Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Supercapacitive carbon nanotube - cobalt molybdate nanocomposites prepared via solvent-free microwave synthesis

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1. TEM micrograph of AF-MWCNTs

Acid functionalized multiwalled carbon nanotubes (AF-MWCNTs) were obtained from Chengdu Organic Chemincal Co, Ltd., Chinese Academy of Sciences. TEM image of AF-MWCNTs used as nucleation sites for $CoMoO_4$ assemblies is shown in Fig. S1. It shows the typical diameter of AF-MWCNTs is ~10nm (Fig. S1).

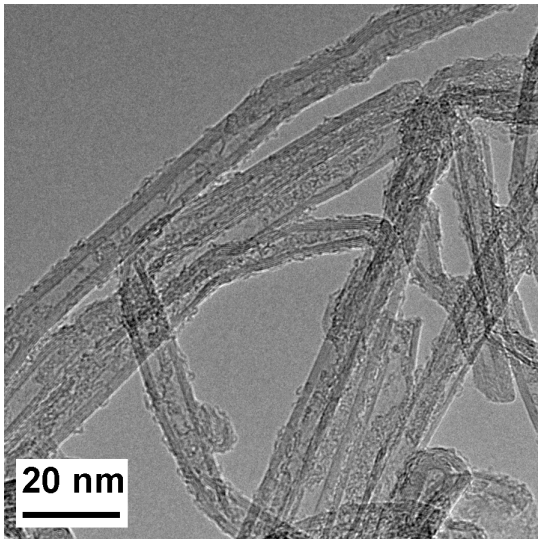

Fig. S1. TEM image of AF-MWCNTs.

2. Experimental

2.1 Synthesis of $CoMoO_4$/MWCNT composite and reference $CoMoO_4$ samples

Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and Cobalt(II) Chloride Hexahydride $CoCl_2\cdot 6H_2O$ were obtained from Sigma Aldrich Co. The MWCNT-molybdate nanocomposite syntheses process was performed using a commercially available Panasonic INVERTER 1200W microwave oven. A mixture of 0.62g (0.50 mmol) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 0.84g (3.53 mmol) $CoCl_2\cdot 6H_2O$, and 0.23 g (19.17 mmol) AF-MWCNTs, was ground to a fine powder using mortar and pestle. The mixture was then transformed to a 100 ml ceramic crucible, which was then heated in the microwave at ambient conditions at a power of 480W for 8.0 min, followed by 720 W for 7.0 min. After cooling to room temperature, the products were washed by water and ethanol for several times. The precipitate was dried under vacuum at 70 ºC overnight. Yield: 0.87 g.

As the control experiments, baseline $CoMoO_4$ samples were synthesized without any carbon additive or using MWCNTs (Aldrich, ~10 nm in diameter, similar as AF-MWCNTs). Yields of the samples are 0.65 g and 0.91 g, respectively.

2.2 Characterization

Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-4800 field emission scanning electron microscope (SEM). Transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 Lab6 TEM, at a 200 kV accelerating voltage. For TEM analysis the samples were dispersed in alcohol with the aid of ultrasonic agitation for several minutes. A drop of the dispersion was deposited onto a copper grid covered by ultra thin carbon film supported by a lacey carbon film. Raman analysis of the samples was performed with a NICOLET AlMEGA XR Dispersive Raman system utilizing a laser power 532 nm-24 mV, resulting in an approximately 2 μm diameter sampling cross section. X-ray diffraction (XRD) analysis of the samples was performed using a Bruker Discover 8 Diffractometer, with Cu Kα radiation (λ = 1.5406 Å) that was monochromatized using a single Gobel mirror. The X-ray photoelectron spectroscopy (XPS) spectra were

recorded on an Axis Ultra spectrometer with Al (Mono) Kα X-ray source (1486.6 eV). The base pressure of the analysis chamber was below 10^{-9} mbar. Thermal gravimetric analysis and differential scanning calorimetry analysis (TGA/DSC) was performed on a SDT Q600, TA Instruments DSC–TGA, in air with a heating rate of 10 °C min^{-1}. The BET specific surface area of the samples was characterized by nitrogen adsorption at 77k using a Quantachrome Nova1200.

