Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Efficient Counter Electrode Material for Dye-sensitized Solar Cells— Flower-structured 1T Metallic Phase MoS_2

Wei Wei[1], Kai Sun[2], and Yun Hang Hu[1,*]

[1]Department of Materials Science and Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931-1295, USA

[2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

1. Experimental section

1.1 Synthesis and characterization of MoS_2.

MoS_2 was synthesized via a typical hydrothermal method: 1mmol of $Na_2MoO_4 \cdot 2H_2O$ and 5mmol of thiourea were dissolved in 60ml of distilled water and stirred vigorously. Then, the obtained mixture was transferred into a 100ml Teflon-lined autoclave. A FTO glass was placed against the wall of the autoclave. The whole system was kept for reactions at 180 or 200 ºC for 24h, which are denoted as MoS_2-180 and MoS_2-200. Finally, the FTO glass covered with MoS_2 film was rinsed with distilled water and ethanol, and then dried in an oven at 80 ºC for 12h. MoS_2 samples were scraped down from the surface of FTO glass before characterization. The products were subjected to X-ray diffraction (XRD) measurements using a Scintag XDS-2000 powder diffract meter with Cu Kα (λ=1.5406Å) radiation. Structures of the samples were characterized by Hitachi-4700 field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS) and the HAADF-STEM images were obtained using a JEOL JEM3100R05 double Cscorrected analytical electron microscope. X-ray photoelectron spectra (XPS) were collected using a Kratos Ulta AXIS DLD XPS with a monochromated Al source. Raman spectra were obtained using an Olympus BX41 spectrometer with a helium-neon laser to excite the samples. Surface area and pore size distribution were measured with a Micromeritics ASAP 2000 surface area measurement analyzer using nitrogen adsorption at liquid-nitrogen temperature (77K). Before nitrogen adsorption measurement, the sample was degassed at 100°C.

1.2 Preparation and characterization of counter electrodes.

A piece of pre-cleaned FTO conducting glass was placed against the inside wall of the Teflon lined autoclave with conduction side facing up. The MoS_2 nanostructure films were directly grown

onto the FTO substrates. The obtained films were rinsed with DI-water and then dried at 80°C for four hours. The FTO glass plates with coated MoS_2 film were directly used as counter electrodes. Cyclic voltammetry measurements were carried out using an electrochemical workstation (EG&G Princeton Applied Research) with a three-electrode system (carbon nanomaterial as a working electrode, Pt wire as a counter electrode, and Ag/AgCl as a reference electrode) containing acetonitrile solution of 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$.

1.3 Preparation of photo electrodes.

FTO glass plates were ultrasonically washed with water and the conducting surface of the FTO was treated with a 0.4mM $TiCl_4$ aqueous solution at 70°C for 30 min. A commercial TiO_2 sol (Solaronix, Ti-Nanoxide T/SP) was used to form a TiO_2 film on a FTO by the doctor-blade method. The TiO_2 film was thermally treated in air at 325°C for 5min, 375°C for 5 min, 450°C for 15min, and 500°C for 15min. The obtained TiO_2/FTO glass plate was post-treated with the 0.4mM $TiCl_4$ solvent at 70°C, followed by heating in air at 500°C for 30min. Finally, the obtained film was immersed in a cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium (N719, 0.3 mM in ethanol) dye solution for 24 hours to achieve dye sensitization.

1.4 Fabrication and performance evaluation of DSSCs.

The sandwich solar cells were assembled using the dye-sensitized TiO_2 photoelectrode and the MoS_2 counter electrode with liquid electrolyte (I^-/I_3^- redox) between them. The electrolyte consists of 0.025 M LiI, 0.04 M I_2, 0.28 M tert-butyl pyridine (TBP), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), and 0.05 M guanidinium thiocyanate in acetonitrile/valeronitrile solvent with 85/15 volume ratio. The effective cell area is 0.25cm^2. The photovoltaic performance of the obtained

MoS_2-based cells was evaluated by Kithley 2400 under illumination of 100Mw cm^{-2} at the range of 320nm-1100nm using a solar simulator (Newport). Electrochemical impedance spectroscopy (EIS) data of DSSCs were obtained at open circuit voltage and 10 mV amplitude over the frequency range of 0.1-100 kHz using CHI 660D electrochemical workstation under dark condition.

