Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Detailed Experiments

Synthesis: All the chemicals were of analytical grade and used without further purification. Sodium tungstate (Na_2WO_4•$2H_2O$) was used as tungsten source, and fumaric acid (COOHCHCHCOOH, for short as FA) supplied the ion of H^+. The detailed process for the synthesis was as follows: 0.196 g Na_2WO_4•$2H_2O$ was dissolved in 35 ml water, following by the addition of FA solution which was dissolved in 40 ml water at 80 ℃ ahead of time (The molar ratio of Na_2WO_4•$2H_2O$ to FA is 0.1). The mixture kept on stirring for several minutes and then transferred to a teflon lined steel autoclave with a capacity of 100 ml, maintained at 180 ℃ for 12 h. After the reaction was completed, the autoclave cooled to room temperature naturally. Precipitates were centrifuged, sequentially washed with water and ethanol for several times to remove the ions possibly remaining in the products, and finally dried at 80 ℃ for 12 h in a vacuum. The contrast experiment were carried out through adjusting the experiment condition.

Characterization: The crystalline structures of the as-prepared samples were characterized by X-ray diffraction (XRD) spectra (Rigaku D/Max-2500, Cu Kα radiation, λ=0.1518 nm). The morphologies were detected by scanning electron microscopy (SEM) on a JEOL JSM-6700F (Field Emission) scanning electron microscope, transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) on a Tecnai G2 F20 TEM. The specific

surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Micromeritics Tristar-3000 surface area and porosity analyzer).

Electrochemical measurements: The as-prepared $WO_3 \bullet 0.33H_2O$ was used as anode material for rechargeable lithium ion batteries. The anode electrode was fabricated by mixing the active material, acetylene black and binder (PVDF) in a weight ratio of 80:10:10, and then coated on Cu foil. The lithium foil served as counter and reference electrode. For the electrolyte, a 1 mol dm^{-3} solution of $LiPF_6$ dissolved in ethylene carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 in volume) was used. The assembly of the testing cells was carried out in an argon filled glovebox, where water and oxygen concentration was kept less than 5 ppm. Galvanostatic charge/discharge measurements were operated on a Land CT2001 automatic battery tester in a voltage range of 0.01-3 V. Cyclic Voltammetry (CV) were performed on a CHI660B electrochemical workstation. All the tests were performed at room temperature.

Table S1 Summary of the experimental parameters and their corresponding morphologies of WO_3•$0.33H_2O$ obtained under various conditions.

T (℃)	time (h)	Na_2WO_4•$2H_2O$ (g)	FA (g)	Morphology
180	12	0.107	0.349	star-like hierarchitectures
180	12	0.196	0.696	perfect chrysanthemum-like hierarchitectures
180	12	0.248	0.879	broken chrysanthemum-like hierarchitectures
180	12	0.196	0.276	irregular clusters
180	12	0.196	0.345	similar chrysanthemum-like hierarchitectures
180	12	0.196	0.828	similar chrysanthemum-like hierarchitectures
180	12	0.196	1.034	broken chrysanthemum-like hierarchitectures
160	12	0.196	0.696	similar chrysanthemum-like hierarchitectures
200	12	0.196	0.696	broken chrysanthemum-like hierarchitectures

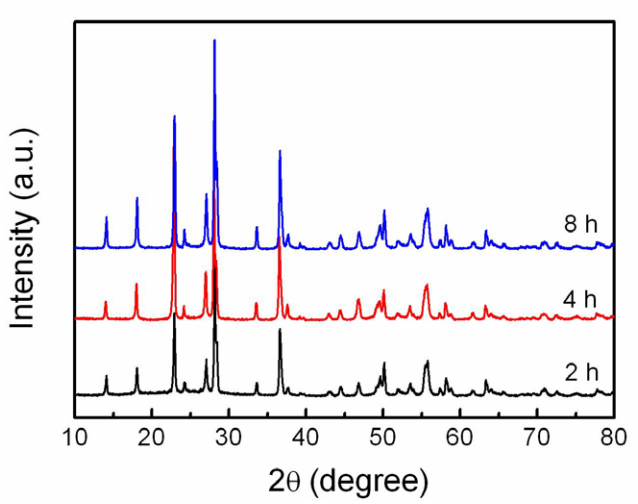

Fig. S1 XRD patterns of WO_3•0.33H_2O collected at 2 h, 4 h, 8 h.

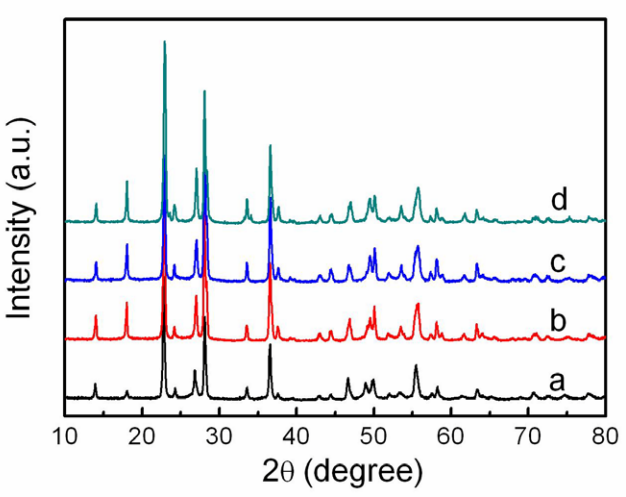

Fig. S2 XRD patterns of samples synthesized with different molar ratio of $Na_2WO_4 \cdot 2H_2O$ to FA : (a) 1:5, (b) 1:8, (c) 1:12, (d) 1:15 (The dosage of $Na_2WO_4 \cdot 2H_2O$ is fixed at 0.196 g). The peaks of all samples can be perfectly indexed to the orthorhombic phase of $WO_3 \cdot 0.33H_2O$ (JCPDS No. 87-1203, space group: Fmm2 (no. 42)).

