

Supporting Information

**WO₃ Nanoparticles Decorated on Both Sidewalls of Highly Porous
TiO₂ Nanotubes to Improve UV and Visible-Light Photocatalysis**

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This file contains Supplementary methods and Figures S1 to S7 with legends.

Materials Synthesis:

1) Preparation of WO₃ nanoparticles on TiO₂ nanofibers(WO₃@TiO₂)

In a typical synthesis process, WO₃@TiO₂ was prepared by four steps, as described below.

The first step was to prepare PVP/titanium acetate composite nanotubes. Typically, 0.60 g tetrabutyl titanate was dissolved in 0.79 g ethanol and 1.05 g ethanoic acid. This mixed solution was stirred for 20 min. Second, 0.2 g poly(vinyl pyrrolidone)(PVP) was dissolved in 0.6 g ethanol and stirred for 20 min. Then these two prepared solutions were mixed together and stirred for 1 h. Thus, a viscous gel of PVP/titanium acetate composite solution was obtained. As for a typical electrospinning process, the spinneret had an inner diameter of 0.6 mm. Grounded aluminum strips (2 cm in width) with parallel gaps of about 1 cm were used as the collectors. A distance of 15 cm and a direct current voltage of 18 kV were maintained between the tip of the spinneret and the collector. During the electrospinning process the environmental temperature was maintained at 90 °C. The temperature of the syringe was maintained at less than 70 °C.

The second step was to prepare TiO₂@Carbon composite nanofibers. After electrospinning, the fibers were

heated from room temperature to 500 °C for 10 min in a vacuum (1×10^{-4} Pa) with a heating rate of 10 °C/min.

The third step was to prepare hierarchical crystalline tungsten carbide nanoparticles on TiO₂@carbon composite nanofibers. We used thermal evaporation to prepare of crystalline WC nanoparticles on nanotubes in both sidewalls. In the thermal evaporation process, the temperature of tungsten filament was ~2450 °C in vacuum (1×10^{-4} Pa), and the temperature of the samples was kept at maintained at 500 °C for 20 min.

The fourth step was to prepare heterostructure WO₃ nanoparticles on TiO₂ nanofibers. The hierarchical crystalline tungsten carbide nanoparticles on TiO₂@carbon composite fibers were heated from room temperature to 500 °C for 120 min in air with a heating rate of 10 °C/min.

2) Preparation of highly porous TiO₂ nanotubes

Highly porous TiO₂ nanotubes were prepared by a two-step process, as described below. In the first step, 0.60 g tetrabutyl titanate was dissolved in 0.79 g ethanol and 1.05 g ethanoic acid. This mixed solution was stirred for 20 min. Second, 0.2 g PVP was dissolved in 0.6 g ethanol and stirred for 20 min. Then the two prepared solutions were mixed together and stirred for 1 h. Thus, a viscous gel of PVP/titanium acetate composite solution was obtained. Third, 0.7 g mineral oil was added to the PVP/titanium acetate composite solution and stirred at room temperature for 48 h to obtain a stable and homogeneous emulsion. As for a typical electrospinning process, the spinneret had an inner diameter of 0.6 mm. Grounded aluminum strips (2 cm in width) with parallel gaps of about 1 cm were used as the collectors. A distance of 15 cm and a direct current voltage of 18 kV were maintained between the tip of the spinneret and the collector. During the electrospinning process the environmental temperature was maintained at 90°C. The temperature of the syringe was maintained at under 70°C.

After electrospinning, the fibers were heated from room temperature to 500 °C at a rate of 2°C min⁻¹, and then held at 500°C for 2 h in air.

3) Preparation of TiO₂ nanofibers

The preparation progress is same with preparation of highly porous TiO₂ nanotubes, except no oil add in the precursor electrospinning solution.

