Supporting Information

Ligand-Free and Size-Controlled Synthesis of Oxygen Vacancy-Rich WO_{3-x} Quantum Dots for Efficient Room-Temperature Formaldehyde Gas Sensing

*Yahui Li, Qiqi Zhang, Xinshi Li, Hua Bai, Wentao Li, Tingting Zeng, and Guangcheng Xi**

Experimental Section

Synthesis of m-WO_{3-x} QDs: In a typical synthesis, 0.05 g of anhydrous tungsten chloride (WCl_6) and 1.0 mL of hydrazine hydrate ($N_2H_4 \cdot H_2O$) were added to 40 mL of anhydrous ethanolin a nitrogen-filled glove box. The obtained blue solution was transferred to a sealed Teflon-lined autoclave. The autoclave was placed in a precision blowing oven with accurate temperature control at 180 °C and was maintained at this temperature for 11 hours. After the reaction, the autoclave was naturally cooled to room temperature, and the obtained blue products were collected by high-speed centrifugation and washed with distilled water and anhydrous ethanol three times. Finally, the sample was dried under vacuum at 50 °C in a vacuum drying box for 4 h.

Characterization: The X-ray diffraction (XRD) patterns of the products were recorded on a Bruker D8 Focus diffractometer using CuKα radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDS) spectra were obtained on a Hitachi S–4800 instrument. Transmission electron microscopy (TEM), high–resolution TEM (HRTEM), and EDS mapping characterizations were performed on a Tecnai G F30 operated at 300 kV. UV–Vis–NIR absorption spectra were recorded on a Shimadzu UV-3600. X-ray photoelectron spectroscopy (XPS) experiments were performed in a Theta probe (Thermo Fisher) using monochromated Al Kα X-rays at hυ = 1486.6 eV. The peak positions were internally referenced to the C1s peak at 284.6 eV. Fourier transform infrared (FTIR) spectra were obtained on a Thermo Iz10 instrument. The Raman spectra were produced at room temperature on a Renishaw-inVia Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm.

Gas-Sensing Measurements: The m-WO_{3-x} QD sensor was fabricated by dip-coating the as-prepared WO_{3-x} quantum dot alcohol colloids to the ceramic tube of the sensor body without an additional aging process. The structure of the WO_{3-x} QDs-based gas sensor is shown in Figure S7. The gas-sensing properties of the WO_{3-x} QDs-based sensor were detected on a gas-sensitive cell testing system (WS-60A, Zhengzhou Winsen Electronics Technology Co., Ltd. China). The structure of the WS-60A instrument is shown in Figure S8. The sensitivity (S) is defined as $S=R_0/R$, where R_0 is the resistance in atmospheric air (relative humidity of approximately 20%) and R is the resistance of the WO_{3-x} quantum dots in formaldehyde-air mixed gas. R_0 was approximately 4.7 MΩ in atmospheric air at room temperature (20-25 °C).

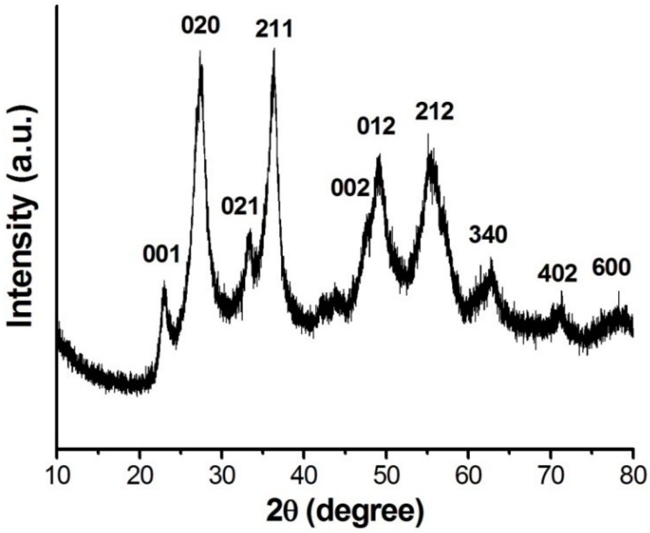

Fig. S1 XRD pattern of the 2.2 ± 0.3 nm WO_{3-x} quantum dots. All the diffraction peaks of the sample were easily indexed as monoclinic-phase WO_{3-x} (PCPDF no. 89-4476). All of the diffraction peaks of the sample wereobviously widened, which strongly suggests a very small crystal grain size. According to the full width at half maximum (FWHM) of the (020) diffraction peak, the average grain size of the m-WO_{3-x} was approximately 2.3 nm.

