Supporting information

Experimental Section

Synthesis of 3D WO₃ nanostructures. 3D WO₃ nanostructures were synthesized by a one-step, high temperature thermal evaporation process. The experimental setup is consisted of a vacuum chamber, two copper electrodes with water cooling, a gas controlling system, a vacuum pump system and an infrared thermometer. A tungsten (W) boat (120 mm \times 20 mm \times 0.3 mm) containing W powders (1g, purity: 99.8%) was placed and fixed on the copper electrodes. Carbon paper strips (5 mm \times 10 mm) were cleaned by ultrasonic cleaning in acetone and methyl alcohol for 3 min, mounted above the boat with one side facing the tungsten boat. The distance between the carbon paper and the W powders is about 3.2 mm. When the vacuum chamber was evacuated down to 1 Pa, mixed gases of high purity argon (99.999%) and oxygen (99.999%) was introduced into the chamber with constant flow rates of 100 and 1 sccm, respectively. The chamber pressure was keep at ~ 70 Pa during the whole evaporation process. The tungsten boat was heated to ~ 1120 °C in 5 minutes, and held at the peak temperature for 10 minutes, then cooled down to room temperature without gas flow. After the evaporation, the 3D WO₃ nanostructures were grown on the carbon paper substrates.

Characterization of the products. The compositions of as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a panlaytical X-pert diffractometer with K α radiation. The phase structures were characterized by Raman spectroscopy (Renishaw inVia). The morphology of the as-grown 3D WO₃ nanostructures was examined by high-resolution field emission Scanning Electron Microscopy FEI Sirion 200 SEM. Transmission electron microscopy (TEM) was performed on 3D WO₃ nanostructures using JEOL 2010F. The chemical compositions of the products were characterized by X-ray photoelectron spectroscopy (XPS, ESCALab 250). The transmission spectrum of the 3D WO₃ nanostructures on quartz

glass substrate was measured by using a Shimadzu UV-2501PC spectrophotometer.

Photoelectrochemical (PEC) cell measurement. The photoelectrochemical property was investigated with a CHI 750a electrochemical workstation (Chenhua, Shanghai) in a conventional three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. The as-prepared 3D WO₃ nanostructures grown on carbon paper were used as the working electrode and a graphite rod acted as the counter electrode. The reference electrode is a saturated calomel electrode (SCE). A 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. Photoelectrochemical response was measured for a specific area (~0.2 cm²) of the 3D WO3 nanostructures electrode under visible light irradiation (> 420 nm, 45 mW/cm²), which provided by a 500W Xe arc lamp with a UV/IR cut-off filter.

Photocatalytic performance measurement. The photocatalytic activity of the synthesized 3D WO3 nanostructures on carbon paper was evaluated by degradation of RB solution. A sample of 3 mL of 1×10^{-5} M RB solution was added into a typical quartz cell. A size of 1 cm \times 0.5 cm carbon paper with 3D WO3 nanostructures was vertically immersed into the RB solution. The quartz cell was irradiated by visible light equipment with a 300 W Xenon lamp. To minimize the heat effect, the sample was placed about 15 cm away from the lamp. The UV-vis absorption spectra of the solution as a function of irradiation time were recorded by using a Shimadzu UV-2501PC spectrophotometer. The sample was removing from the solution when measuring the absorption spectra, and then the sample was placed back into the solution for further irradiation. To study the self-degradations of RB solution, the same size carbon paper without WO₃ nanostructures was added into the RB solution under the same irradiation conditions, as show in Fig. S1.

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Figure S1 UV-vis absorption spectra of RB solution as a function of irradiation time with the absence of 3D WO₃ nanostructures on carbon paper.

The surface morphology of WO₃ nanostructures after photocatalytic experiment which have been exposed under a 300 W Xenon lamp for 11 hours, was analyzed by scanning electron microscope. Figure S2 (a) and (b) are the low-magnification and high-magnification SEM images of the 3D WO₃ nanostructures after dye degradation experiments, respectively. The SEM images show that the 3D WO₃ nanostructures retained their original morphology and structure after the photodegradation reaction. This implys the high stability of the 3D WO₃ nanostructures.



Figure S2 (a) Low-magnification and (b) High-magnification SEM images of 3D WO₃ nanostructures after dye degradation experiments.