Supplementary Material (ESI) for Chemical Communications

Supporting Information

Hexagonal single crystal growth of WO_3 nanorods along a [110] axis with enhanced adsorption capacity

Jian Zhu,[a] Songling Wang,[a] Songhai Xie,[b] Hexing Li*,[a]

[a]The Education Ministry Key Lab of Resourse Chemistry, Shanghai Normal University, Shanghai 200234, China. [b]Department of Chemistry, Fudan University, Shanghai 200234, China.

1. Sample preparation

The WO_3-110-1 was synthesized according to the following procedure. 1.2 g $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ was dissolved in 40 mL aqueous solution. The acid of solution was adjust to pH = 1 by dropwise addition of 0.60 M H_2SO_4 with constant magnetic stirring at room temperature. Then, the solution was transferred into a Teflon-lined 50 mL autoclave for hydrothermal treating at 100°C for 24 h. After being cooled down to room temperature, the prepared WO_3 powders were filtrated and washed thoroughly with water, followed by drying at 100°C for 12 h. TheWO_3-110-2 was synthesized in the same way by using 1.2 M HCl instead of 0.60 M H_2SO_4. Calcination of the WO_3-110-1 at 350°C for 5 h resulted in the WO_3-110-3.

The WO_3-001-1 was prepared in the similar way to that used for synthesizing WO_3-110-1 by using 1.6 g $Na_2WO_4\cdot 2H_2O$ instead of 1.2 g $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ in 0.60 M H_2SO_4 aqueous solution. The WO_3-001-2 was obtained by using 1.2 M HCl instead of 0.60 M H_2SO_4.

For comparison, the WO_3-R1 was also synthesized according to the procedure reported elsewhere. Briefly, 10 g $H_2W_2O_7\cdot 1.5H_2O$ was dispersed in 66 mL n-octylamine and 330 mL heptane at room temperature. After being stirred for 72 h, the as-received white solid was washed thoroughly with ethanol, followed by drying at 100°C for 12 h. Then, the solid product (10 g) was dispersed in500 mL aqueous solution containing 24 wt% HNO_3. A yellow suspension was obtained after reaction

for more than 2 days, which were collected and washed with H_2O and ethanol, followed by drying at 100^oC and calcining at 450^oC for 2 h at a heating rate of 2^oC/min, leading to the final product WO_3-R1.

2. Adsorption test

In each run of tests, 0.070 g WO_3 was added into 50 mL aqueous solution containing different amount (40, 80, 100, 120, 320, and 560 mg/L) of rhodamine B (RhB) or methylene blue (MB). The solution was oscillated for 12 h at 25°C in a water bath (SHA-C) to reach adsorption equilibrium. The RhB or MB left in the solution was determined by UV-visible spectrophotometer from which the adsorption capacity could be calculated.

