Supplementary Materials

In situ grown Bi_2WO_6@$CoMoO_4$ layered cladding structure on carbon nanofibers by two-step solvothermal method and Ti mash substrate as advanced counter electrodes for dye-sensitized solar cells

Xiaoyu Zhang[a], Xueyan Peng[a], Xuan Wang[a], Qian Zhang[a], Zixin Wang[a], Ling Li[a]*

[a] *Hebei Key Lab of Optic-electronic Information and Materials, College of Physics Science and Technology, Institute of Life Science and Green Development, Hebei University, Baoding 071002, P. R. China*

[b] *Key Laboratory of Digital Medical Engineering of Hebei Province, College of Electronic and Information Engineering, Hebei University, Baoding 071002, P. R. China*

Experimental

1. *Chemicals*

Polyacrylonitrile (PAN, M_w=150 000, aladdin), N, N-dimethylformamide (DMF, M_w=73.09, 99.9%, aladdin), $Bi(NO_3)_2 \cdot 5H_2O$ (M_w=485.07, analytical reagent, aladdin), $Na_2WO_4 \cdot 2H_2O$ (M_w=329.87, analytical reagent, Tianjin Guangfu), $Co(NO_3)_2 \cdot 6H_2O$ (M_w=291.03, analytical reagent, aladdin), $Na_2MoO_4 \cdot 2H_2O$ (M_w=241.95, analytical reagent, aladdin), urea (M_w=60.06, analytical reagent, aladdin), ethylene glycol (M_w=62.08, analytical reagent, Tianjin Huihang), LiI (M_w=133.85，aladdin), I_2 (M_w=253.81, 99.8%, Tianjin Fuchen), 4-tert-butylpyridine (TBP, M_w=135.21, aladdin), 1, 2-dimethyl-3-propylimidazolium iodide (DMPI, M_w=266.13, aladdin), acetonitrile (M_w=41.05, analytical reagent, Tianjin Fuchen).

2. *Preparation of CNFs*

Mix the DMF and PAN at a weight ratio of 9:1, and stir on a magnetic mixer for 24 h to obtain a transparent and clear solution, then transfer the spinning solution to a 10 ml syringe, cooperate with an electrostatic spinning machine to obtain white cloth fibers at a voltage of 20 kV and a flow rate of 1 $ml \cdot h^{-1}$. Dry the white cloth fiber in a blast drying oven at 80 ℃ for 6 h to remove the residual solution on the fiber surface. After that, the dried white cloth fibers were annealed by 1000 ℃ at nitrogen atmosphere in a tubular furnace for 2 h, and CNFs was obtained after carbonization.

3. Synthesis of CNFs@Bi_2WO_6

Pour 4 mmol $Bi(NO_3)_2 \cdot 5H_2O$ and 2mmol $Na_2WO_4 \cdot 2H_2O$ into 60 ml ethylene glycol and stir magnetically at room temperature for 30 min. Put 0.1 g CNFs into 100 ml Teflon lining, transfer the stirred solution into the lining and heat it in a blast drying oven at 150 ℃ for 4 h. After natural cooling to room temperature, fully rinse with deionized water and absolute ethanol, dry in a blast drying oven at 60 ℃ for 6 h, and then anneal at 400 ℃ (with heating rate of 5 $℃ \cdot min^{-1}$) in a tubular furnace for 2h to obtain CNFs@Bi_2WO_6.

4. Synthesis of CNFs@Bi_2WO_6@$CoMoO_4$

Dissolve 2 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 2 mmol $Na_2MoO_4 \cdot 2H_2O$ in 60 ml deionized water in 500 r/min at room temperature, and add 10 mmol urea after complete dissolution. Then transfer the solution together with CNFs@Bi_2WO_6 into 100 ml Teflon lining, heat it in a blast drying oven at 120 ℃ for 6 h, after natural cooling to room temperature, dry the washed material at 60 ℃ for 8 h, and anneal it

with heating rate of 5℃·min^{-1} to 500 ℃ in nitrogen atmosphere in a tubular furnace for 1 h get CNFs@Bi_2WO_6@$CoMoO_4$ material.

5. Make Ti mesh CNFs@*Bi_2WO_6@$CoMoO_4$ CEs*

Before making the CEs, the slurry is prepared according to the following formula: 0.3 g ethyl cellulose, 2 ml absolute ethanol and 0.6 g terpineol. The colorless and transparent viscous liquid is obtained by stirring at room temperature for 24 h. Firstly, cut the titanium mesh into a size of 2*5 cm^2, paste the Ti mesh on the desktop with 3M transparent tape, leave a 7 mm gap longitudinally, and control the film thickness of the CEs by controlling the number of layers of 3M tape. In a mortar, grind the prepared CNFs@Bi_2WO_6@$CoMoO_4$ into powder, then drop the above slurry and continue grinding for 20 min. Finally, scrape and apply the ground material evenly on the Ti mesh with a scraper. The Ti mesh was dried at 80 ℃ for 4 h and annealed at 500℃ in nitrogen atmosphere for 30 min to obtain the Ti mesh CNFs@Bi_2WO_6@$CoMoO_4$ CEs.

6. Fabrication of DSSCs

The preparation of photoanode is obtained by uniformly printing TiO_2 slurry on clean FTO conductive glass for 5 times by screen printing and annealing at 500 ℃ for 30 min. The effective area of photoanode is 0.36 cm^2. Soak the photoanode in the prepared N719 ethanol solution for 24 h for color sensitization. Dissolve 0.2 M I_2, 0.3 M LiI, 0.4 M TBP and 0.36 M DMPI into 10 ml acetonitrile to prepare iodine electrolyte. During the test, the dye-sensitized photoanode and CEs are combined together, and the electrolyte is injected in the middle to assemble a complete DSSCs.

7. Measurement

The micro surface morphology and lattice spacing of the material samples were tested by scanning electron microscope (SEM, FEI, NOVA NanoSEM 450) and transmission electron microscope (TEM, JEOI, JEM-2100 Plus). The crystal structure of the material was detected by X-ray diffraction (XRD, D8-Advance, Bruker AXS). The elemental composition of the material and the valence states of each element were measured by X-ray photoelectron spectroscopy (XPS, Thermo VG, ESCALAB250). The specific surface area and average pore diameter of the samples were obtained by Brunauer-Emmett-Teller measurement (BET). All the electrochemical performance results of the CEs were tested on the electrochemical workstation (CHI 660E, Chenhua, Shanghai). The Tafel test is used to show the polarization characteristics of the CEs. During the test, two identical CEs are opposite and together, electrolyte is injected into the middle to assemble a virtual battery, and the potential is scanned from -0.7 V to 0.7 V at a scanning rate of 20mV·s^{-1} on the electrochemical workstation. The electrochemical impedance spectrum (EIS) test was used to characterize the electron transfer resistance of the CEs and the diffusion resistance of the electrolyte, scanning from 0.1 Hz to 1 MHz at a bias voltage of 0.1 V. The cyclic voltammetry (CV) curve can intuitively show the catalytic oxidation-reduction ability of the CEs. During the test, a three electrodes system was adopted: Ag/AgCl electrode is the reference electrode, Pt is the CEs, and the electrode that was tested is the working electrode, it is scanned from potential -0.2 V to 1.0 V at the scanning rate of 10 mV·s^{-1}.