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Ionic liquid-modulated preparation of hexagonal tungsten trioxide mesocrystals for lithium-ion batteries

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Experimental Section

Materials

1-*n*-butyl-3-methyl imidazolium acetate ([Bmim][CH_3COO]) was obtained from Lanzhou Greenchem ILS, LICP. CAS. China. Other chemicals were purchased and used without further purification. The water used was deionized.

Synthesis of hexagonal tungsten trioxide (h-WO_3) mesocrystal

In the typical synthesis procedure, 5 mL of [Bmim][CH_3COO] was put into 20 mL of deionized water under stirring to form a homogenous solution. Subsequently, 2.7 g of $H_2C_2O_4$ (0.03 mol) was added into the above homogenous solution under continuous stirring. then 0.33 g of $Na_2WO_4 \cdot 2H_2O$ (1 mmol) was added into the solution and continued to stir for 10 min, the total solution was transferred into a stainless-steel autoclave with a capacity of 33 mL, sealed and heated at 180 ℃ for 24 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant product was collected and washed with deionized water and anhydrous ethanol for several times. The final product was dried in a vacuum at 80 ℃ for 3 h. Varying the amount of [Bmim][CH_3COO] could produce h-WO_3 with different morphologies. The synthetic conditions for preparing the typical samples are summarized in Table S1.

Characterizations

The products were characterized by XRD, SEM, TEM and HR-TEM measurements. XRD measurements were performed on a Rigaku D/max 2500 diffractometer with Cu Kα radiation (λ= 0.154056 nm) at V= 40 kV and I = 150 mA, and the scanning speed was 8°/min. Morphology observations were performed on a Hitachi S4800 field emission scanning electron microscope (FE-SEM). TEM and HR-TEM images were recorded with a Tecnai G2 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 kV.

Electrochemical Test

Electrochemical studies were characterized in CR2016-type coin cell with a multi-channel current static system Arbin (Arbin Instruments BT 2000, USA). The working electrodes were prepared by a slurry coating method on a copper foil with 80 wt% active material (h-WO_3), 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) dispersed in *N*-methyl-2-pyrrolidone (NMP). Test cells were assembled in an argon-filled glove box with water and oxygen contents less than 1 ppm using Li foil as the combined reference and counter electrode and polypropylene film (Celgard 2400) as separator. The electrolyte was 1 M $LiPF_6$ in a 1:1 (V/V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were galvanostatically discharge-charged at different current density between 0.01 and 3 V at the room temperature. Cyclic voltammetry (CV) was conducted on an electrochemical workstation (CHI660E) at a scan rate of 0.1 mV s^{-1} from 0.01 to 3.0 V.

Table S1. Summary of the Experimental Parameters and Their Corresponding Morphologies of Hexagonal WO_3 Obtained under Different Conditions.

No.	n($Na_2WO_4 \cdot 2H_2O$) (mmol)	n($H_2C_2O_4$) (mol)	V([Bmim][CH_3COO]) (mL)	Morphology
S1	1	0.03	0	spherical polycrystal
S2	1	0.03	5	biconical mesocrystal
S3	1	0.03	10	rodlike single-crystal

All the reactions were conducted at 180 ºC for 24 h.

Table S2. Summary of Refined Cell Parameters of the Samples and JCPDS Card 33-1387.

No.	*a* (Å)	*b* (Å)	*c* (Å)	*α*	*β*	*γ*	volume (Å^3)
Standard	7.298	7.298	3.899	90	90	120	179.84
S1	7.29386	7.29386	3.88869	90	90	120	179.16
S2	7.29352	7.29352	3.88845	90	90	120	179.15
S3	7.28235	7.28235	3.87831	90	90	120	179.12