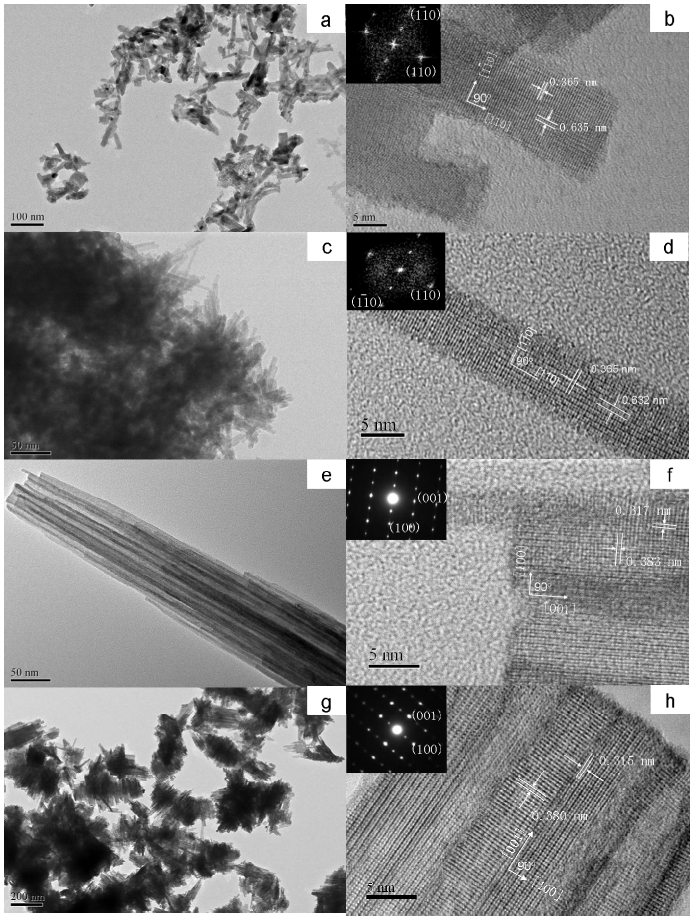


Fig. S1 TEM and HRTEM images of (a, b) WO_3-110-3, (c, d) WO_3-110-2, (e, f) WO_3-001-1, (g, h) WO_3-001-2. The insets are the FFT images (b, d) and the SAED patterns.

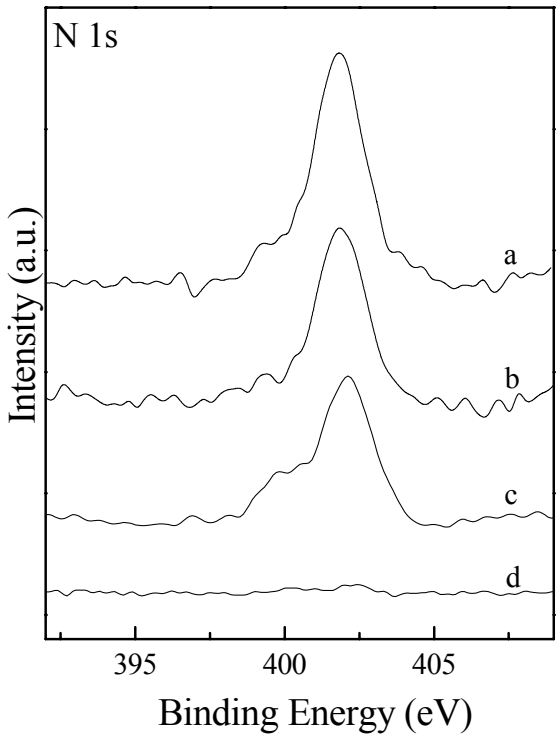


Fig. S2 N 1s XPS spectra of (a) the WO_3-110-1, (b) the WO_3-110-1 after being immerged in 0.50 M HCl aqueous solution for 12 h, (c) the WO_3-110-4 obtained by immerging WO_3-110-3 NH_4Cl solution for 24 h at 25^oC, and (d) WO_3-110-3.

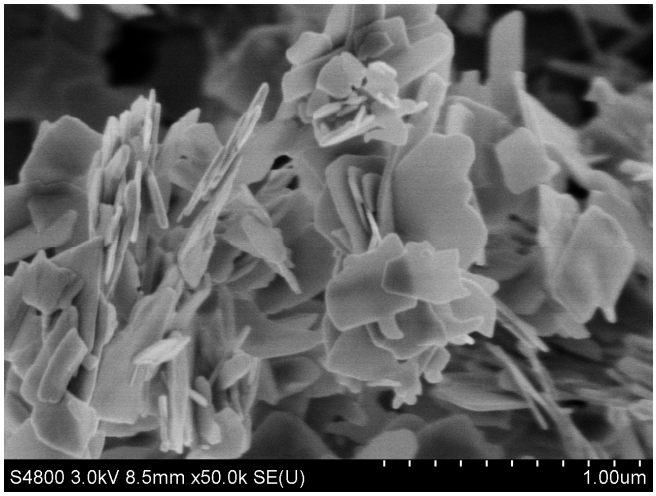


Fig. S3 SEM image of the WO_3-R1.

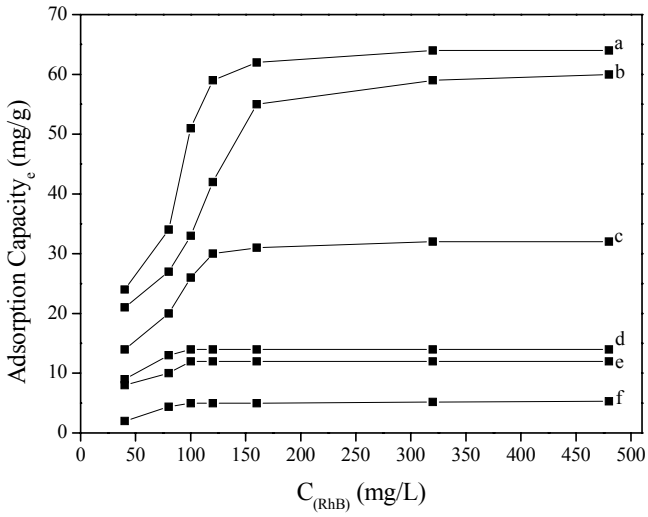


Fig. S4 Adsorption isotherms of different samples for RhB at 25°C. (a) WO_3-110-2, (b) WO_3-110-1, (c) WO_3-110-3, (d) WO_3-001-2, (e) WO_3-001-1, (f) WO_3-R1.

