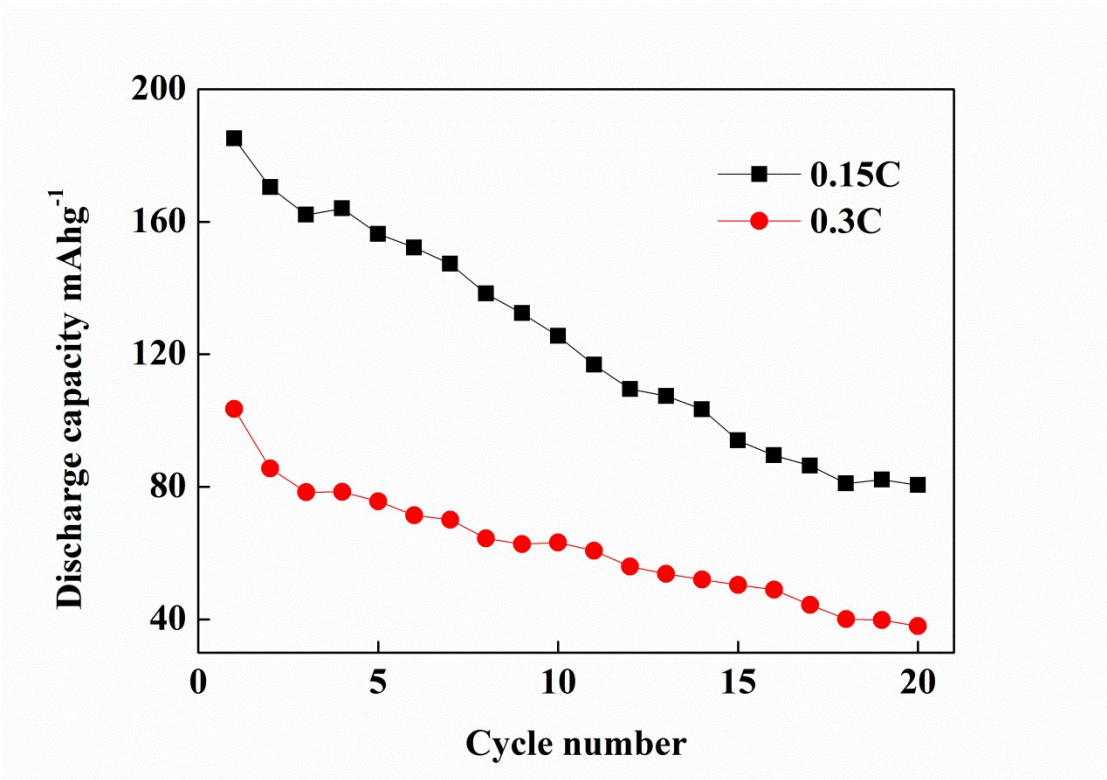

Figure S4. Cycling curves for the lithium ion battery at 0.15C and 0.3C in dark.

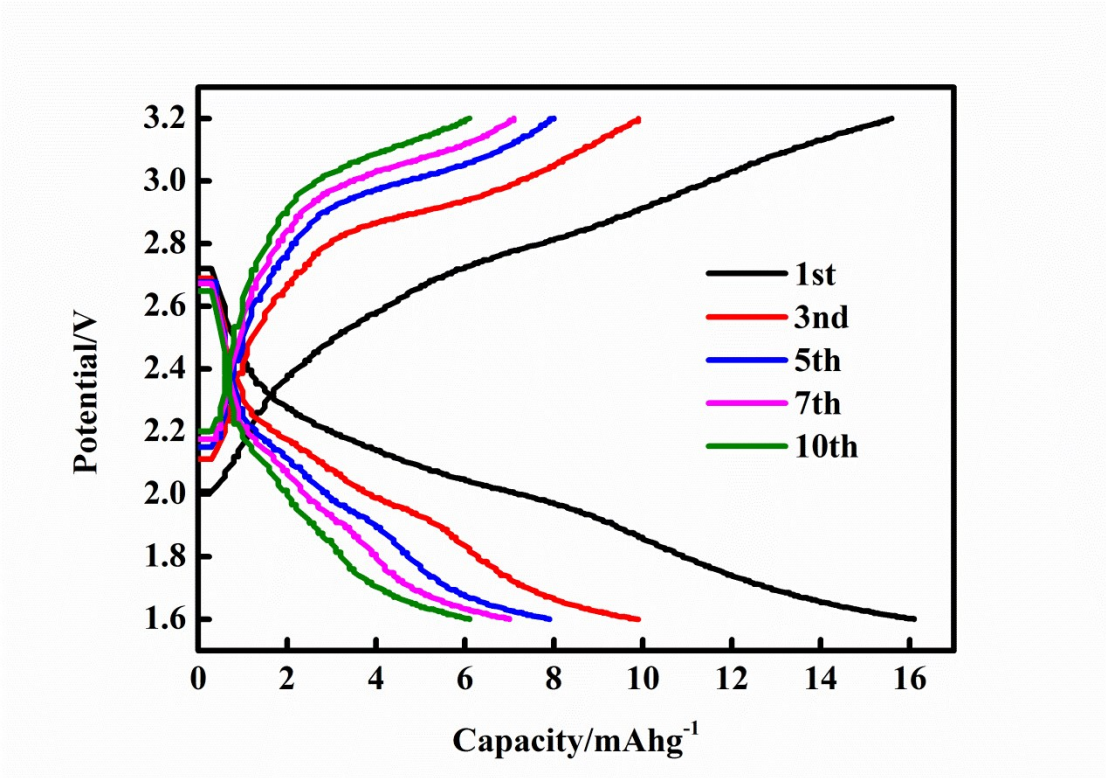

Figure S5. Galvanostatic charge (with illumination)-discharge (without illumination) curves for 10 cycles.

Reference

1 J. R. Jennings, Y. Liu, F. Safari-Alamuti and Q. Wang, J. Phys. Chem. C, 2011, **116**, 1556-1562.

2 H. Zhang, J. Tong, W. Fang, N. Qian and Q. Zhao, ACS Appl. Energy Mater., 2018, **1**, 1355-1363.