Supplementary Information

Highly efficient Mo_2C nanotubes as a counter electrode catalyst for organic redox shuttles in dye-sensitized solar cells

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Synthesis of Mo_2C particles (Mo_2C-Ps): 2.73 g of $MoCl_5$ was added to 8 mL ethanol under stirring for 30 min to form Mo-orthoester. Next, 3.00 g of urea was added to the obtained Mo-orthoester solution and stirred until the urea was completely dissolved. Subsequently, the viscous solution was dried at 120 °C to get rid of the residual solvent and got the urea-metal precursor. After sintered urea-metal precursor at 800 °C for 4 h under N_2 atmosphere, Mo_2C particles were collected.

Synthesis of Mo_2C nanotubes (Mo_2C-NTs): 2.48 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 40 mL of deionized water under stirring followed by adding 3.34 g of phenylamine. The pH of the above solution was around 10. Adding hydrochloric acid (I M) drop by drop to regulate the pH to 4~5, until white amounts of floccules appeared. Keep the solution under 50 °C for 6 h and collected the white wirelike precursor (Fig. S1). After sintered at 750 °C or 1000 °C for 3.5 h under N_2 atmosphere, Mo_2C nanotubes with different diameter were achieved. Fig. S2 showed the XRD patterns of the prepared Mo_2C-NTs at 750 and 1000 °C. The diffraction peaks at 34.42, 37.64, 39.48, 52.06, 61.94, 69.34, 72.54, 74.86, 75.76, and 81.28 ° can be assigned to the crystal planes of (100), (002), (101), (102), (110), (103), (200) (112), (201), and (004), respectively for Mo_2C (No. 11-0680, PDF-2 Database). At 750 °C, the diffraction peak showed a low intensity, indicating a weak crystallinity. In

contrast, the Mo_2C nanotubes synthesized at 1000 ^{o} gave a high crystallinity. Fig. 3S and 4S showed the SEM image of the prepared Mo_2C-NTs at different sinter temperature. The diameter of the Mo_2C-NTs at 750 ^oC was around 25 nm, a slight aggregation was observed. However, under the high sinter temperature of 1000 ^oC the thin Mo_2C-NTs aggregated to form thick nanotubes, and the diameter was increased to 350~500 nm.

Cell Fabrication: The Mo_2C counter electrode (CE) was prepared with spray coating technique. In detail, 100 mg of the Mo_2C nanotubes (or particles) were dispersed in 5 mL of isopropanol, ultrasonically dispersed for 30 min, and the Mo_2C-NTs paste was achieved. The prepared paste was then sprayed onto FTO glass. Subsequently, the FTO glass coated with Mo_2C-NTs paste was sintered under N_2 atmosphere at 450 °C for 30 min and the Mo_2C-NTs CE was obtained. The thickness of Mo_2C film was controlled around 20 μm. The Pt CE on FTO glass was fabricated by thermal decomposition as follows: isopropanol solution containing 0.5 wt% chloroplatinic acid was sprayed on FTO conductive glass for 5 s. The resulting conductive glass was sintered at 450 °C for 30 min, and the Pt CE was obtained. 10 μm thick layer of TiO_2 sensitized with N719 dye (Solaronix) was used as the photoanode. The T^-/T_2 electrolyte contains 0.4 M $Me_4N^+T^-$, 0.4 M di-5-(1-methyltetrazole) disulfide (T_2), 0.05 M $LiClO_4$, and 0.5 M TBP in 6:4 (v/v) acetonitrile/ethylene carbonate. The DSC was assembled with a photoanode, a CE, and an electrolyte. The active area of the DSC was 0.16 cm^2. Symmetrical cells were fabricated with two identical counter electrodes clipping the electrolyte. The cells were sealed with a hot-melt surlyn film.

Measurements: The as-prepared Mo_2C particles and nanotubes were assessed by X-ray diffraction (XRD) measurements using an automatic X-ray powder diffractometer (D/Max 2400, Rigaku). The morphologies of Mo_2C were characterized by scanning electron microscopy (SEM, S−4800, Hitachi, Japan) and transmission electron microscopy (TEM, h−7650, Hitachi, Japan). Nitrogen adsorption-desorption isotherms were measured with an Antosorb-1 Apparatus (Antosorb-1, Quantachrome, USA) to check the BET surface area of Mo_2C nanotubes and particles. The current density−voltage performance of the DSC was carried out under simulated AM 1.5

illumination (I = 100 mW cm^{-2}, PEC−L01, Peccell, Yokohama, Japan) with an electrochemical workstation system (CHI 660E, Chenhua, Shanghai). EIS experiments were characterized with symmetrical cells in the dark with a computer-controlled potentiostat (Zennium Zahner, Kronach, Germany). The measured frequency ranged from 100 mHz to 1 MHz. The amplitude of the alternating current was set at 10 mV. Tafel-polarization measurements were carried out with the electrochemical workstation system (CHI 660E, Chenhua, Shanghai) in a symmetrical dummy cell. The scan rate was 10 mV s^{-1}. CV measurements were carried out in a three electrode system in an argon-purged electrolyte solution at a scan rate of 20 mV s^{-1} using the electrochemical workstation system (CHI 660E, Chenhua, Shanghai). Pt served as the counter electrode, and Ag/AgCl worked as the reference electrode. The T^-/T_2 electrolyte in CV measurements contained 100 mM $Me4N^+T^-$, 10 mM T_2, and 0.2 M $LiClO_4$ in acetonitrile.