Figure S1

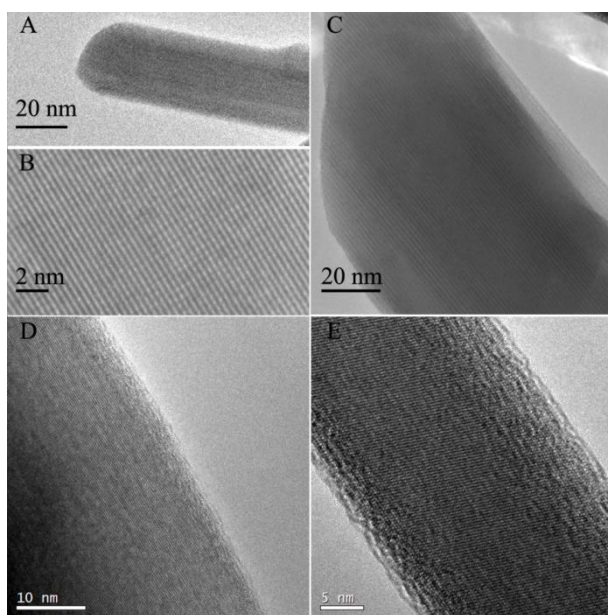


Figure S1 Transmission electron microscopy images of the single crystal WC. The single crystal WC were preparation by thermal evaporation, in the process, the temperature of tungsten filament is ~2450 °C in a vacuum (1×10^{-4} Pa), and the temperature of the samples(PVP nanofibers) ~500 °C for 2 h.

Figure S2

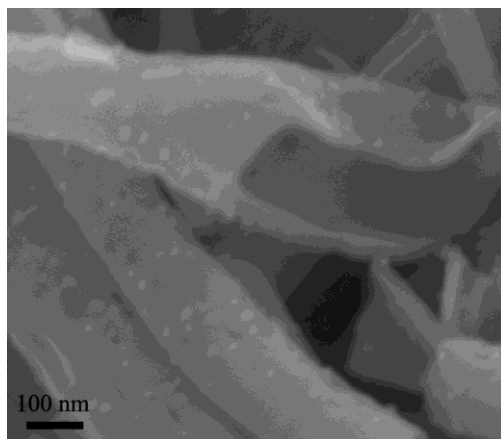


Figure S2 Scanning electron micrographs of heterostructure of WO_3 nanoparticles on highly porous TiO_2 nanotubes on both sidewalls ($\text{WO}_3@ \text{TiO}_2 @ \text{WO}_3$) after ten times cycling catalytic measurements. The micrographs showed that there was almost no change in the morphology. This means that the $\text{WO}_3@ \text{TiO}_2 @ \text{WO}_3$ were stable enough to be used in photocatalysis.

Figure S3

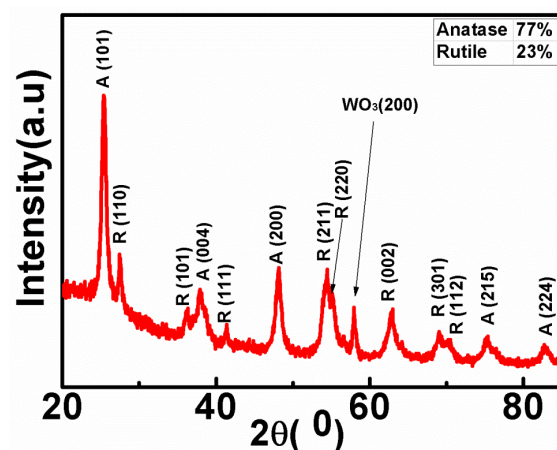


Figure S3 X-Ray diffraction pattern of the WO_3 nanoparticles on highly porous TiO_2 nanotube along both internal and external sidewalls; the inset table shows the ratio between the anatase and rutile phases of TiO_2 .

