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Supporting Information Available:

Synthesis of WO_3 nanostructures and their ultraviolet photoresponse property

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Synthesis of WO_3 nanostructures

We have synthesized WO_3 nanostructures such as nanowires, nanorods bundles and nanotubes bundles by a facile hydrhtermal method described as follows: First, two kinds of acid solutions were prepared, one was hydrochloric acid solution (2M) by adding concentrated hydrochloric acid (12M) to de-ionized water with the volume ratio of 1:5, another was citric acid solution (2M) by dissolving citric acid power (12.61 g) into 30 ml de-ionized water. Then sodium tungstate power (0.66 g) was dissolved in 20 ml de-ionized water under vigorous magnetic stirring and then ammonium sulfate (0.53 g) was dissolved in the Na_2WO_4 solution (a compared experiment was also conducted without $(NH_4)_2SO_4$), after stirring for 30 min, 2M HCl solution was slowly dropped into the mixed solution under magnetic stirring until the pH value of the solution reached 0.5-2 and then the solution was transferred into a Teflon-lined 50 ml capacity autoclave, and maintained at 180 ^oC for 4 h. After reaction, the autoclave cooled down naturally to room temperature and the precipitate was centrifuged and washed with de-ionized water and absolute ethanol for 2-3 times to remove ions that possibly remained at the final products, then dried at 60 ^oC for 12 h. Meanwhile, another experiment was carried out with 2M citric acid solution as the acidification agent instead of 2M HCl solution to adjust the pH value of solution in the presence of ammonium sulfate while keeping other conditions unchanged.

Growth procedure of WO_3 nanorods bundles (Sample B)

The growth procedure of WO_3 nanorods bundles may be involved with two stages. At the early stage, WO_3 nanoparticles form immediately and aggregate to nanorods with $(NH_4)_2SO_4$ as capping agent, subsequently, the formed nanorods bond compactly together to form larger rods crystals under Van der Waals force. As the reaction proceeds, the concentration of H^+ decreases sharply and the WO_3 crystal growth is initiated preferentially from the active nanoparticles regarded as the WO_3 nucleation sites on the surface of nanorods bundles.[S1]

Growth process and mechanism of WO_3 nanotubes bundles (Sample C)

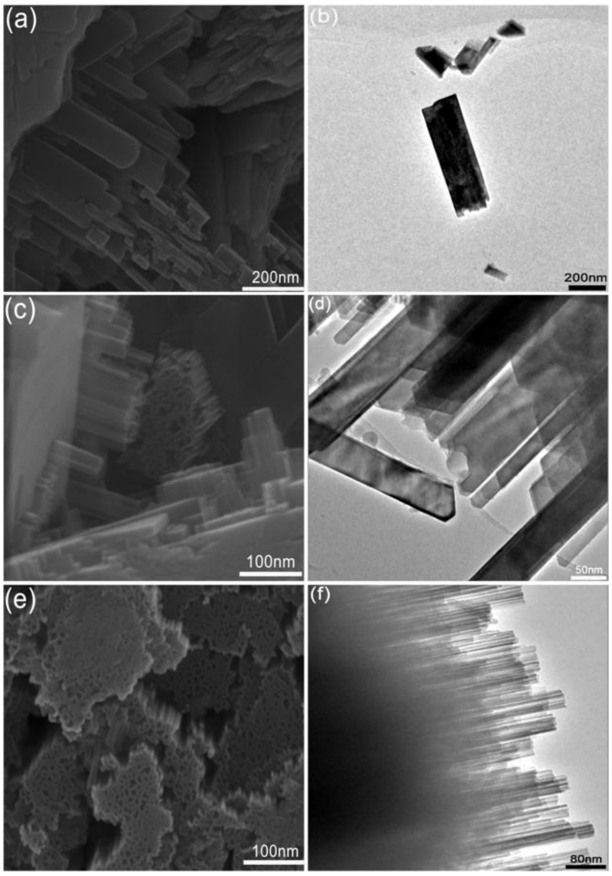

Fig. S1 SEM images (a, c, e) and TEM images (b, d, f) of WO_3 nanotubes bundles prepared at different times: (a, b) 1h; (c, d) 2h and (e, f) 4h.

Fig. S1 show the corresponding SEM and TEM images and present the morphology evolvement of WO_3 nanotubes bundles. At the original stages as shown in Fig. S1(a, b), the intermediate products collected after 1h are irregular quadrate or rectangle WO_3 plates, which start to assemble together to form larger WO_3 plates after reaction for 2 h, and Fig. S1(c) shows that WO_3 nanotubes clusters start to grow on the surface of the WO_3 plates. When the reaction time is further increased to 4 h, the whole surface is almost covered with the large numerous, highly aligned, and closely packed nanotubes shown in Fig. S1(e, f). Based on the above experimental results, the formation process of the nanotubes bundles can be illustrated as follows: at the beginning stage of hydrothermal reaction, the WO_3 nanoparticles form quickly and aggregate to quadrate or rectangle building blocks under high concentration of H^+, due to the weak interaction, the building blocks further assemble to larger plates. As the reaction proceeds, the concentration of H^+ is reduced sharply, and the hydrothermal reaction becomes slow, subsequently the new WO_3 crystal growth is initiated preferentially along the dangling bonds acting as nucleation sites, which have been proved to exist by the Raman and XPS Spectra, on the surface of the plates. Finally, the closely arranged nanotubes bundles form on the whole surface of the WO_3 plates.