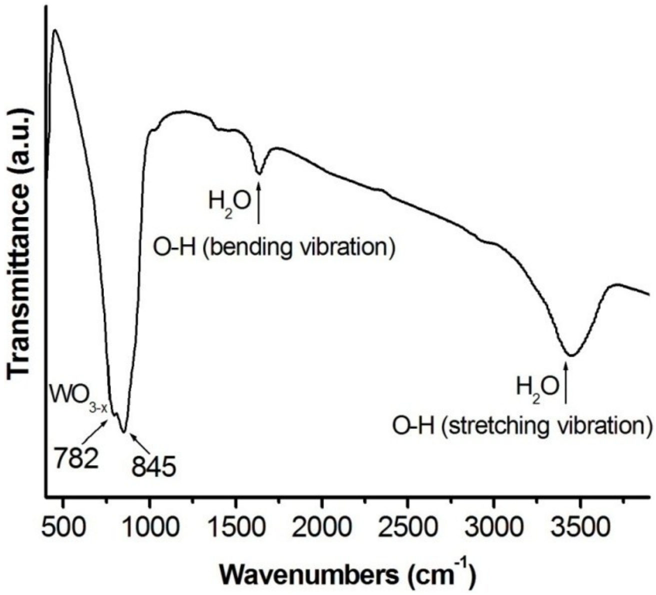

Fig. S2. FTIR spectrum of the 2.2 ± 0.3 nm WO_{3-x} QDs. The bands in the region of 1000–500 cm^{-1} are attributed to the W-O (845 cm^{-1}) units and the stretching vibrations of the bridging oxygen atoms O-W-O (782 cm^{-1}).

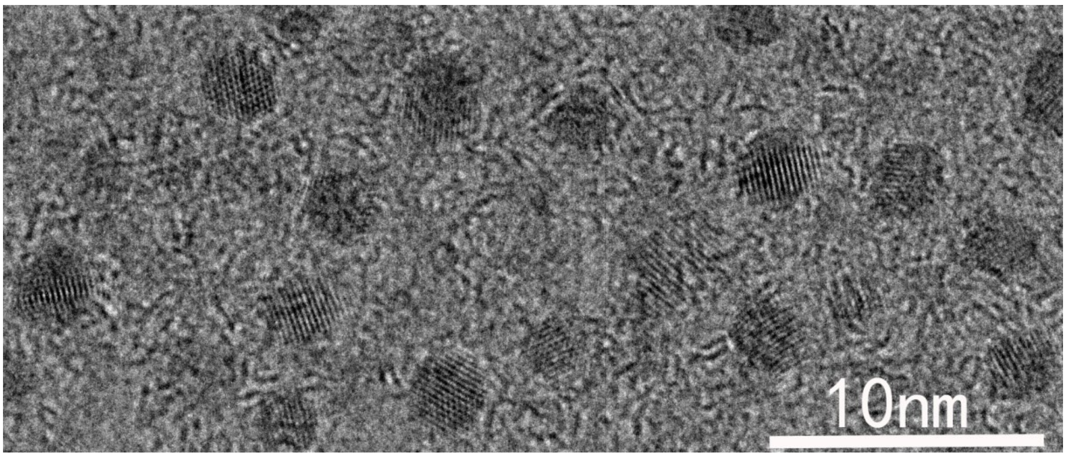

Fig. S3. HRTEM image showing a wide-area view of the as-prepared 2.2 ± 0.3 nm m-WO_{3-x} QDs. The clear crystal lattice fringes indicate that the m-WO_{3-x} QDs were highly crystalline.