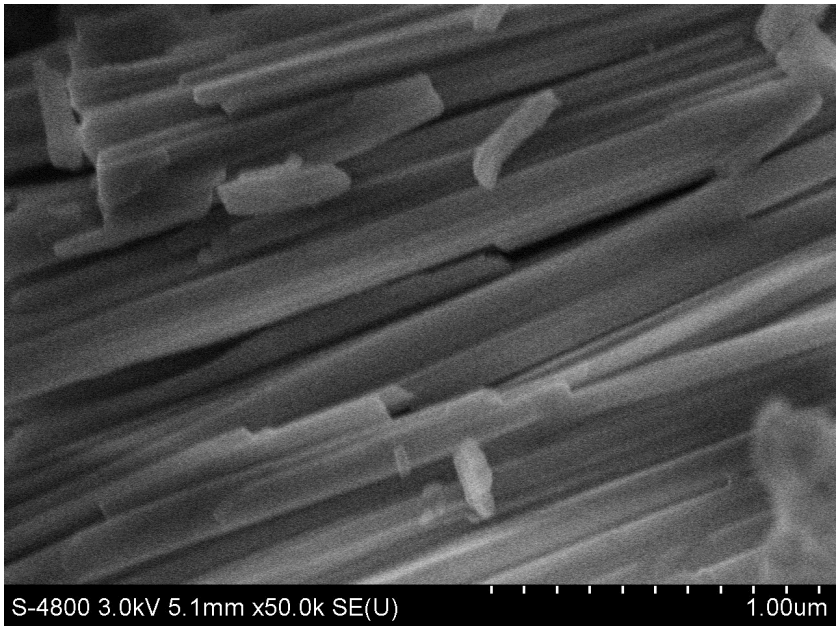

Fig. S1. SEM image of the wirelike precursor of the Mo_2C-NTs.

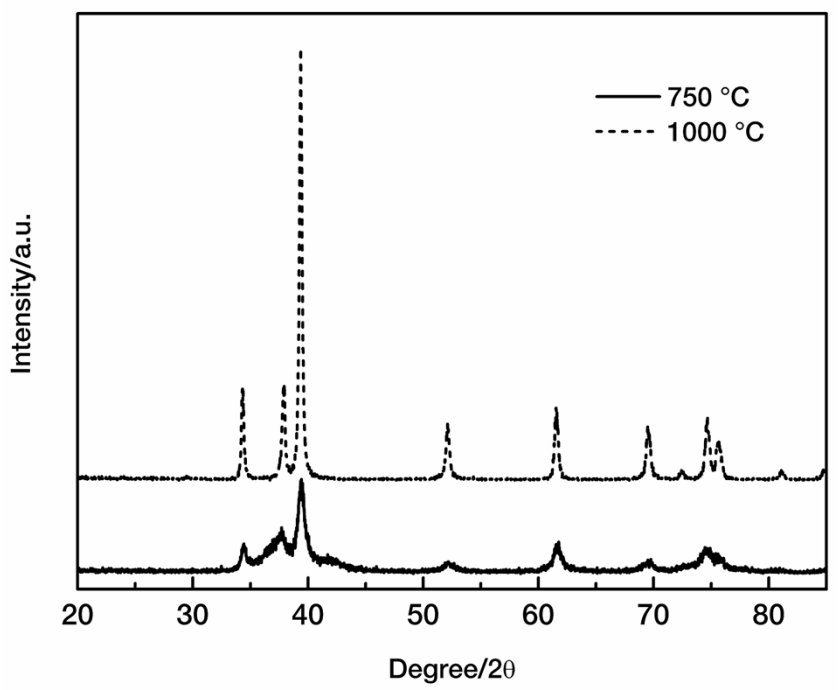

Fig. S2. XRD patterns of the prepared Mo_2C-NTs at different sinter temperature.

