

Supporting Information

Self-assembly Synthesis of Tungsten Oxide Quantum Dots with Enhanced Optical Properties

Songling Wang, ‡ *Stephen V. Kershaw,* § *Guisheng Li**§, and *Michael K. H. Leung,* *, ‡

§Key Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai, China.

‡Ability R&D Energy Research Centre, School of Energy and Environment, City University of Hong Kong, Hong Kong, China.

§Department of Applied Physics, City University of Hong Kong, Hong Kong, China.

E-mail: *mkh.leung@cityu.edu.hk*, Fax: (852)34420688, Tel: (852)34424626;
Liguisheng@shnu.edu.cn, Fax: +(86)21-64322272, Tel: +(86)21-64321673.

(1) Chemicals and characterizations

Tungsten chloride (WCl_6) ($\geq 99.9\%$), ethanol (99.9 %), and ethylene glycol (99.8 %) were purchased from Sigma-Aldrich. UV-visible Absorption spectrum was measured with a Varian Cary 50 Conc UV-Visible spectrometer. Photoluminescence spectrum was measured with a Varian Cary UV-Visible photospectrometer. Transmission Electron Microscopy (TEM), High-resolution Transmission Electron Microscopy (HRTEM) was performed using TEI Tecnai G220 Scanning TEM. X-Ray Diffraction (XRD) pattern was recorded on D/MAX-2000 diffractometer with high-intensity $\text{CuK}\alpha$ irradiation ($\lambda=1.5406 \text{ \AA}$). X-Ray Photoelectron Spectroscopy (XPS)

measurements were done on Perkin-Elmer PHI 5000C XPS system with a monochromatic Al-K α source and a charge neutralizer. All the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. Gas chromatography-mass spectrometry (GC-MS) was performed on the Agilent GC/MS (Agilent 7890A GC/Agilent 5975C MS). The analysis information: column (DB-5MS 30 m x 250 μ m x 0.25 μ m); oven Program(40 °C for 3 min, 15 °C/min to 150°C for 0 min, 25 °C/min to 260 °C for 2 min) Split Ratio: 30:1; injection Volume (1 μ L); mass range (36-600 amu).

(2) Experimental sections

Synthesis of the tungsten oxides, titanium oxides, copper oxides, and iron oxides nanoparticles:

In a typical synthesis, tungsten chloride (WCl₆) (0.1 g) was added to ethylene glycol (10 mL) under stirring at room temperature. After WCl₆ dissolving completely, the solution became colorless and transparent. Then, this solution was transferred into a Teflon-lined double-walled digestion vessel (50 mL) in the microwave digestion system (Ethos TC, Milestone) for microwave treatment at 160 °C, power 800 W, for 40 min. After microwave irradiation, the microwave system was cooled to room temperature, and a yellowish colloidal solution was obtained. The as-prepared sample was washed 3 - 4 times by acetone and ethanol to remove the rest organics. Finally, the yellowish tungsten oxides (WO₃) quantum dots (QDs) precipitates were obtained by centrifugation. In order to investigate the formation mechanism of WO₃ QDs,

different microwave reaction time (10, 15, 20, and 30 min) were chosen for obtaining various sample. Based on the same experimental conditions, other ultrafine metal oxides nanoparticles could be also prepared, including TiO_x (0.05 ml TiCl_4 , 160 °C, 10 min), CuO_x (0.1 g CuCl_2 , 180 °C, 60 min), and FeO_x (0.1 g FeCl_3 , 180 °C, 45 min).

UV-vis absorbance and photoluminescence measurements of the WO_3 QDs:

The as-synthesized WO_3 QDs was dispersed in ethylene glycol (10 mL) for obtaining a transparent suspension solution A. Then 3 mL of the above solution was sampled in a quartz cell (5 mL) for UV-vis absorbance and photoluminescence measurements.

Thermal/photonic stabilities measurements of the WO_3 QDs:

For thermal-stability assessment, the above suspension solution A was sealed in a Teflon cell and then kept in oven for heat treatment under different temperatures (60 °C, 1h; 120 °C, 1h; 120 °C, 1d; 120 °C, 2d; 120 °C, 4d). Then, the resulted samples (0.05, 0.1, 0.15, 0.2 mL) were diluted with ethylene glycol (4 mL) for PL spectra. The thermal stability of WO_3 QDs can be obtained through comparing the PL maximum positions of these samples with that of as-prepared WO_3 QDs without heat treatment. For photo-stability measurement, the suspension solution A was exposed to UV light irradiation (with the wavelength of 365 nm) for different time (1 to 24 h), and then their PL spectra were recorded. The relative decrease of maximum PL intensities were plotted to directly evaluate the photo-stability of WO_3 QDs at extending UV light exposure time.