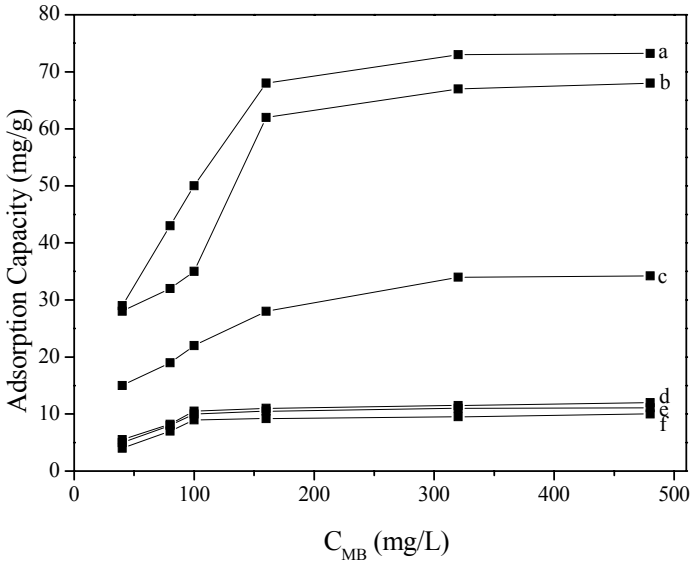


Fig. S5 Adsorption isotherms of different samples for MB at 25°C. (a) WO_3-110-2, (b) WO_3-110-1, (c) WO_3-110-3, (d) WO_3-001-2, (e) WO_3-001-1, (f) WO_3-R1.

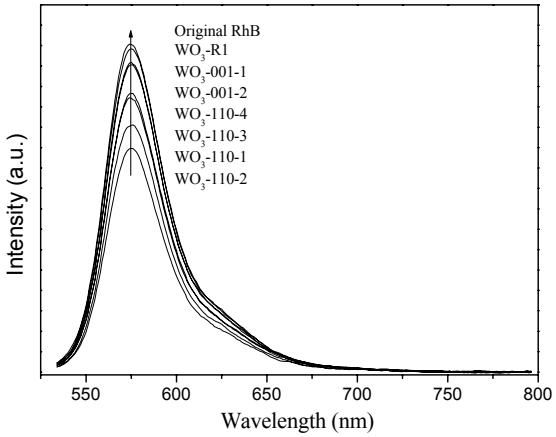


Fig. S6 Fluorescence spectra of RhB solution after adsorbed by different WO_3 samples. Conditions: RhB initial concentration = 320 mg/L, exciting light = 520 nm. The RhB solution was diluted for 2500 times by water before fluorescence measurement.

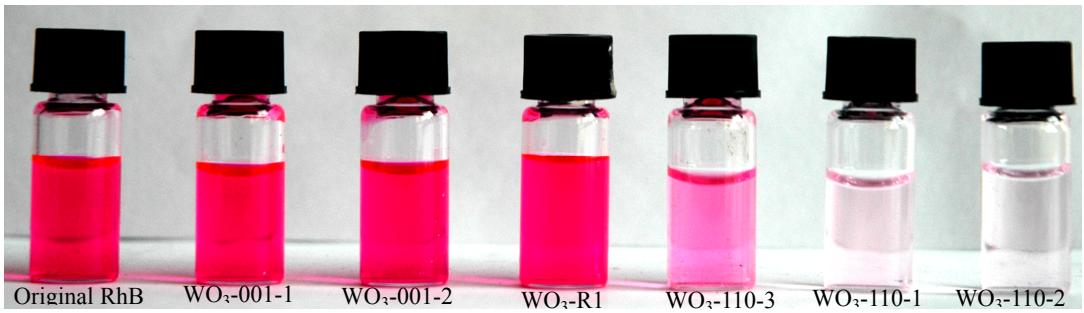


Fig. S7 Adsorption test for RhB over (a) WO_3-110-2, (b) WO_3-110-1, (c) WO_3-110-3, (d) WO_3-001-2, (e) WO_3-001-1, (f) WO_3-R1 samples. Adsorption conditions: RhB initial concentration = 40 mg/L, temperature = 25^{o}C.

