Supporting Information

Ultrathin Ag nanoparticles anchored on urchin-like WO$_3$·0.33H$_2$O for enhanced photocatalytic performance

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Experimental

Sample preparation

Synthesis of urchin-like WO$_3$·0.33H$_2$O. In a typical synthesis, a solution of peroxopolytungstic acid (PTA) was prepared firstly by adding 0.56 g of tungsten powder into 1 mL distilled water and 10.0 mL of hydrogen peroxide (H$_2$O$_2$, 30%) at 60 °C for 24 h. Then, the above PTA sol was transferred to a 50 mL autoclave. And then 0.19 g of NaCl and 7 mL distilled water were added into the above autoclaves. Finally, the autoclaves were sealed and maintained at 180 °C for 8 h. After the reaction, the formed precipitates were filtered, washed with deionized water and ethanol, and dried at 60 °C for 24 h.

Synthesis of Ag/WO$_3$·0.33H$_2$O. Typically, 0.5 mL of AgNO$_3$ (0.01 g/mL) aqueous solution was slowly dropped into the above as-synthesized WO$_3$·0.33H$_2$O suspension (0.2 g/40 mL) under strong stirring. After 4 h, additional 0.5 mL AgNO$_3$ solution was dropped into the suspension. After 8 h, additional 0.9 mL AgNO$_3$ solution was further dropped into the suspension. After 24 h stirring, the final product was collected, washed with distilled water and ethanol for several times, and dried in air at 60 °C for 12 h.

Characterization

Powder X-ray diffraction (XRD) pattern was performed on a Shimadzu (XRD-7000) diffractometer operated at 40 kV voltage and 40 mA current using Cu Ka radiation in the range

(20 ~ 80°). The morphology of the product was observed by a Zeiss (MERLIN Compact) field-mission scanning electron microscope (FESEM) at an accelerating voltage of 15 kV. The transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) analysis images were performed on a JEOL JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 kV. The chemical composition of the products was investigated by electron energy dispersive X-ray (EDX) analysis. The photoluminescence (PL) spectrum was measured by a Horiba Fluoromax-4 spectrophotometer. The work function of $WO_3 \cdot 0.33H_2O$ was obtained by an ultraviolet photoemission spectrophotometer.

Photocatalytic experiment

The catalytic activity experiments for the oxidation and decoloration of the rhodamine B (RhB) dye under solar light irradiation were carried out at ambient temperature. The original solution was prepared by adding 50 mL RhB solution (10 mg/L), then 50 mg catalyst was added into the solution to form the aqueous dispersion, and was magnetically stirred in the dark for 60 min to ensure an adsorption–desorption equilibrium was established. Afterwards, the dispersion was irradiated by a 300 W xenon lamp equipped under magnetic stirring. At given time intervals, the dispersion was sampled and centrifuged to separate the catalyst. They were centrifuged at 10000 rpm for 2 min. UV-vis absorption spectra were recorded at different intervals to monitor the reaction using a UV/vis/NIR spectrophotometer (Hitachi U-4100).
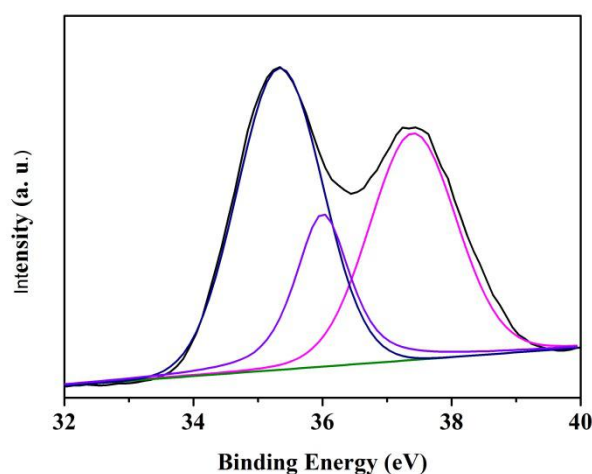

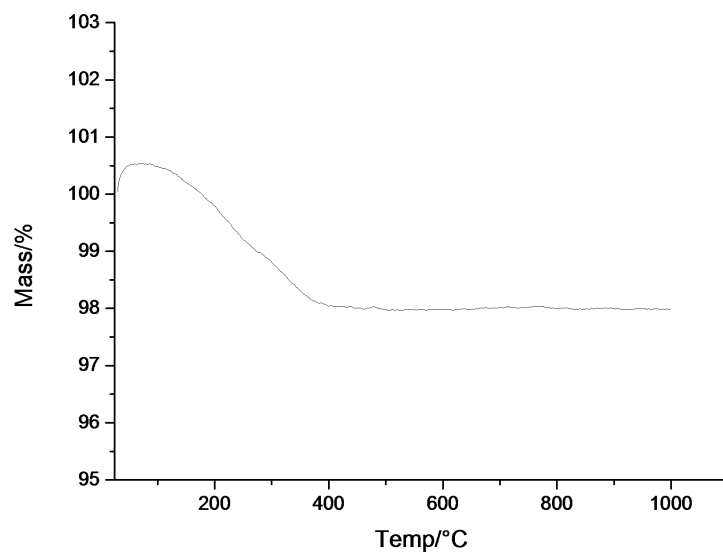**Fig. S1** XPS spectrum of the tungsten element of the as-synthesis of $WO_3 \cdot 0.33H_2O$.