Photochromism and UV-vis absorbance measurements of the WO_3 QDs:

The as-prepared WO₃ QDs were dispersed in the water (20 mL) to form a colorless suspension solution. The solution became blue upon being exposed to solar-light (the light source: CEL-HXF300/CEL-HXUV300, Power: 300 W) for 10 s. Then, the blue solution was tested by UV-vis absorbance. For the de-coloration measurement, the blue solution was kept in dark for different time (10, 20, and 40 min) and then was analyzed by UV-vis absorbance.

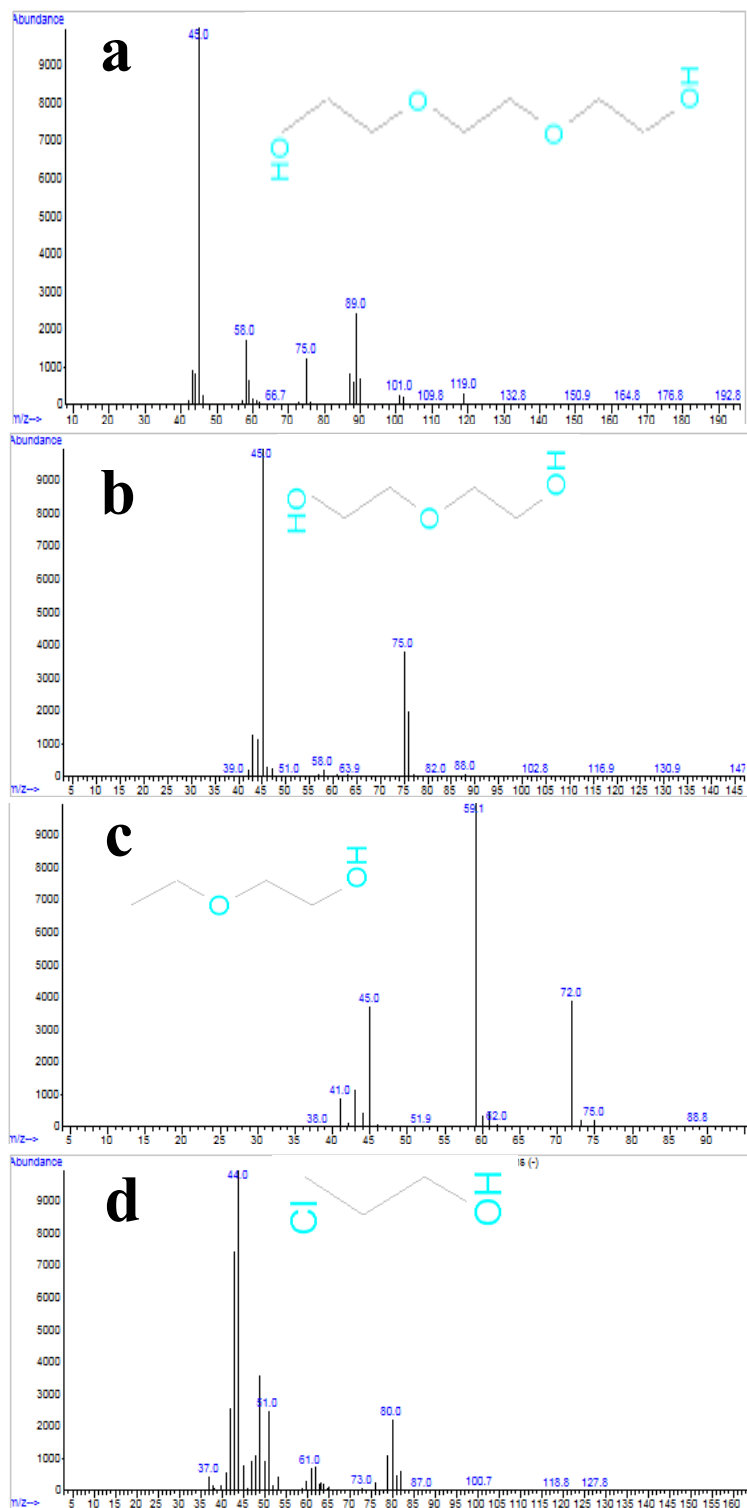


Figure S1. Gas chromatography-mass spectrometer (GC-MS) of chain-like linkage ethers detected in the supernatant solution of as-prepared WO₃ QDs obtained by the microwave treatment for 40 min.

