Supporting Information

Template-Free Synthesis and Characterizations of Mesoporous Tungsten Nitride Nanoplates

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Experimental Section

Synthesis. To prepare mesoporous tungsten nitride particles, layered tungsten oxide was prepared by a hydrothermal method. For the layered tungsten oxide, ammonium tungstate ((NH₄)₁₀H₂(W₂O₇)₆, Aldrich, 99.99 %) as a precursor was dissolved in 5 M hydrochloric acid solution (Aldrich, 35%) with constant stirring at 25 °C for 1 h and then kept at 120 °C for 2 h. After the hydrothermal process, the resulting precipitate was cooled to room temperature, washed several times with ethanol and distilled water, and then filtered by using a filtration. The yellow layered tungsten oxide powder was obtained after drying in 50 °C oven. For mesoporous tungsten nitride structures, the layered tungsten oxide powder was loaded into a quartz boat, which was inserted into a vitreous quartz tube inside a cylindrical furnace, heated to reaction temperatures (600 and 700 °C) for 1 h, and then maintained at the temperature for duration times such as 3, 6, and 12 h in the NH₃ flow of 100 mL min⁻¹. The samples were cooled down to room temperature in flowing NH₃, and passivated for 2 h in flowing 1% air in order to avoid drastic reoxidation to WO₃ when they were exposed to air. Also, tungsten trioxide (WO₃, Fluka, 99.9%), was used as a precursor for nitride formation to compare with the present work.

Characterizations. The as-prepared samples were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6700F system) and field-emission transmission electron microscopy (FE-TEM, a Tecnai G2 F30 system) operating at 300 kV. The TEM samples were prepared by placing a drop of the nanoparticle suspension in ethanol on a carbon-coated copper grid. Structural analysis of the samples was carried out by an X-ray diffraction (XRD) method using a Rigaku diffractometer equipped with a Cu Kα radiation source of λ = 0.15418 nm with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2θ between 20° and 80° was explored at a scan rate of 5° min⁻¹. The surface area and porosity of the synthesized samples were analyzed by a nitrogen adsorption measurement (Micromeritics ASAP 2020 adsorption analyzer).
Figure S1. TEM images of layered tungsten oxide (a), samples prepared at 600 °C (b) and 700 °C (c) using the layered tungsten oxide in NH₃ atmosphere, and sample prepared at 700 °C (d) using commercial WO₃ in NH₃ atmosphere.
Figure S2. X-ray diffraction (XRD) patterns of as-prepared layered tungsten oxide (a) and samples (b,c) heated at 600 and 700 °C using the layered tungsten oxide in NH₃ atmosphere for 3 h and sample (d) heated at 700 °C using commercial WO₃ in NH₃ atmosphere for 3 h.
Figure S3. Characteristic curves of nitrogen adsorption-desorption isotherms and pore size distributions of W2N samples.
Figure S4. XRD patterns of samples prepared at 700 °C for 3 h (a), 6 h (b), and 12 h (c) in NH₃ atmosphere using layered tungsten oxides.
Figure S5. XRD patterns of as-prepared mesoporous tungsten nitride (a), tungsten oxide (b) prepared at 400 °C in air atmosphere using mesoporous tungsten nitride, and mesoporous tungsten nitride (c) prepared at 700 °C in NH₃ atmosphere using tungsten oxide.
Figure S6. Characteristic curves of nitrogen gas adsorption-desorption isotherms (a) and pore size distributions (b) of tungsten nitride and tungsten oxide nanoparticles.
Figure S7. CVs of W$_2$N electrodes synthesized using (a) layered tungsten oxide and (b) commercial WO$_3$, in 1 M KOH with different scan rates at 25 °C.
**Figure S8.** Specific capacitance of W$_2$N electrodes in 1 M KOH with different scan rates at 25 °C.