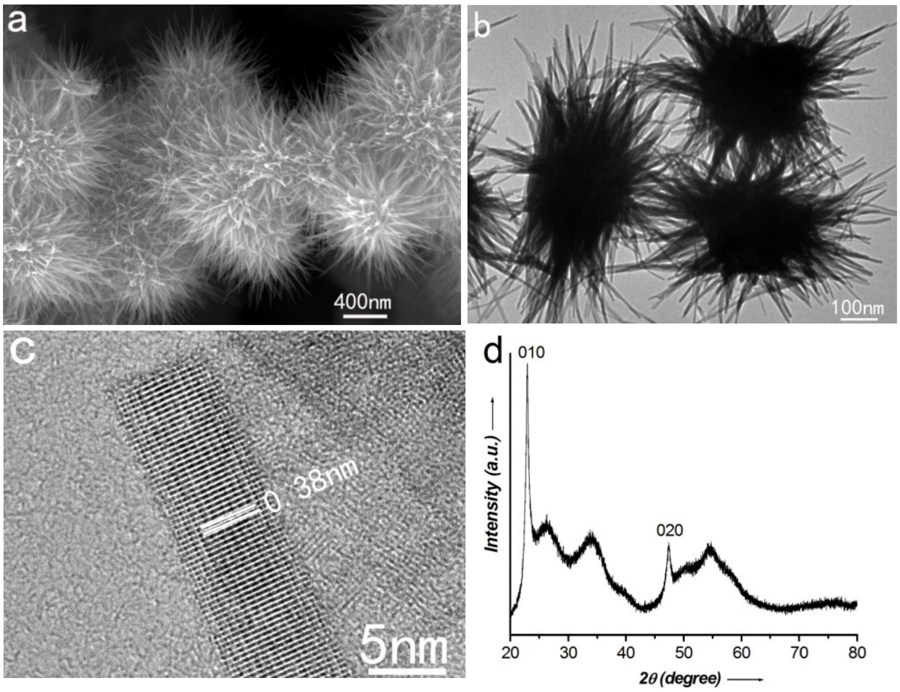

Fig. S4. Keeping the other reaction conditions unchanged, comparative experiments showed that only urchin-like $W_{18}O_{49}$ nanowire aggregates were prepared by directly hydrolysing WCl_6 in ethanol without $N_2H_4 \cdot H_2O$: a) SEM and b) TEM images of the urchin-like $W_{18}O_{49}$ nanowire aggregates; c) HRTEM image of the $W_{18}O_{49}$ nanowires, for which the lattice fringes with aspacing of 0.38 nm can be indexed as the (010) crystal plane of monoclinic-phase $W_{18}O_{49}$; d) XRD pattern of the $W_{18}O_{49}$ nanowires, which can be indexed as monoclinic $W_{18}O_{49}$ (JCPDS No.: 05–0392).[1,2]

References

[1] G. C. Xi, S. X. Ouyang, P. Li, J. H. Ye, Q. Ma, N. Su, H. Bai, C. Wang, *Angew. Chem. Int. Ed*., **2012**, *51*, 2395–2399.

[2] W. Cheng, Y. R. Ju, P. Payamyar, D. Primc, J. Y. Rao, C. Willa, D. Koziej, M. Niederberger, *Angew. Chem. Int. Ed*., **2015**, *54*, 340–344.

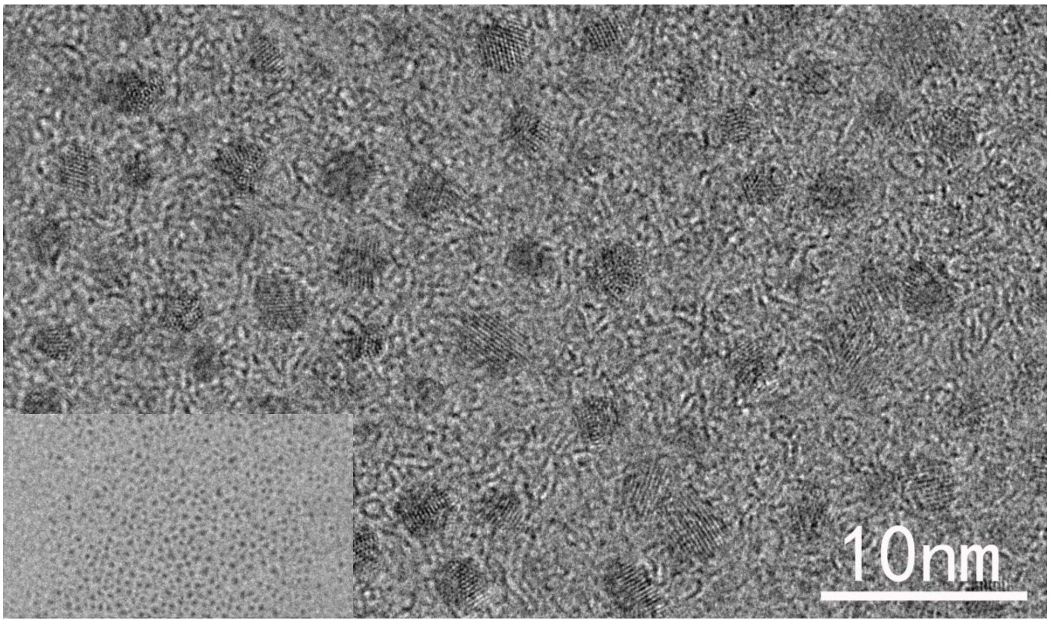

Fig. S5 HRTEM and TEM (inset) images of the WO_3 QDs prepared by oxidizing the blue m-WO_{3-x} QDs (2.2 ± 0.3 nm) with a dilute aqueous H_2O_2 solution (1 M) at room temperature.