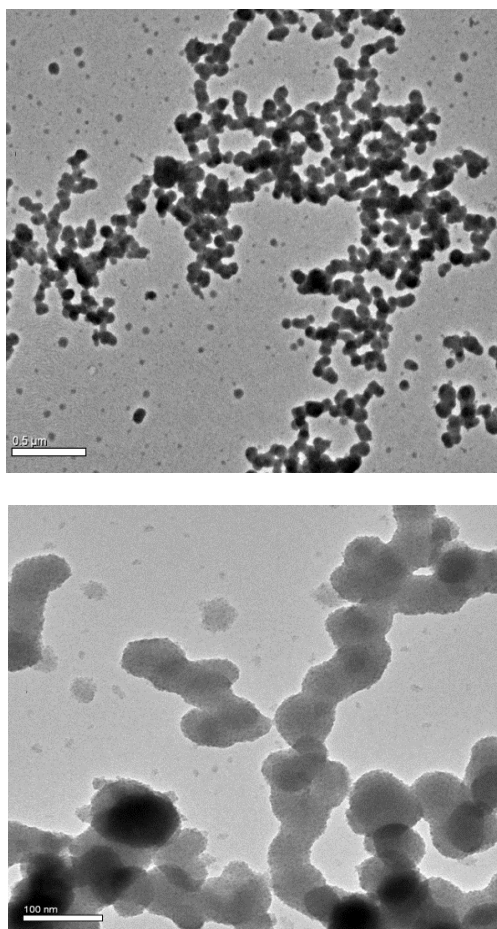


Figure S2. Low-magnification TEM image of as-prepared tungsten oxide sample synthesized by microwave reactions for 10 min.

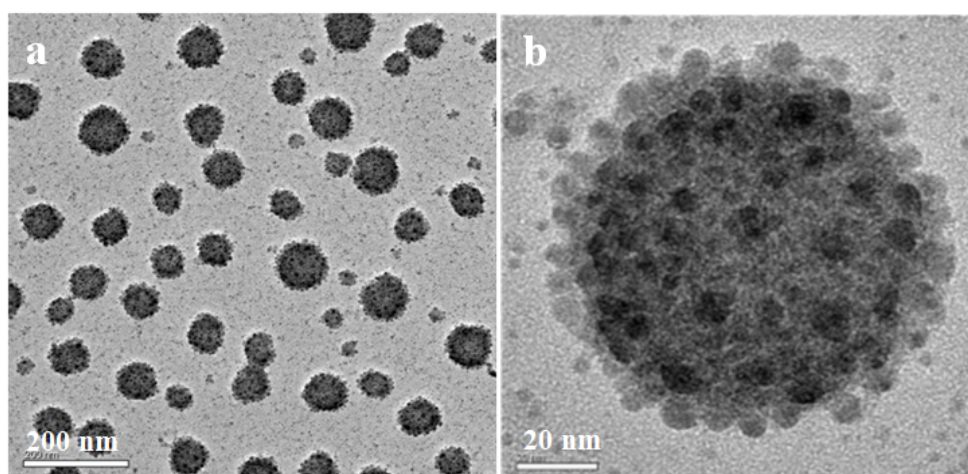


Figure S3. Low-magnification (a) and high-magnification (b) TEM images of the sample fabricated by microwave reactions for 20 min.