2. FESEM images of 1Tphase MoS_2

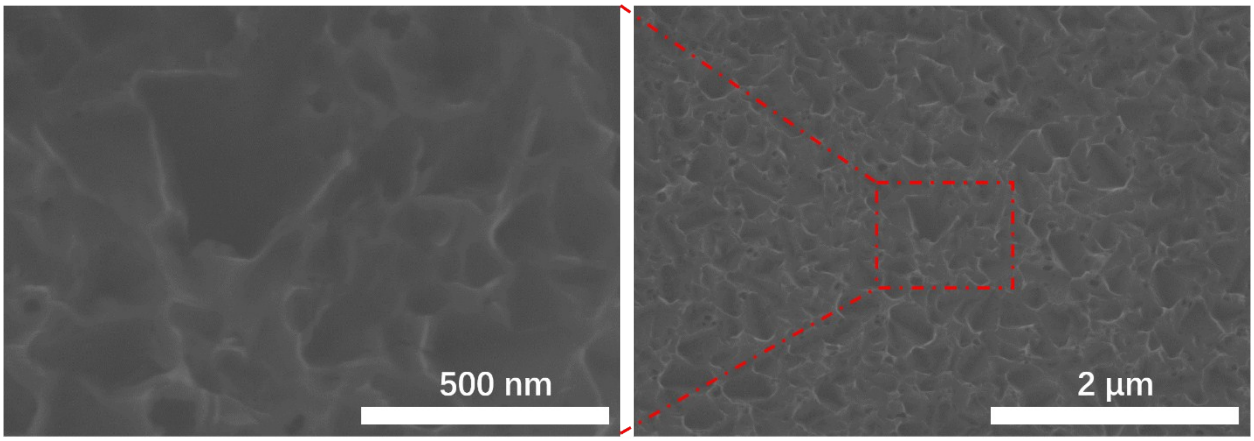

Fig. S1 FESEM images of flower-structured 1T phase MoS_2.

As shown in Fig. S1, the MoS_2 are composed of large, uniform nanosheets, which gathering together to form a flower-like structure.

3. Efficiency of DSSC with Pt as counter electrode

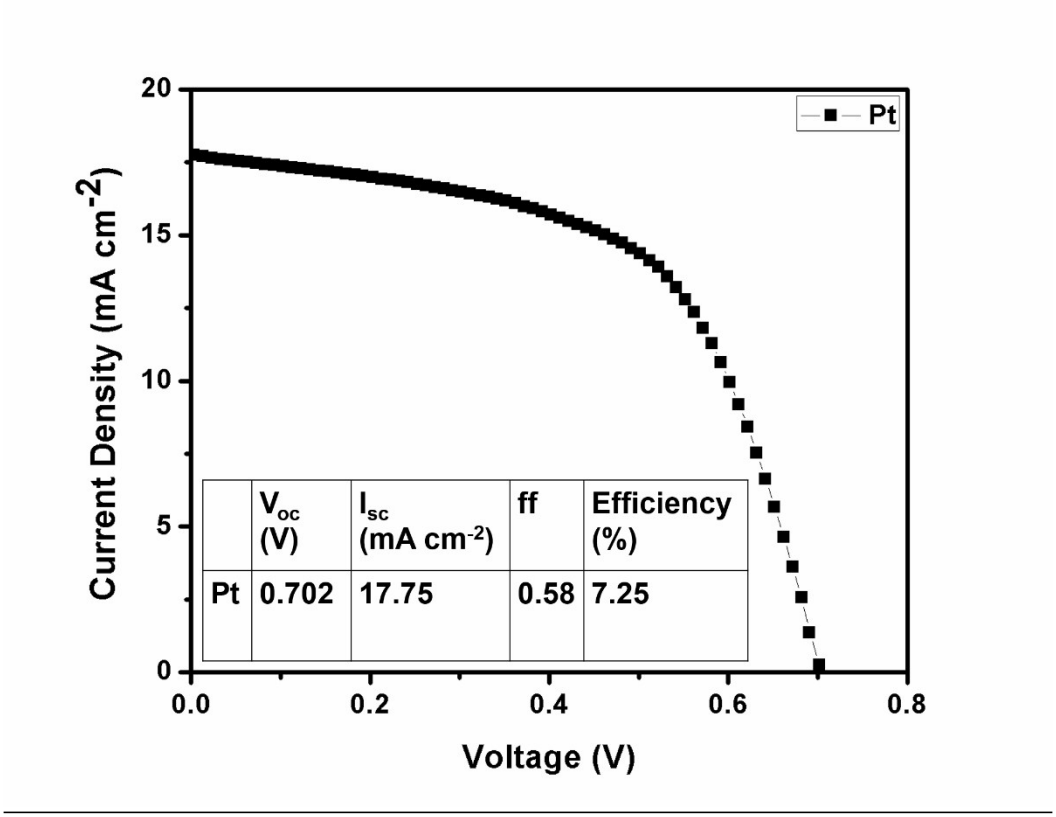

Fig. S2 J-V curve of DSSC with Pt counter electrode with photovoltaic parameter inset.