Figure S4

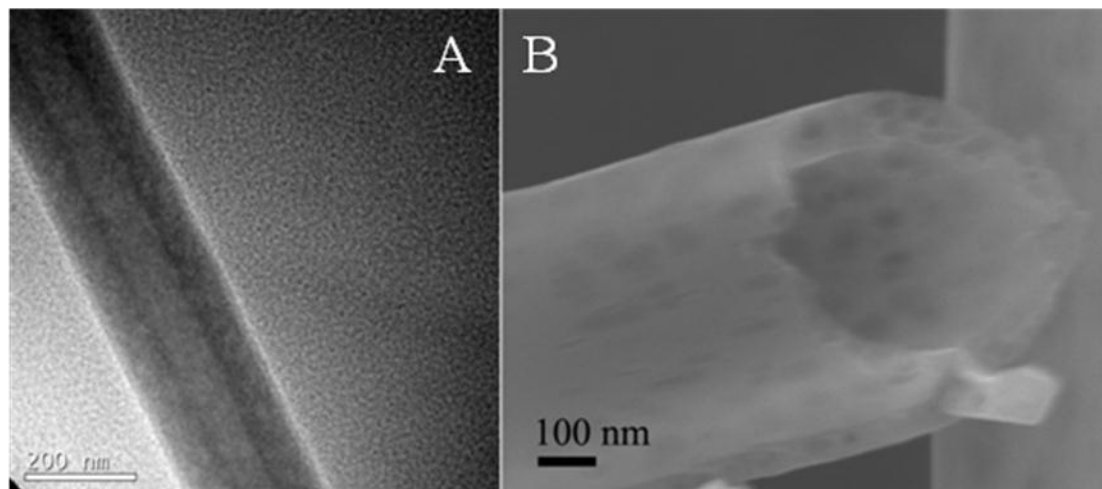


Figure S4 Transmission electron microscopy images of nanotubes: A) as-spun nanotubes without annealing; B) after under annealing (without under thermal evaporation). From A can know, the surface of nanotubes is very smooth, and without porous on the surface.

Figure S5

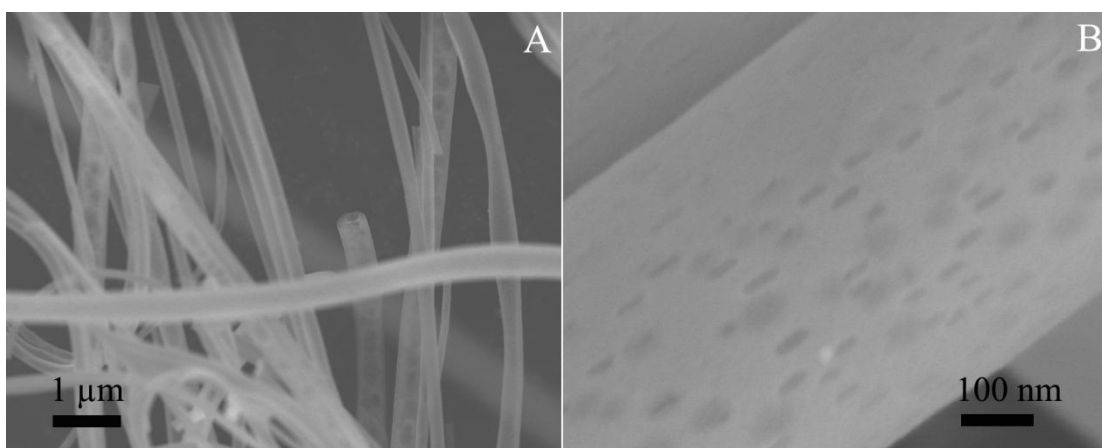


Figure S5 Scanning electron micrographs of nanotubes. The nanotubes via the same procedure with heterostructure of WO_3 nanoparticles on highly porous TiO_2 nanotubes on both sidewalls except that in the

thermal evaporation process, the temperature of tungsten filament is $\sim 2000^{\circ}\text{C}$. It can be found that the surface of the nanotubes almost no particles.