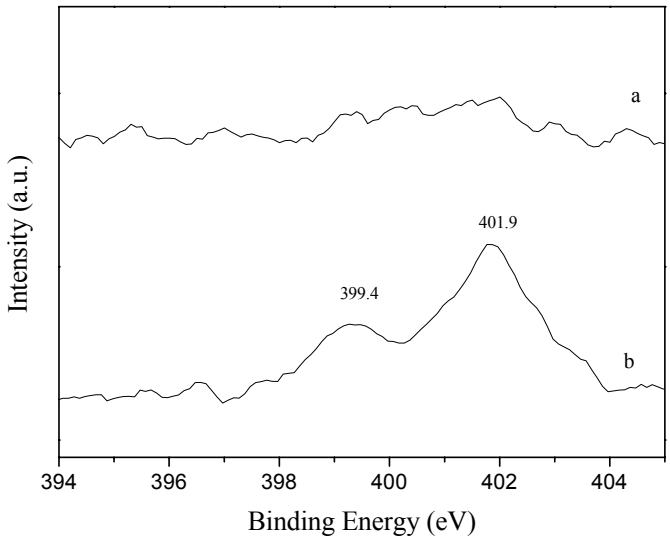


Fig. S8 N 1s XPS spectra of RhB adsorbed on WO_3-001-1(a) and WO_3-110-3(b).

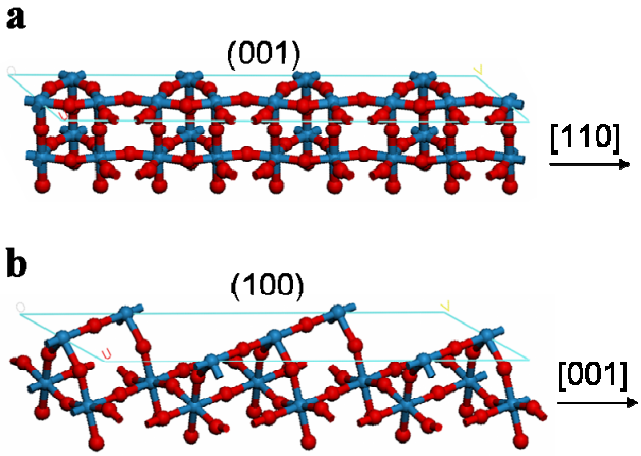
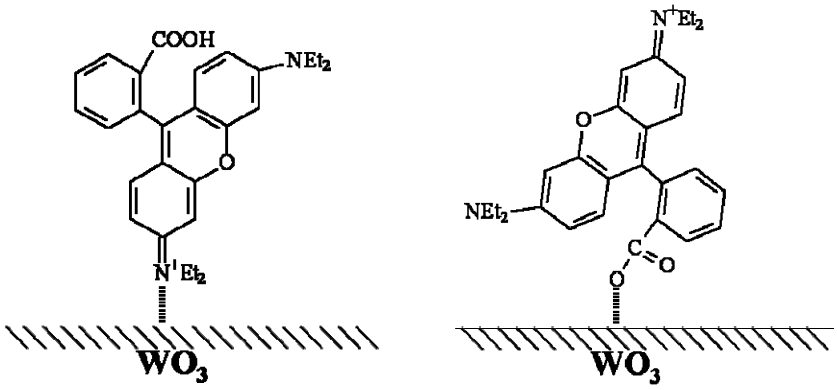


Fig. S9 Theoretical model of (a) (001) and (b) (100) surface structure of the WO_3 hexagonal single crystal. The O and W atoms are present in red and blue balls.

Table S1 Adsorption capacities calculated from fluorescence spectra for RhB solution[a]

Samples	Capacity (mg/g)	Samples	Capacity (mg/g)
WO_3-110-1	52	WO_3-001-1	11
WO_3-110-2	65	WO_3-001-2	12
WO_3-110-3	34	WO_3-R1	4
WO_3-110-4	30		

[a]Adsorption conditions are given in Figure S5.



Scheme S1 Plausible adsorption models of RhB on the WO_3-110-3