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 ºC. The temperature of the syringe was maintained at less than 70 ºC.

The second step was to prepare TiO₂@Carbon composite nanofibers. After electrospinning, the fibers were
heated from room temperature to 500 ºC for 10 min in a vacuum (1×10⁻⁴ Pa) with a heating rate of 10 ºC/min.

The third step was to prepare hierarchical crystalline tungsten carbide nanoparticles on TiO₂@carbon composite nanofibers. We used thermal evaporation to prepare crystalline WC nanoparticles on nanotubes in both sidewalls. In the thermal evaporation process, the temperature of tungsten filament was ~2450 ºC in vacuum (1×10⁻⁴ Pa), and the temperature of the samples was kept at maintained at 500 ºC 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 ºC for 120 min in air with a heating rate of 10 ºC/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 ºC at a rate of 2ºC min⁻¹, and then held at 500°C for 2 h in air.
3) Preparation of TiO$_2$ nanofibers

The preparation progress is same with preparation of highly porous TiO$_2$ 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 WO₃ nanoparticles on highly porous TiO₂ nanotubes on both sidewalls (WO₃@TiO₂@WO₃) after ten times cycling catalytic measurements. The micrographs showed that there was almost no change in the morphology. This means that the WO₃@TiO₂@WO₃ were stable enough to be used in photocatalysis.

Figure S3

Figure S3 X-Ray diffraction pattern of the WO₃ nanoparticles on highly porous TiO₂ nanotube along both internal and external sidewalls; the inset table shows the ratio between the anatase and rutile phases of TiO₂.
Figure S4

Figure S4 Transmission electron microscopy images of nanotubes: A) as-spun nanotubes without annealing; B) after under annealing (without under thermal evaporation). Form 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 WO₃ nanoparticles on highly porous TiO₂ 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

![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 (WO\(_3\)/TiO\(_2\)/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 WO\(_3\)/TiO\(_2\)/WO\(_3\) under lump was much faster than that that using heterostructure WO\(_3\) nanoparticles on TiO\(_2\) nanofiber.](image)

Figure S7
Figure S7 X-Ray diffraction pattern of the TiO$_2$ nanofibers and highly porous TiO$_2$ nanotube.

Figure S8 X-Ray diffraction pattern of the crystalline WC nanoparticles on amorphous carbon-highly porous TiO$_2$ nanotubes.
Figure S9 Photographs of A) TiO$_2$@C@WC; and B) WO$_3$@TiO$_2$@WO$_3$. The color of the TiO$_2$@C@WC is black, and after annealing in air to form WO$_3$@TiO$_2$@WO$_3$, the color changed into white.

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