2.3 Electrochemistry

For the electrochemical testing, a slurry of 95% (by weight) $CoMoO_4$/MWCNTs and 5% binder (PVDF) suspended in N-methylpyrrolidone was coated onto glassy carbon disc. The disk was then dried at 110 ^oC overnight in a vacuum oven. It was then sealed in a Teflon electrode assembly using epoxy resin. The electrochemical experiments were performed in Teflon beakers with a Pt wire as a counter electrode and Hg/HgO as a reference electrode. The electrolyte was 1M KOH. Cyclic voltammetry and galvanostatic charge-discharge cycling were performed using a Solatron 1470E Multichannel Potentiostat/Cell Test System. The specific capacitance is calculated as $It/m\Delta E$, where I is the change/discharge current, t is the discharging time, m is the mass of the electrode material and ΔE the potential window.

3. XPS analysis

The overall XPS spectrum shows the surface of the obtained products consist of 45.32% C, 8.94% Co, 9.00% Mo and 36.73% O by atomic composition (Fig. S2A). The Co 2p XPS spectra of the obtained product show two peaks at 796.7 and 781.2 eV, corresponding to the Co $2p^{1/2}$ and Co $2p^{3/2}$ of $CoMoO_4$, respectively (Fig. S2B).[1,2] The Mo 3d XPS spectra of the composite display two peaks at 235.8 and 232.9 eV, agreeing well with Mo $3d^{3/2}$ and Mo $3d^{5/2}$ assigned to Mo^{6+} species in an oxidic surrounding, respectively (Fig. S2C).[1]O 1s XPS show two strong peaks, around 529.3 and 530.7 eV, this doublet line can be regarded as characteristic of $CoMoO_4$,[1] A weak peak at 532.9 eV of the O 1s XPS, is a typical peak of O 1s in the organic acid chemical environment, is also in agreement with the oxygen (belong to –COOH) of

AF-MWCNTs (Fig. S2D).[3]

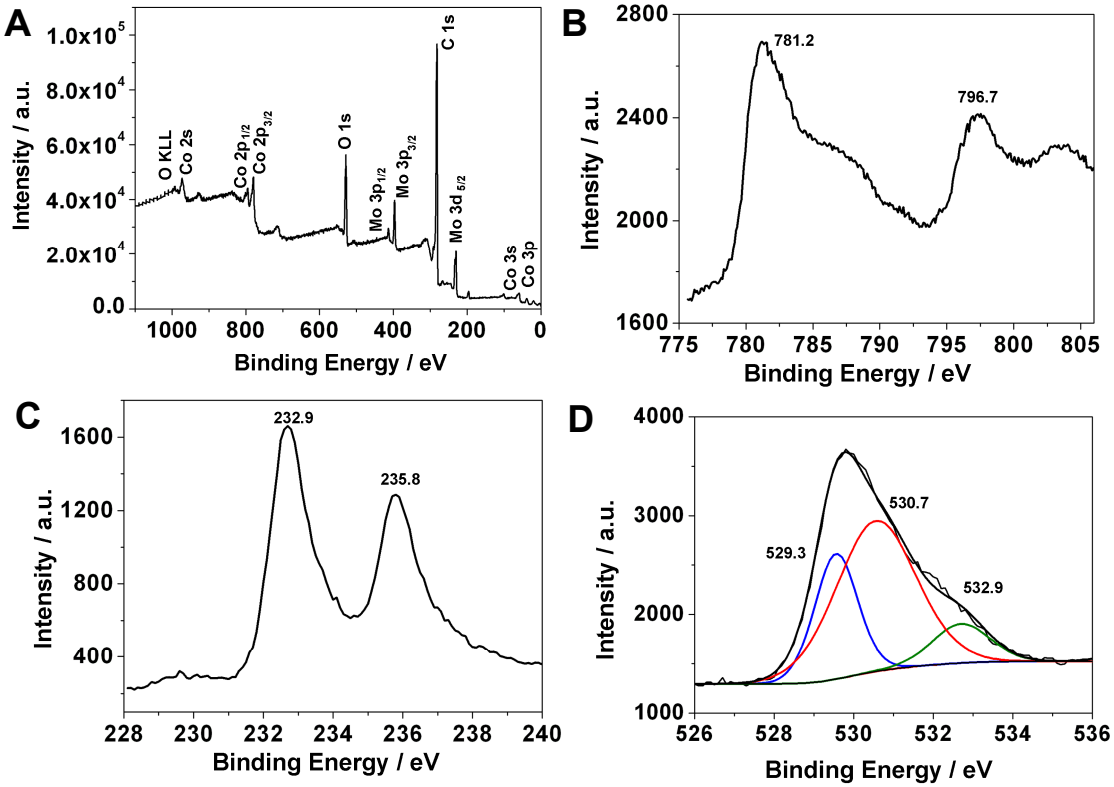

Fig. S2. (A) Overall XPS, (B) Co 2p, (C) Mo 3d and (D) O 1s XPS spectra of $CoMoO_4$/MWCNT composite.