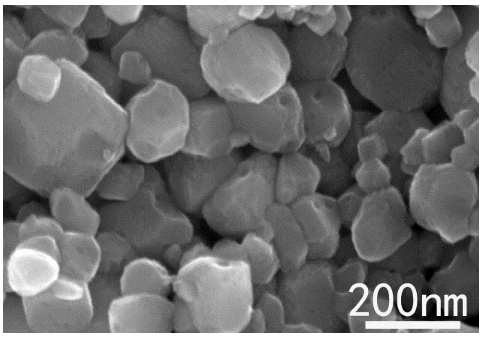

Fig. S6 SEM image of commercial monoclinic-phase WO_3 powder.

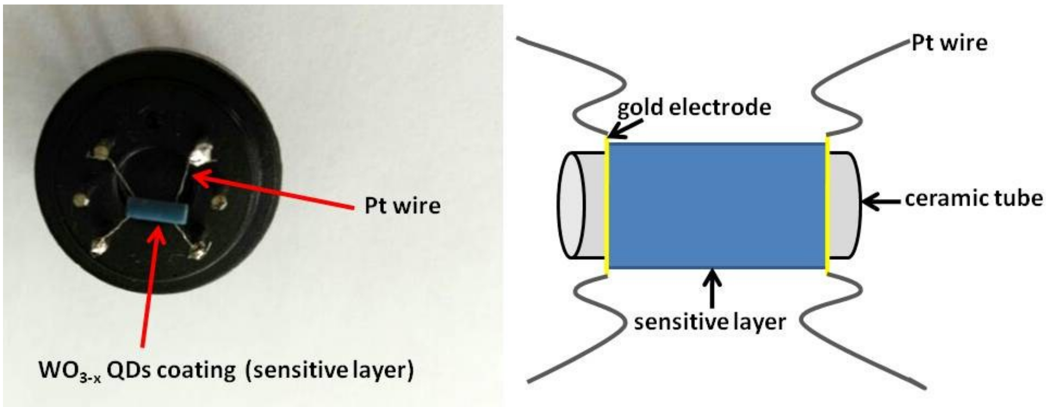

Fig. S7. Structure of the WO_{3-x} QD-based gas sensor.

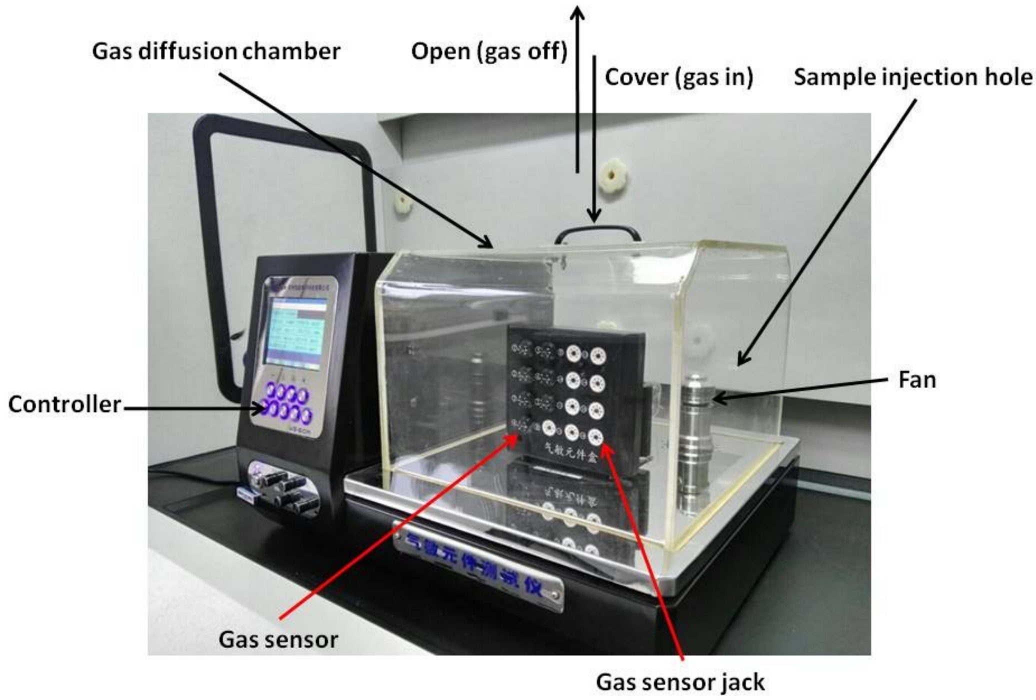

Fig. S8. Structure of the gas-sensing measurement system (WS-60A, Zhengzhou Winsen Electronics Technology Co., Ltd. China).