Figure S6

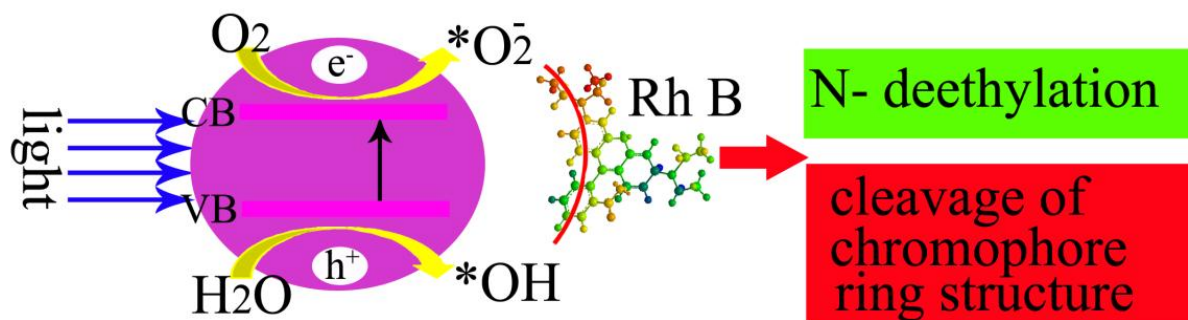


Figure S6 Schematic diagram of semiconductor photocatalysis decomposed Rhodamine B. Due to oxygen can react with electrons in the photocatalysis process, and usually materials with larger specific surface areas that adsorb more oxygen on the surface. The heterostructure of WO_3 nanoparticles on highly porous TiO_2 nanotubes on both sidewalls ($\text{WO}_3/\text{TiO}_2/\text{WO}_3$) which have larger surface areas than the heterostructures deposited only on the outside wall of nanotubes can absorb more oxygen. So the photodecomposition rate of RhB by the heterostructure of $\text{WO}_3/\text{TiO}_2/\text{WO}_3$ under lump was much faster than that that using heterostructure WO_3 nanoparticles on TiO_2 nanofiber.

Figure S7

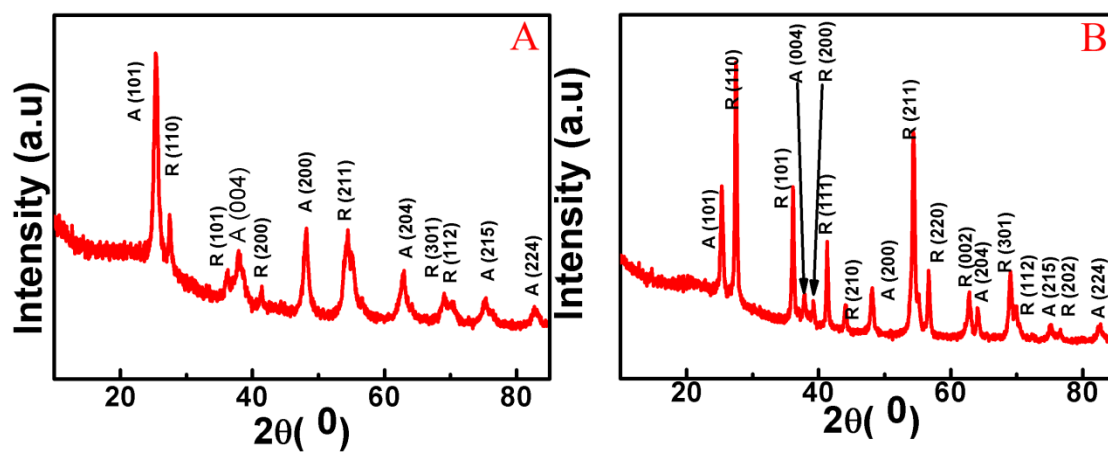


Figure S7 X-Ray diffraction pattern of the TiO₂ nanofibers and highly porous TiO₂ nanotube.