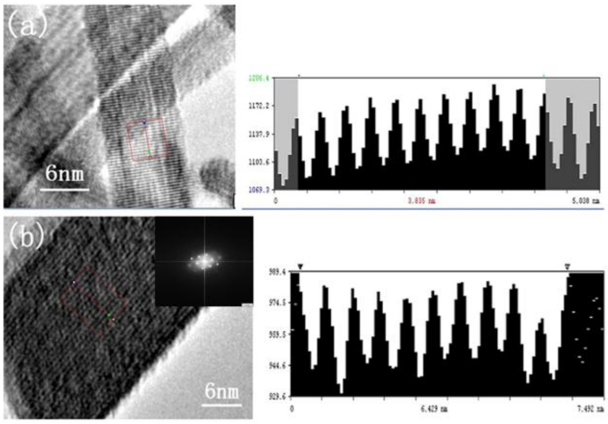

Fig. S2 HRTEM images of (a) WO_3 nanowires (Sample A) and (b) WO_3 nanotubes bundles (Sample C) (the inset is SEAD image)

Fig. S2a shows the HRTEM images of WO_3 nanowires (Sample A), ten lattices spacing (3.835 nm) is measured shown in the right image. So the lattice spacing is 0.3835 nm, corresponding to the d-spacing in (002) plane of WO_3 nanowires. The lattice spacing is 0.6429 nm for WO_3 nanotubes bundles as shown in the Fig. S2b.

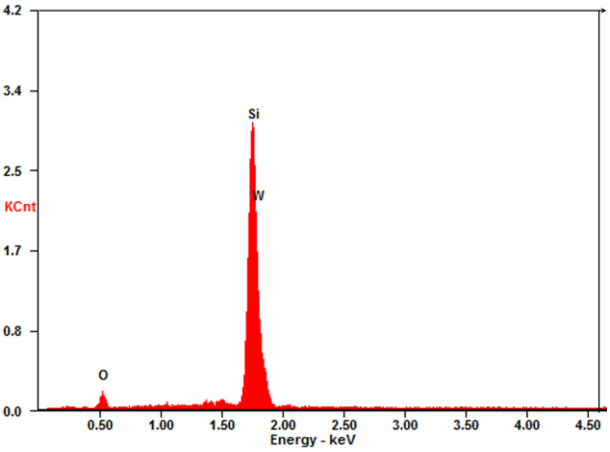

Fig. S3 EDX spectra of WO_3 nanowires (Sample A) prepared with HCl.

The EDX spectra of WO_3 nanowires present the existence of W and O elements and the Si signal is from the substrate used in the test. Software analysis indicates that the atomic ratio of O/W is close to 3 for WO_3 nanowires.

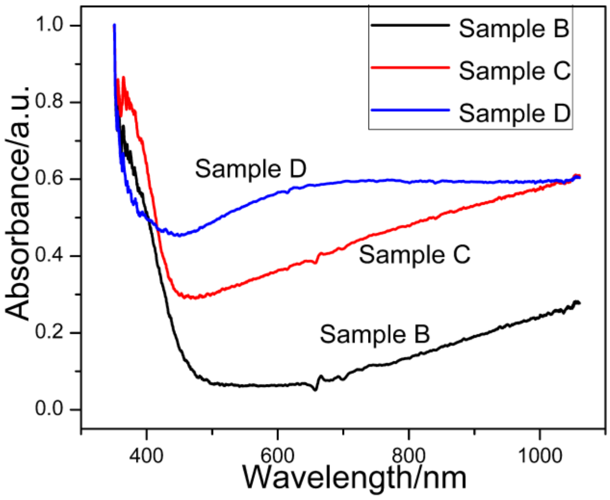

Fig S4 UV-Vis absorption spectra of WO_3 nanostructures. Sample B (nanorods bundles), Sample C (nanotubes bundles), Sample D (blue nanowires).

All the absorption spectra of three WO_3 samples start to rise sharply at about 450 nm resulting from the inter-band absorption, indicating that the band gap of these WO_3 samples is similar, which is about 2.76 eV. Fig. S4 obviously shows that the different WO_3 samples present different absorbance. According to Y. A. Yang [S2], the absorbance of MoO_3 film increased with an increasing amount of the injected H^+ ions, in our case, the exists of low valence W species (W^{5+}) result in the different absorbance, and the content of the defects (low valence W species) in these samples arranges as Sample D > Sample C > Sample B, which is consist with the Raman and XPS analysis.

References

S1 Z. Gu, T. Zhai, B. Gao, X. Sheng, Y. Wang, H. Fu,Y. Ma, and J. Yao, *J. Phys. Chem. B*, 2006, **110**, 23829.

S2 Y. A. Yang, Y. W. Cao, B. H. Loo and J. N. Yao, *J. Phys. Chem. B*, 1998, **102**, 9392.