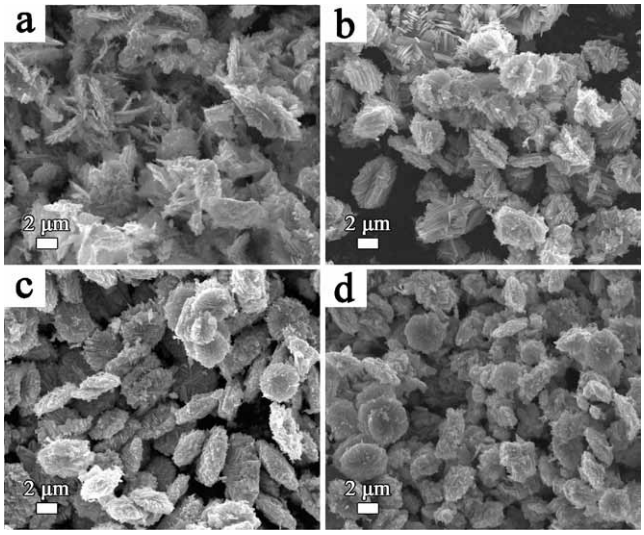

Fig. S3 SEM images of samples synthesized with different molar ratio of $Na_2WO_4 \cdot 2H_2O$ to FA: (a) 1:5, irregular clusters, (b) 1:8, similar chrysanthemum-like hierarchitectures, (c) 1:12, similar chrysanthemum-like hierarchitectures, (d) 1:15, broken chrysanthemum-like hierarchitectures, (The dosage of $Na_2WO_4 \cdot 2H_2O$ is fixed at 0.196 g).

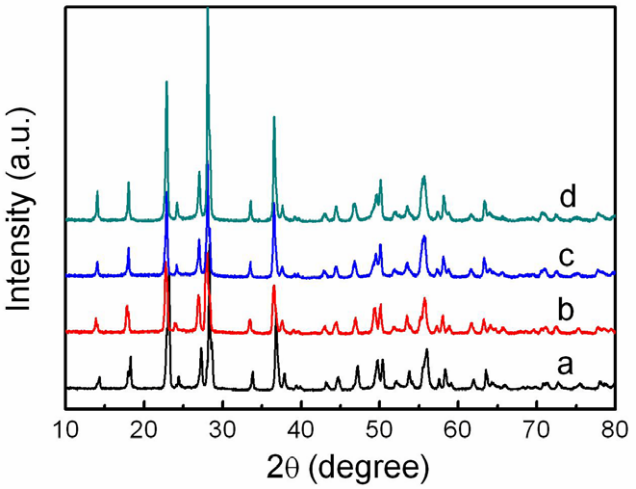

Fig. S4 XRD patterns of samples synthesized with different dosage of Na_2WO_4•$2H_2O$: (a) 0.107 g, (b) 0.248 g (the molar ratio of Na_2WO_4•$2H_2O$ to FA is 0.1), and the patterns of samples synthesized at (c) 160 ℃, (d) 200 ℃ for 12 h, respectively. The peaks of all samples can be perfectly indexed to the orthorhombic phase of WO_3•$0.33H_2O$ (JCPDS No. 87-1203, space group: Fmm2 (no. 42)).

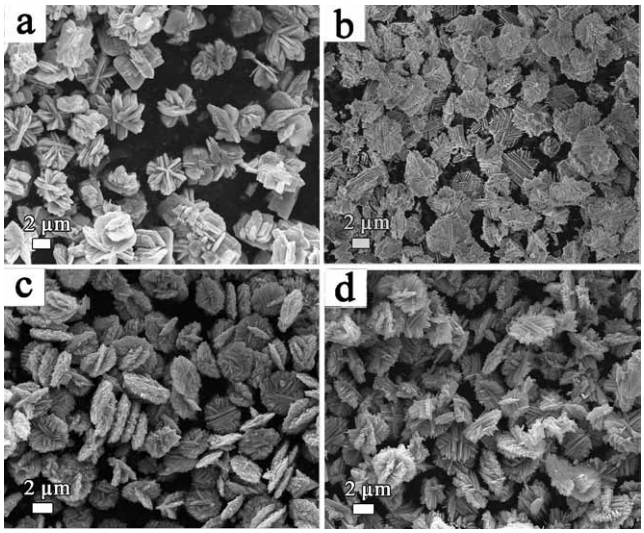

Fig. S5 SEM images of samples synthesized with different dosage of $Na_2WO_4 \cdot 2H_2O$: (a) 0.107 g, star-like hierarchitectures (b) 0.248 g, broken chrysanthemum-like hierarchitectures, (the molar ratio of $Na_2WO_4 \cdot 2H_2O$ to FA is 0.1), and the images of samples synthesized at (c) 160 ℃, similar chrysanthemum-like hierarchitectures, (d) 200 ℃, broken chrysanthemum-like hierarchitectures, for 12 h, respectively.