Electronic Supplementary Information

Au nanoparticles decorated WO₃ photoelectrode for enhanced photoelectrochemical properties

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Experimental details

1. Synthesis of WO₃ nanoparticles

All of the reagents were of analytical grade and were used without further purification. WO₃ nanoparticles were prepared via hydrothermal method reported recently with some modification. The typical experimental procedure was as follows: 0.125 g of H₂WO₄ and 0.5 mL H₂O₂ (30 wt%) were dissolved into 2 mL of distilled water and then stirred intensely at 100 ºC for 30 min. After being cooled, 0.35 mL of HCl (37 wt%), 0.0315 g oxalic acid dehydrate, 7.5 mL ethanol and 7.5 mL distilled water were added to the above solution. The obtained solution was transferred to 25 mL Teflon-lined autoclave at a constant temperature of 180 ºC for 4 h. The precipitate was collected and washed repeatedly with distilled water, and was then dried at 60 ºC under vacuum followed by calcinations in air at 550 ºC for 2 h.

2. Fabrication of WO₃/FTO photoelectrode

F: SnO₂ coated conductive glass flakes (FTO, 1.5*2.5 cm²) were cleaned by distilled water, ethanol and acetone. Firstly, a paste was prepared by adding hydroxypropyl cellulose (Aldrich) into diethylene glycol with a concentration of 10 wt% and heated at 100 ºC for 5 h. Then, WO₃ nanoparticles were dispersed into the paste with the quality ratio of 1:3, and absolute ethanol was added and grounded in an agate mortar to form viscous slurry. Finally, the slurry was dropped onto a piece of FTO glass by doctor blading method, and the film was heated up to 550 ºC at a rate of 5 ºC min⁻¹ and maintained for 30 min after drying naturally.

3. Preparation of Au decorated WO₃ photoelectrode
The Au nanoparticles sol was prepared by reducing HAuCl$_4$ using NaBH$_4$ as reductant in the present of polyvinyl pyrrolidone (PVP). Briefly, 0.01 g PVP was added into 10 ml of 1 mM HAuCl$_4$ aqueous solution and was heated at 100°C in a round bottom flask for 30 min. Then, 1 ml of 0.04 M NaBH$_4$ aqueous solution was added and kept reaction for 30 min, and finally Au nanoparticles sol was obtained.

For preparation of Au nanoparticles decorated WO$_3$ photoelectrode, 20 μL of the Au sol was dropped onto WO$_3$ film, and was then calcined at 300 °C at a rate of 3 °C min$^{-1}$ for 2 h. One drop-coating process was defined as one cycle. For comparison, a series of Au decorated WO$_3$ film with 1, 5, 10, 15, 20 cycles were prepared, and the samples were denoted as WO$_3$-1Au, WO$_3$-5Au, WO$_3$-10Au, WO$_3$-15Au, WO$_3$-20Au respectively.

4. Characterization

The phase structure of the products were characterized by X-ray diffraction (XRD) using a Bruker advance-D8 with Cu Kα radiation. The field emission scanning electron microscopy (FESEM) images were obtained on Carl Zeiss AG SUPR40. The transmission electron microscope (TEM) images were obtained on JEOL JSM-100, and the high-resolution transmission electron microscope (HRTEM) images were observed on FEI Tecnai G220. The UV-Vis optical absorption of the samples was carried out on a Perkin-Elmer Lambda 950 UV-Vis spectrometer.

5 Electrical and photoelectrochemical measurements

The photoelectrochemical measurements were carried out on a CHI 660D electrochemical workstation (shanghai chenhua, China) with a standard three-electrode electrochemical cell with a flat quartz window with Au decorated WO$_3$ photoelectrode, Ag/AgCl and Pt foil using as working electrodes, reference electrode and counter electrode. All the electrodes were performed in a 0.5 M Na$_2$SO$_4$ (pH=7) solution. The 500 W Xe lamp was used as irradiation source with a light intensity of 100 mW/cm$^2$. By recording the wavelength-dependent photocurrent densities ($I$) generated at specific wavelengths ($\lambda$) and the monochromatic light intensities ($J_{light}$) of the light source, the incident photon to electron conversion efficiency (IPCE) can be calculated using the following equation:

$$ IPCE = \frac{1240I(mA/cm^2)}{[\lambda(nm)J_{light}(mW/cm^2)]} $$

Capacitance measurements were carried out at the AC frequency of 1 kHz in the dark.
Electrochemical impedance spectroscopy (EIS) was applied to explore the conductivity of the resulting electrodes under illumination.

References


**Fig. S1.** SEM image of WO$_3$ nanoparticle.

**Fig. S2.** Bode phase diagram for WO$_3$ and WO$_3$-Au electrode.
**Tab. S1.** Elemental ration of WO$_3$-10Au

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<th>element</th>
<th>Quality percent</th>
<th>Atomic percent</th>
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<td>W M</td>
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<td>Au M</td>
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<td>total</td>
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**Tab. S2.** The exact contents (wt %) of Au in the Au decorated WO$_3$ with different cycles

<table>
<thead>
<tr>
<th>Sample</th>
<th>WO$_3$-1Au</th>
<th>WO$_3$-5Au</th>
<th>WO$_3$-10Au</th>
<th>WO$_3$-15Au</th>
<th>WO$_3$-20Au</th>
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<tr>
<td>Contents (wt%)</td>
<td>0.47</td>
<td>0.65</td>
<td>1.20</td>
<td>1.40</td>
<td>2.01</td>
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