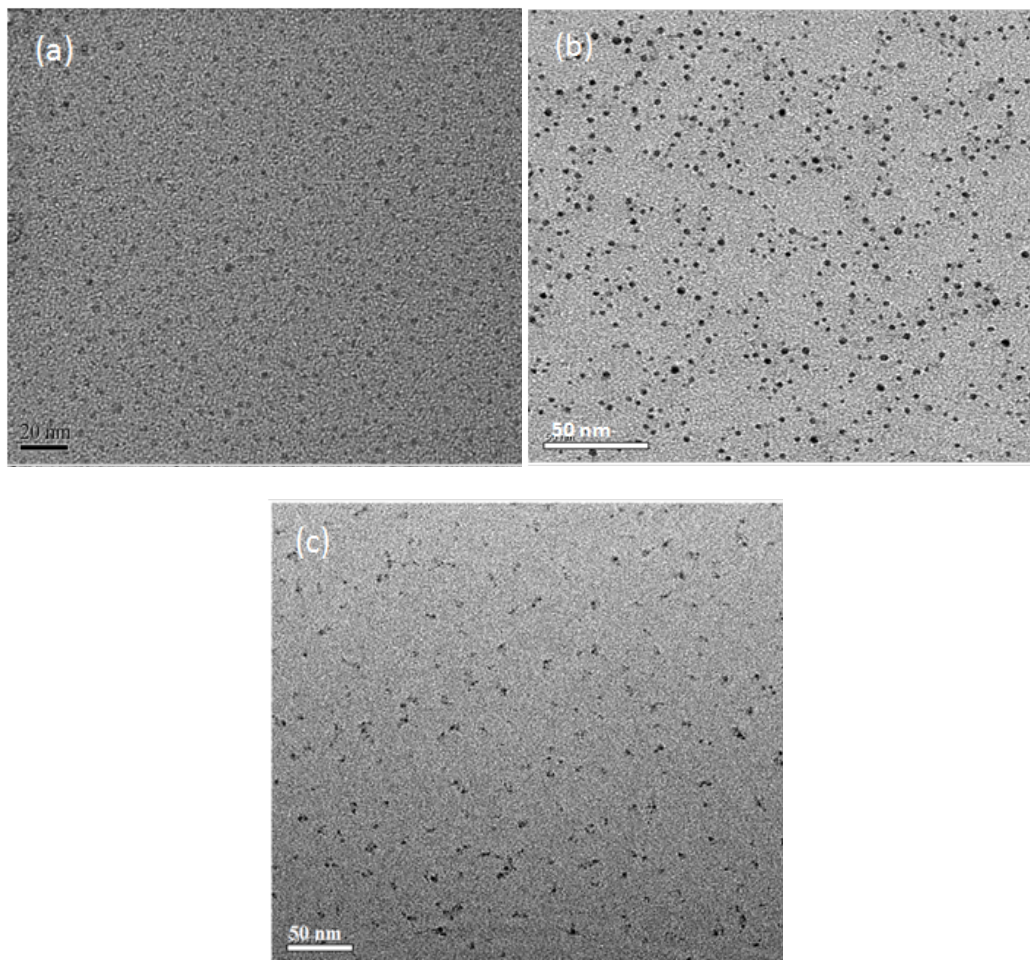


Figure S4. TEM images of ultrafine metal oxides obtained by microwave reactions at different conditions: (a) Titanium oxide, 160 °C, 10 min; (b) Copper oxide 180 °C, 60 min; (c) Iron oxies, 180 °C, 45 min.

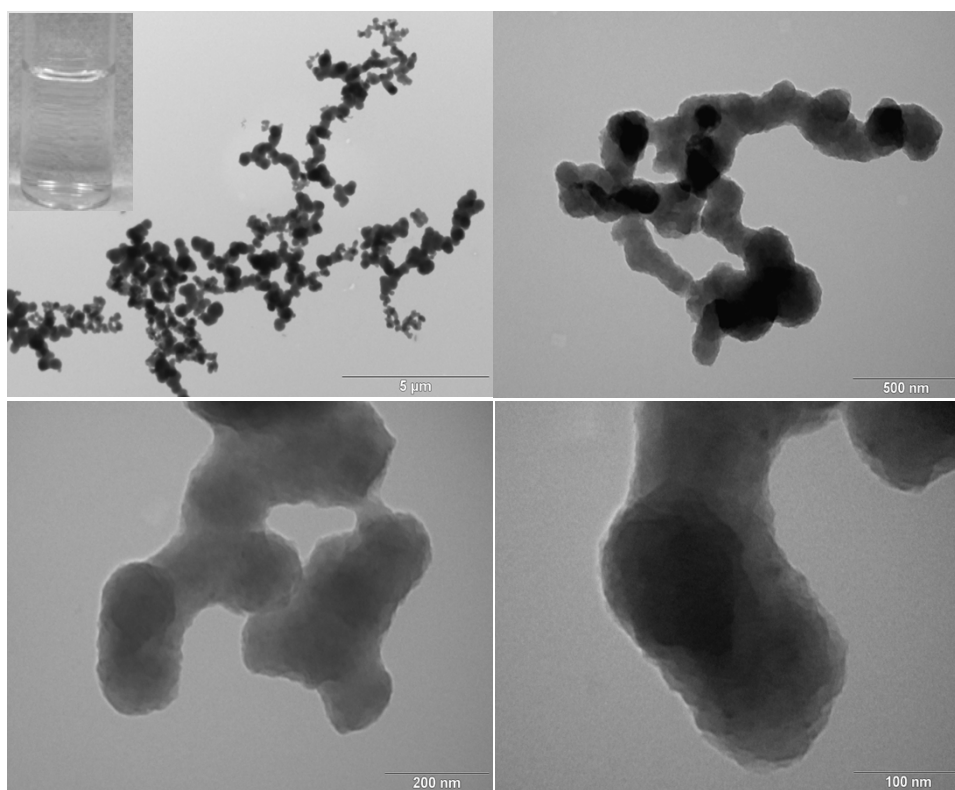


Figure S5. The digital picture and TEM images of the pure ethylene glycol after microwave irradiation at 160 °C for 40 min.

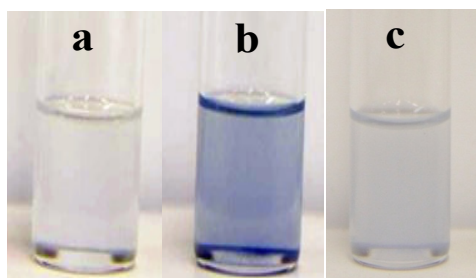


Figure S6. The digital pictures of the as-synthesized WO_3 QDs dispersed in water: (a) before solar-light irradiation, (b) after 10s of solar-light irradiation, (c) the bleached state after 40 min in dark.