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Supporting Information

Solar Rechargeable Battery based on Sodium Ion Storage Mechanism with $Fe_2(MoO_4)_3$Microspheres as Anode Materials

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Experimental section

1. Preparation of photo-anode

The photo-anode was prepared as per the following procedure: a piece of fluorine-doped tin oxide glass (FTO, 15 Ω cm^{-2}, Nippon Sheet Glass) substrate was firstly washed with redistilled water, ethanol, acetone and anhydrous ethanol sequentially. Then the FTO substrate was treated by immersing in 40 mM aqueous $TiCl_4$ solution at 70 ºC for 30 min, washed with redistilled water and ethanol, and calcined at 500 ºC for 30 min followed by cooling to ambient temperature. Then, the photo-anode was fabricated by doctor-blading a commercial TiO_2 sol (CNANE) onto a treated FTO substrate to form a mesoporous TiO_2 film followed by sintering the anode at 500 ºC in a muffle furnace at a heating rate of 5 ºC min−1 for 30 min. For sensitization, the TiO_2 electrodes (1cm×1cm) were impregnated with an ethanol solution containing 5.0×10−4 mol L-1 Z907 dye (Solaronix, Sweiss) for 24 h at room temperature. The sensitizer-coated TiO_2 films were then rinsed with anhydrous ethanol and dried in air. The electrolytes used in dye-sensitized solar cells are composed of 0.05 M I2, 0.1 M LiI, 0.6 M 1, 2-dimethyl-3-propylimidazolium (DMPII) and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile.

2. Preparation of Pt-Ti mesh

A large piece of raw Ti mesh with a thickness of 0.5 mm was cut into small rectangle pieces of 20 mm×20 mm, which were then cleaned with alcohol and acetone solution, respectively. After this process, the Ti meshes were washed with diluent HF acid and alcohol in a supersonic cleaner, then fully rinsed with distilled water. This Ti mesh was platinised by thermal decomposition of Hexachloroplatinic acid, H_2PtCl_6. 0.2 M H_2PtCl_6isopropanolicsolution was the source material for Pt. The thermal decomposition method was as follows: Dip the mesh into 0.2 M H_2PtCl_6 solution, gently place the sample to achieve a uniform coat. And then put the sample into the oven at 400ºC for 1 h.

3. Preparation of $Fe_2(MoO_4)_3$ material

$Fe_2(MoO_4)_3$ microspheres were synthesized by a simple hydrothermal method using $Fe(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_6Mo_7O_{24}$ as precursor. In a typical procedure, $(NH_4)_6Mo_7O_{24}$ (0.02 mmol) and $Fe(NO_3)_3$ (1mmol) were individually dissolved in distilled water. Then $(NH_4)_6Mo_7O_{24}$ solution was slowly added into the $Fe(NO_3)_3$ solution under magnetic stirring to form a homogeneous solution at room temperature. The pH was adjusted to a specific value (pH=1.65) using HNO_3 (1mol/L) solution. The resulting precursor suspension was transferred into a 50 mL Teflon-lined stainless autoclave. The autoclave was sealed and maintained in an oven at 140 ºC for 12 h, then allowed to cool to room temperature naturally. The products were filtered off, washed several times with distilled water and absolute ethanol, and finally dried in a vacuum at 60 ℃ for 4 h. The crystalline structure of the as-prepared $Fe_2(MoO_4)_3$ sphere was characterized by X-ray diffractometry on a Rigaku Mini Flex II diffractometer. The morphology of the $Fe_2(MoO_4)_3$ sphere was visualized using scanning electron microscopy (SEM, Supra 55vp-25-62).

4. Preparation of FTO-$Fe_2(MoO_4)_3$ electrode

The cathode was prepared by a slurry of 85wt% $Fe_2(MoO_4)_3$, 10 wt% carbon black, and 5 wt% polyvinylidenefluoride (PVDF) dispersed in Nmethyl-2-pyrrolidone (NMP). The powder mixture was then casted on a FTO and dried at 120 ℃ for 12h.

5. Apparatus and characterization

The $Fe_2(MoO_4)_3$ electrode were characterized using cyclic voltammetry (CV) technique by a three-electrode system. The photo-electrochemical responses of the photocatalytic rechargeable solar cell (discharge curves) and dye-sensitized solar cell (I-V curves) were recorded with a CHI 600A electrochemical workstation (CH Instruments, Shanghai, China). The light source used in this work was a Xe lamp (Oriel 91160-1000, USA) with a 500-1100 nm filter, operated at a power density of 100 mW cm-2. The intensity of the incident light was measured with a radiant power/energy meter (Oriel, 70260) before each experiment.

6. Electrochemical performance of $Fe_2(MoO_4)_3$ electrode

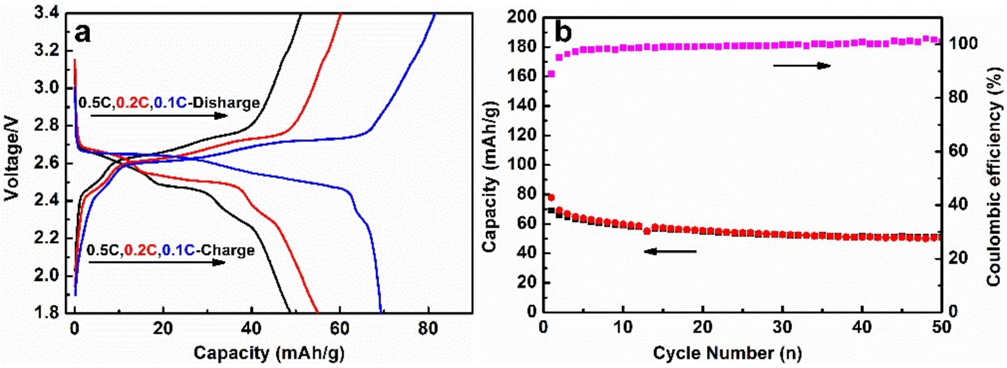

Figure S1. (a) The charge/discharge curves of $Fe_2(MoO_4)_3$/Na cell at current rates of 0.1C (9 mA/g), 0.2C (18 mA/g) and 0.5C (45mA/g) in the potential region of 1.8-3.4V (vs Na/Na^+). (b) The cycling performances of $Fe_2(MoO_4)_3$ at a current density of 0.03 mA.

The charge/discharge curves and cycle performance of $Fe_2(MoO_4)_3$ are shown in **Figure S1**. At 0.1C rate, the charge/discharge capacities of $Fe_2(MoO_4)_3$ are around 80 and 70 mAh/g, implying the transformation of Fe^{3+} to Fe^{2+}. At 0.5C rate, the sample is still able to deliver the higher capacity of 50 mAh/g. With the increased current rate, especially at high current, the discharge capacity is decreased due to the effect of increasing electrochemical polarization. Due to the irreversible capacity loss, the Coulombic efficiency of the initial two cycles is low. The Coulombic efficiency from 3rd to 50th cycle is around 100%, showing good reversible cycling after the surface reaction are completed. A decrease in capacity is observed with cycling for up to 30 cycles before a stable performance.