Cell parameters indexed using MDI Jade

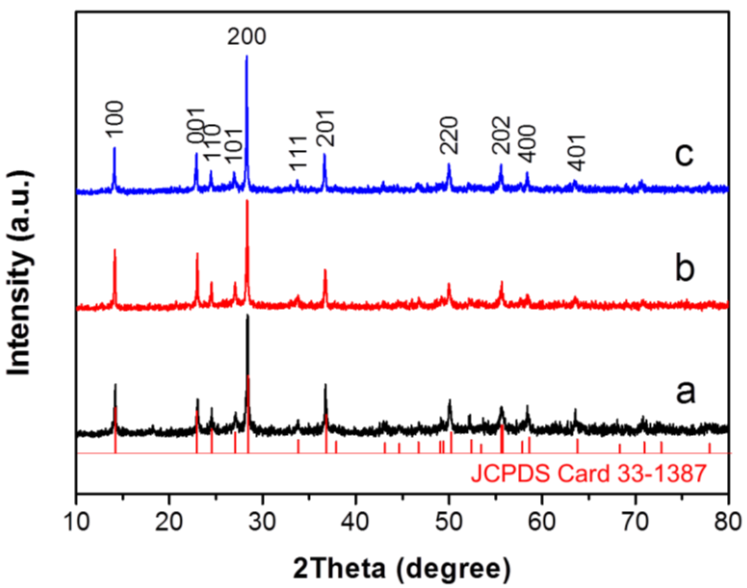

Figure S1. XRD patterns of as-synthesized hexagonal tungsten trioxides with different morphologies: (a) S1, spherical polycrystal; (b) S2, biconical mesocrystal; (c) S3, rodlike single-crystal. All of the diffraction peaks can be indexed to the hexagonal structure of tungsten trioxide, which are consistent with the reported values (JCPDS Card 33-1387).

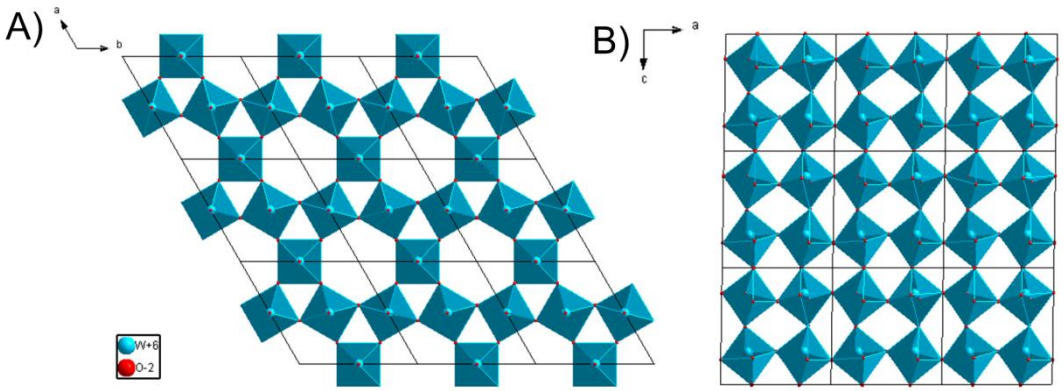

Figure S2. Structural illustrations of (A) hexagonal tungsten trioxide and (B) monoclinic tungsten trioxide (3 × 3 × 3 cells).

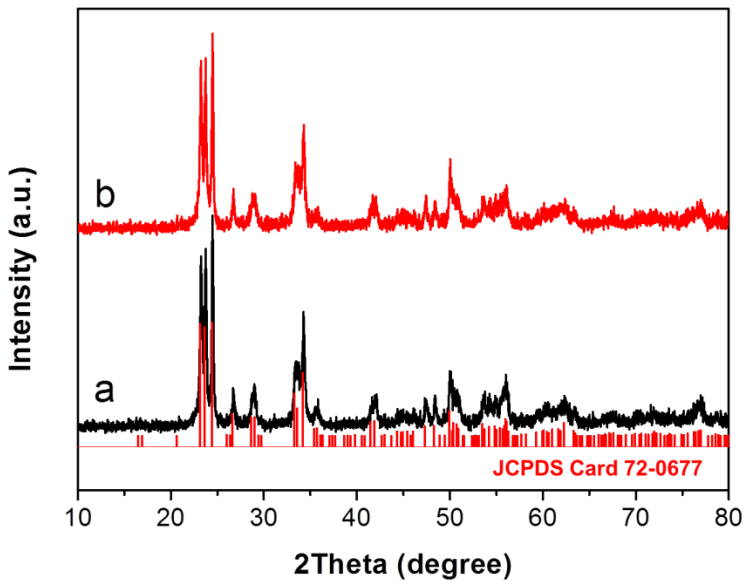

Figure S3. XRD patterns of as-synthesized monoclinic tungsten trioxides in the presence of different inorganic acid: (a) nitric acid; (b) hydrochloric acid. All of the diffraction peaks can be indexed to the monoclinic structure of tungsten trioxide, which are consistent with the reported values (JCPDS Card 72-0677).