4. Thermal analysis

TG and DSC data show that the initial mass loss of the AF-MWCNTs and the obtained $CoMoO_4$/MWCNT composite are ~3.5% and 3.6% in the range between ~80 and 250 ^oC, respectively, and several small peaks of DSC curve below 250^oC in the curve can be observed, attributed to the evaporation of physically adsorbed water (Fig. S3).[4] As to AF-MWCNTs, the exothermal peak ~ 515 ^oC can be assigned to the ignition of AF-MWCNTs (Fig. S3A, blue line), and there is a corresponding 94.6% weight loss in the TG curve (Fig. S3A, black line). The ignition residue is chiefly cobalt oxide, which comes from cobalt used as catalyst to synthesize MWCNTs.[4] To $CoMoO_4$/MWCNT composite, the exothermal peak ~495 ^oC can be assigned to the ignition of AF-MWCNTs (Fig. S3B, blue line), corresponding 23.7% weight loss in the TG curve (Fig. S3B, black line). The ignition residues are chiefly cobalt oxide and

$CoMoO_4$. Compared with the TG and DSC data of AF-MWCNTs and $CoMoO_4$/MWCNTs, it can be inferred that the $CoMoO_4$/MWCNT composite contains of ~24.6% AF-MWCNTs and ~75.4% of $CoMoO_4$.

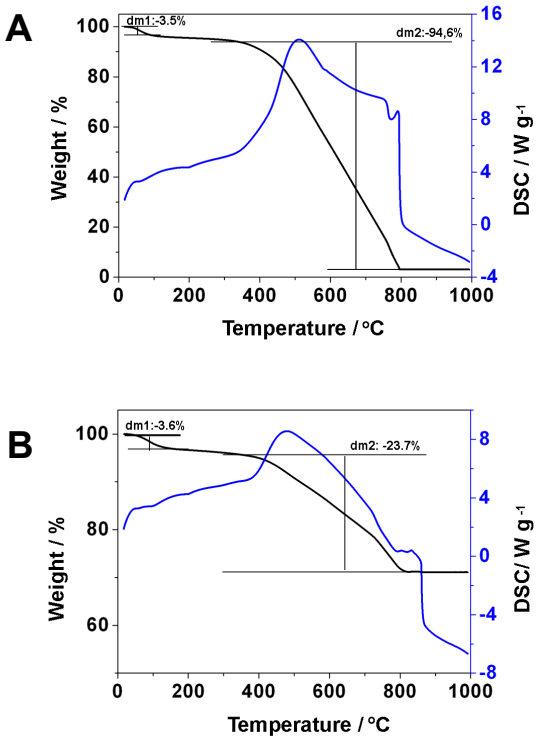

Fig. S3. TG–DSC curves of (A) AF-MWCNTs and (B) $CoMoO_4$/MWCNT composite

5. The BET surface area

The BET surface area of $CoMoO_4$/MWCNT composite is 58.1 m^2 g^{-1}, the $CoMoO_4$/MWCNT composite contains of ~24.6% AF-MWCNTs and ~75.4% of $CoMoO_4$ and the surface area of AF-MWCNTs is 110.0 m^2 g^{-1}. Given that the surface of AF-MWCNTs is completely exposed, it can be inferred that the minimum of the BET specific surface area of $CoMoO_4$ assemblies is 41.2 m^2 g^{-1}.

6. Raman shifts and SEM images of the reference $CoMoO_4$ samples

Raman spectrum of the reference $CoMoO_4$ synthesized via similar microwave solid phase synthesis method but without any carbon additive is shown in Fig. S4A. There are five bands the positions around 330, 353, 806, 868 and 926 cm^{-1}, can be assigned to $CoMoO_4$. The SEM image of $CoMoO_4$ synthesized by microwave without any

carbon additive shows an irregular bulk morphology (Fig. S4B). Also, it is hard to do SEM characterization for the reference $CoMoO_4$ due to its poor conductivity.