Fig. S2 TGA data of the pristine $WO_3 \cdot 0.33H_2O$.

In theory, the weight percent of H_2O can be calculated by the following formula:

$$\frac{M_{H2O} * n}{M_{H2O} * n + M_{WO3}}$$

Where M is the molar number, and n is the stoichiometry of the hydrated water.

According to the TGA data, we can calculate the loss of H_2O is about 2.55%. When the n value is 0.33, the theoretical lose of water can be 2.50%, thus the stoichiometry of the hydrated water in the oxide can be identified as 0.33, and the XRD pattern can be further confirmed this viewpoint.
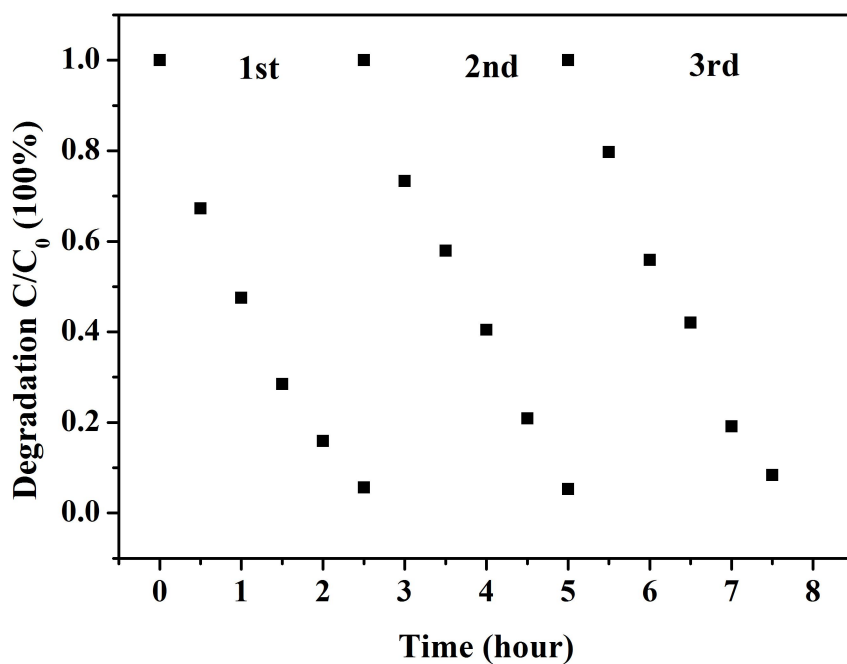
Fig. S3 The recycled photodegradation performance of the urchin-like $WO_3 \cdot 0.33H_2O$ sample.

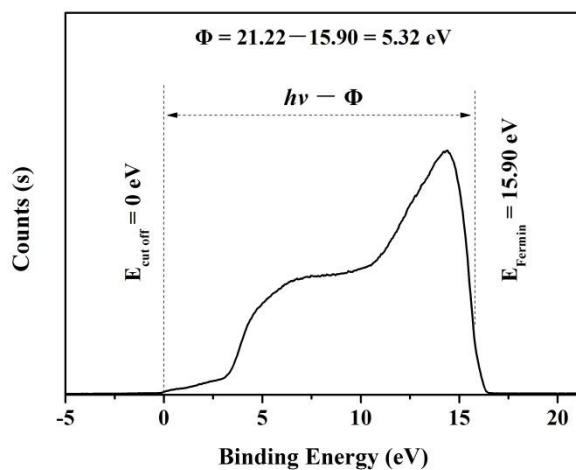**Fig. S4** Ultraviolet photoemission spectrum of the urchin-like $WO_3 \cdot 0.33H_2O$ sample.

Fig. S4 is the ultraviolet photoemission spectrum by using electronic kinetic energy for the x-axis. It can be seen that the electrons from the Fermi level are escaping the $WO_3 \cdot 0.33H_2O$ with about 15.90 eV of kinetic energy. Since the total photo energy is 21.22 eV (Vacuum = 3×10^{-8} Pa), the remaining energy represents the $WO_3 \cdot 0.33H_2O$'s work function of 5.32 eV. Note, the zero in kinetic energy appears at the secondary energy cut-off.