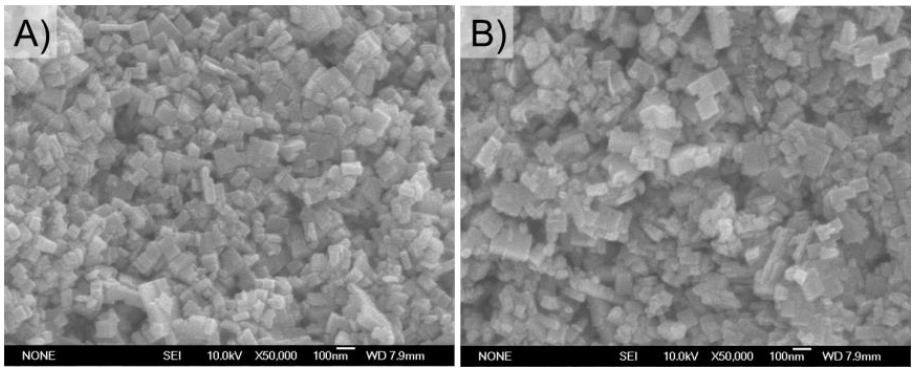

Figure S4. SEM images of as-synthesized monoclinic WO_3 nanoplates in the presence of different inorganic acid: (a) nitric acid; (b) hydrochloric acid.

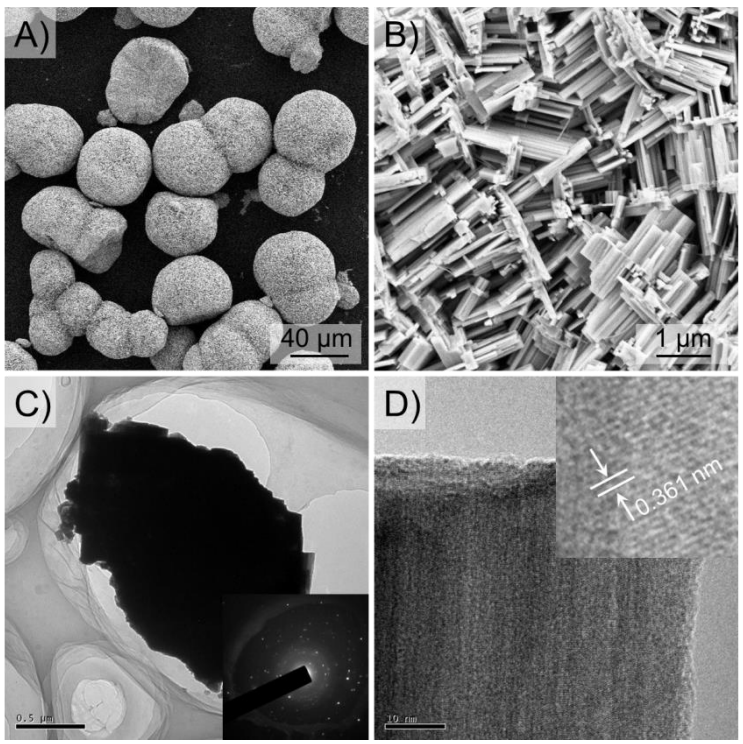

Figure S5. (A) Low- and (B) high-magnification SEM images, (C) low-magnification and (F) corresponding HRTEM images of as-prepared h-WO_3 spherical polycrystals.

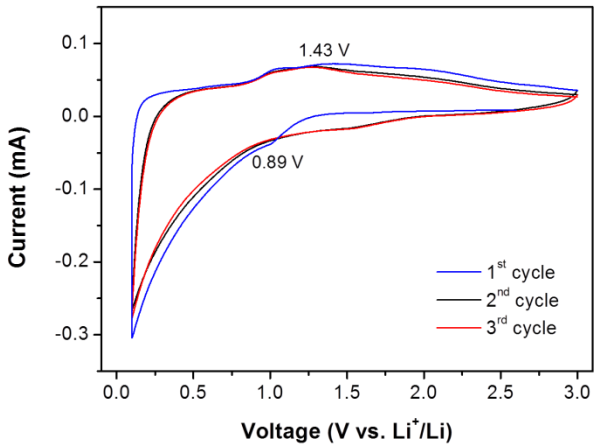

Figure S6. Cyclic voltammetry curves of h-WO_3 biconical mesocrystalline electrodes at a rate of 0.1 mV/s for the first 3 cycles.