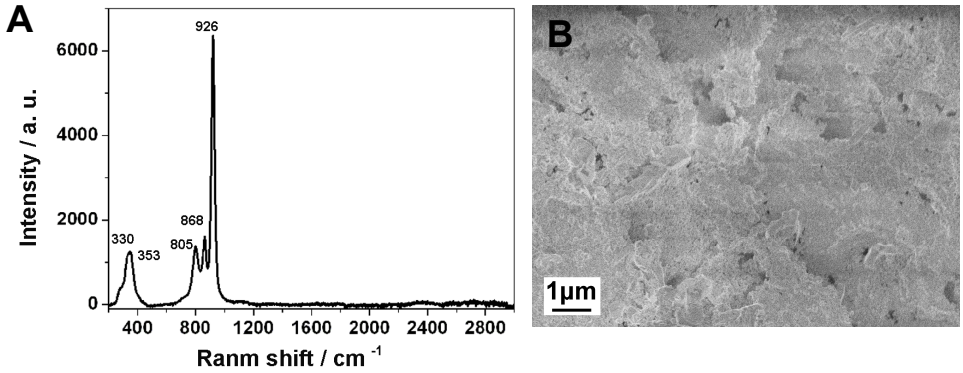

Fig. S4. (A) Raman spectra and (B) SEM image of the reference $CoMoO_4$ without any carbon additive

Raman spectrum of the reference $CoMoO_4$ synthesized via similar microwave solid phase synthesis method using MWCNTs shows eight bands. The bands in the positions around 330, 353, 806, 868 and 926 cm^{-1}, are typical bands of $CoMoO_4$, and the bands around 1346, 1577 and 2665 cm^{-1} are the D band, G band and 2D band of MWCNTs, respectively (Fig. S5A). The SEM image of $CoMoO_4$ synthesized by microwave using MWCNTs shows many large particles with several hundreds nanometers pack together (Fig. S5B).

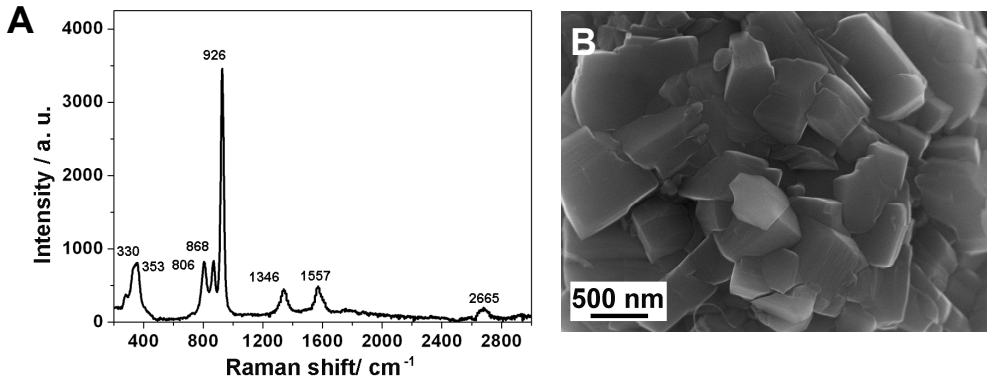

Fig. S5. (A) Raman spectra and (B) SEM image of the reference $CoMoO_4$ with MWCNTs

7. CV curves of the reference $CoMoO_4$ and $CoMoO_4$/MWCNTs

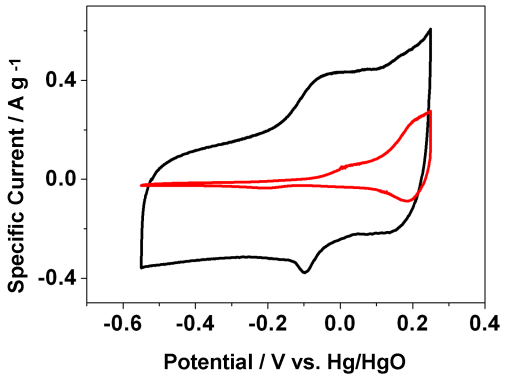

Fig. S6 CV curves of the reference $CoMoO_4$ (red line) and $CoMoO_4$/MWCNTs(black line) in 1 mol L^{-1} KOH, scan rate: 2 mV s^{-1}.

References

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