Figure S8

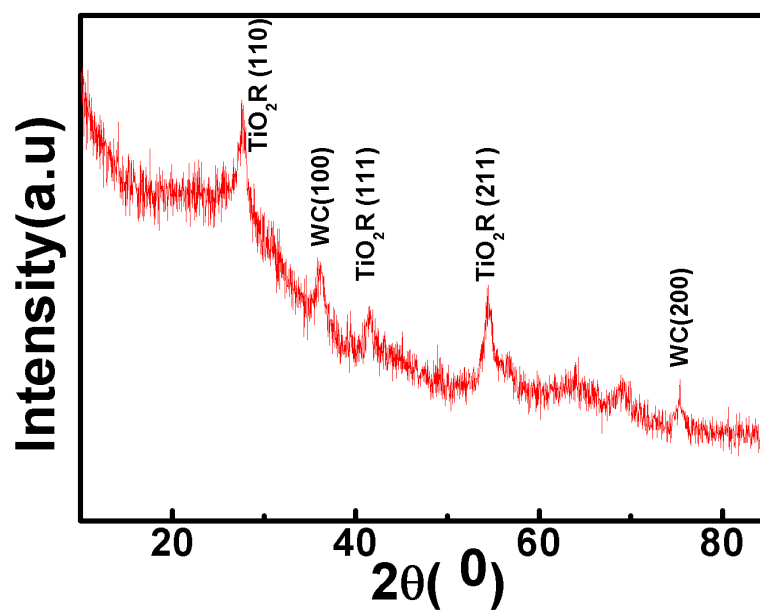


Figure S8 X-Ray diffraction pattern of the crystalline WC nanoparticles on amorphous carbon-highly porous

TiO₂ nanotubes.

Figure S9



Figure S9 Photographs of A) $\text{TiO}_2@\text{C}@\text{WC}$; and B) $\text{WO}_3@\text{TiO}_2@\text{WO}_3$. The color of the $\text{TiO}_2@\text{C}@\text{WC}$ is black, and after annealing in air to form $\text{WO}_3@\text{TiO}_2@\text{WO}_3$, the color changed into white.

Figure S10

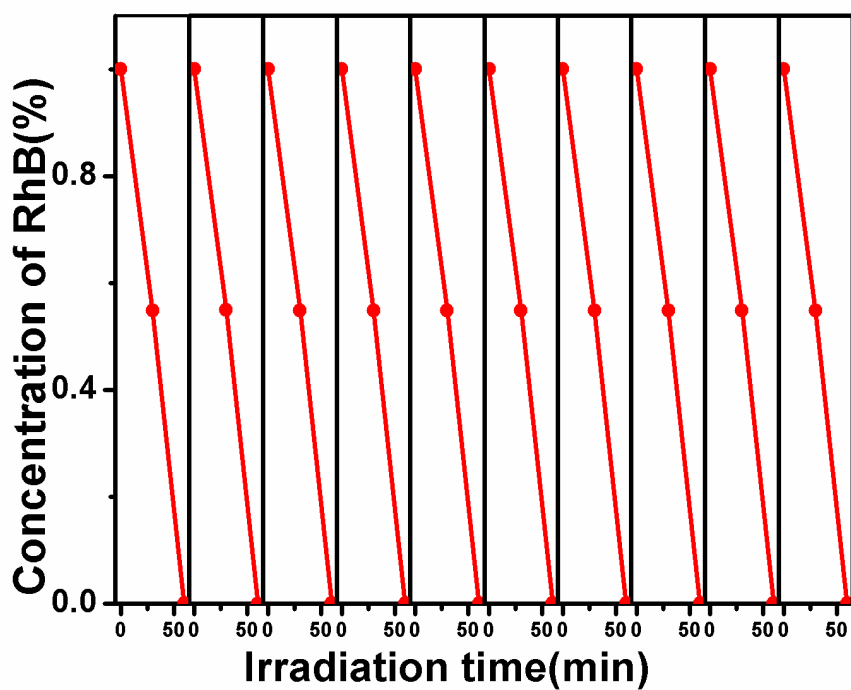


Figure S10 Cycling tests of photocatalytic activity (RhB decomposition) of the heterostructure of $\text{WO}_3@\text{TiO}_2@\text{WO}_3$ as photocatalysts under visible light.