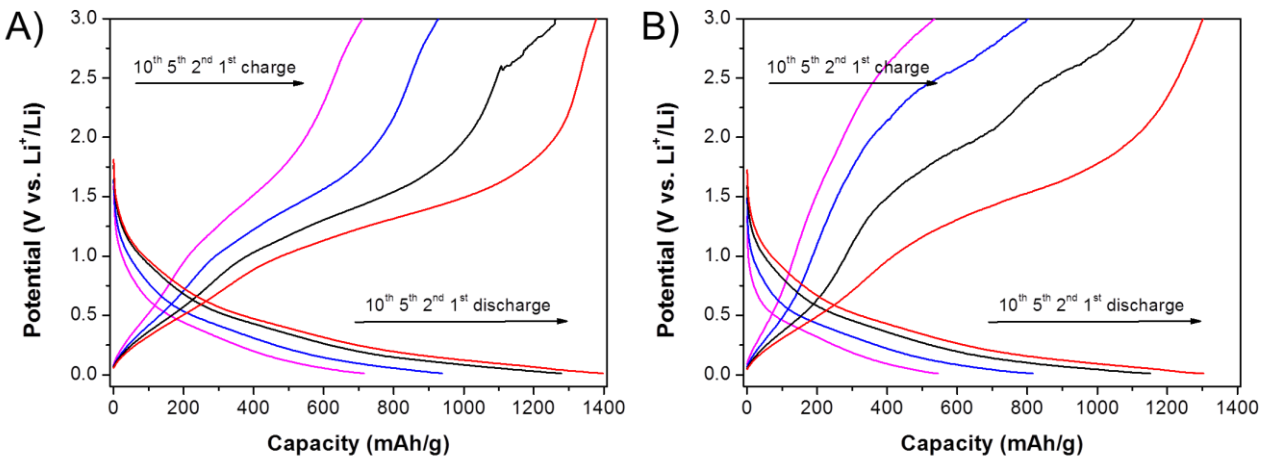

Figure S7. Galvanostatic charge-discharge profiles of h-WO_3 electrodes measured at 50 mA/g current density in the potential range of 0.01-3.0 vs. Li^+/Li: (A) rodlike single-crystals; (B) spherical polycrystals.

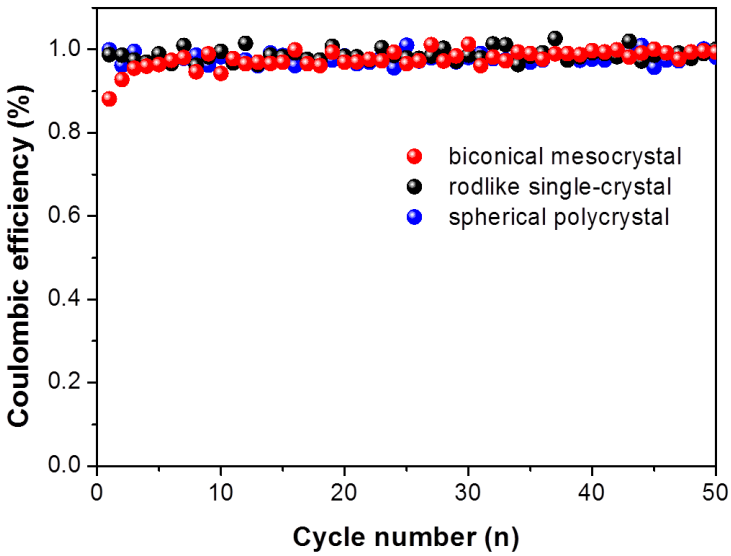

Figure S8. Coulombic efficiency versus cycle number plots of as-prepared h-WO_3 electrodes with different morphologies and crystal forms at 50 mA/g current density.

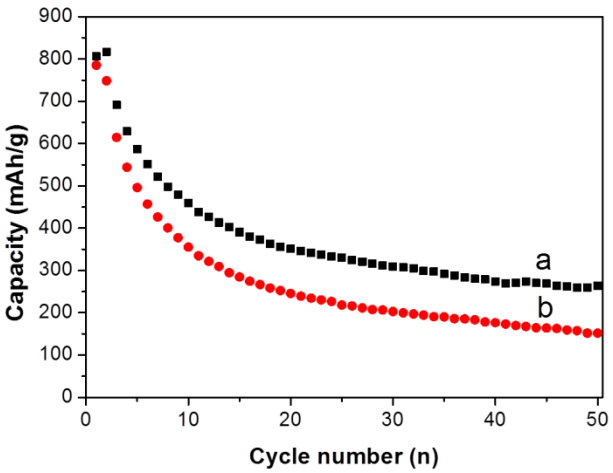

Figure S9. Cycling performance of as-synthesized monoclinic WO_3 nanoplates in the presence of different inorganic acid: (a) nitric acid; (b) hydrochloric acid. The current density is 50 mA/g.