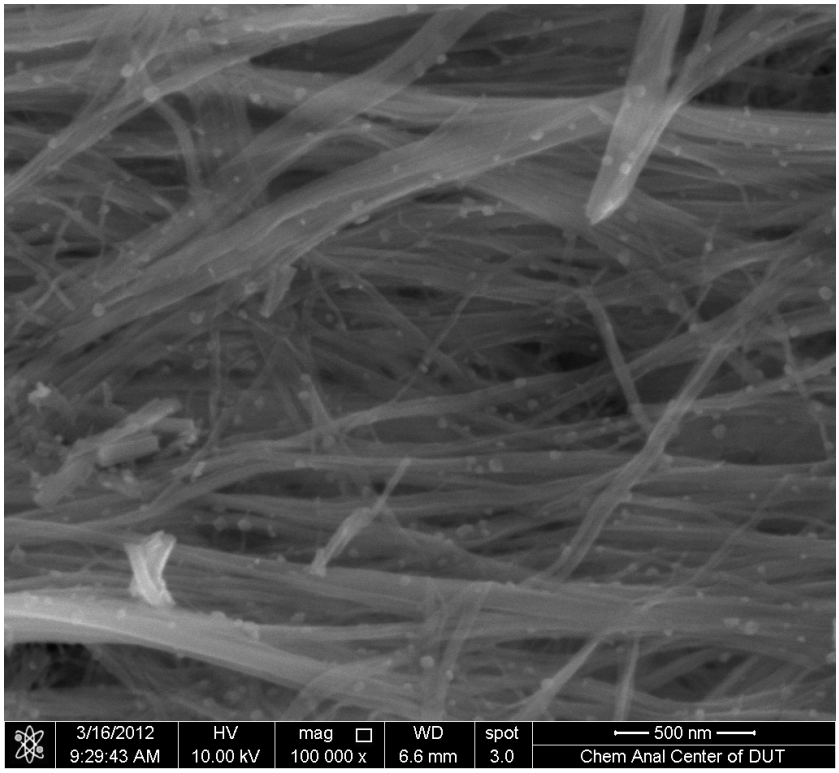

Fig. S3. SEM image of the Mo_2C-NTs sintered at 750 °C.

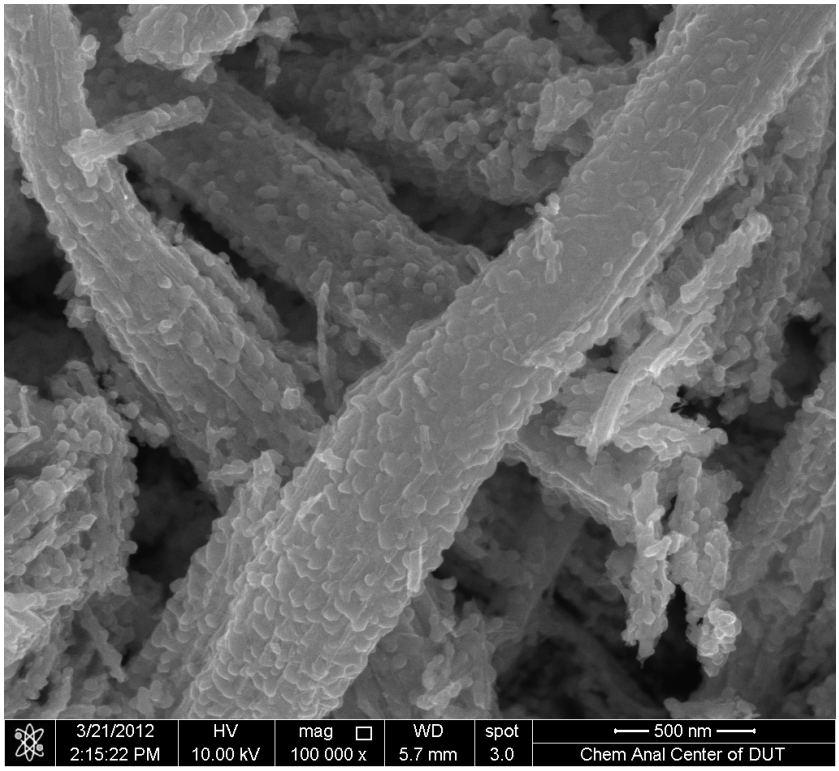

Fig. S4. SEM image of the Mo_2C-NTs sintered at 1000 °C

Table S1 Photovoltaic parameters of the T^-/T_2 electrolyte based DSC and EIS parameters of the symmetrical cells using different electrodes.

Counter electrodes	*V*oc/mV	J_{sc}/mA cm^{-2}	*FF*	PCE/%	R_s /Ω	R_{ct} /Ω	Z_N /Ω
Pt	625	13.05	0.479	3.91	12.8	8.1	23.2
Mo_2C-Ps	636	13.66	0.633	5.50	12.9	2.0	16.7
Mo_2C-NTs	637	14.06	0.694	6.22	13.2	0.8	4.5

V_{oc}: open-circuit voltage, J_{sc}: short-circuit current density, FF: fill factor, PCE: power conversion efficiency R_s: series resistance, R_{ct}: charge transfer resistance, Z_N: Nernst diffusion impedance.