Electronic Supplementary Information

Au nanoparticles decorated WO_3 photoelectrode for enhanced photoelectrochemical properties

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Experimental details

1. Synthesis of WO_3 nanoparticles

All of the reagents were of analytical grade and were used without further purification. WO_3 nanoparticles were prepared via hydrothermal method reported recently with some modification[26]. The typical experimental procedure was as follows: 0.125 g of H_2WO_4 and 0.5 mL H_2O_2 (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 WO_3/FTO photoelectrode

F: SnO_2 coated conductive glass flakes (FTO, 1.5*2.5 cm^2) 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, WO_3 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 WO_3 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_2SO_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 (λ) and the monochromatic light intensities (J_{light}) of the light source, the incident photon to electron conversion efficience (IPCE) can be calculated using the following equation:

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

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

1 H. He, S. P. Berglund, P. Xiao, W. D. Chemelewski, Y. Zhang and C. B. Mullins, *Journal of Materials Chemistry A*, 2013, **1**, 12826-12834.

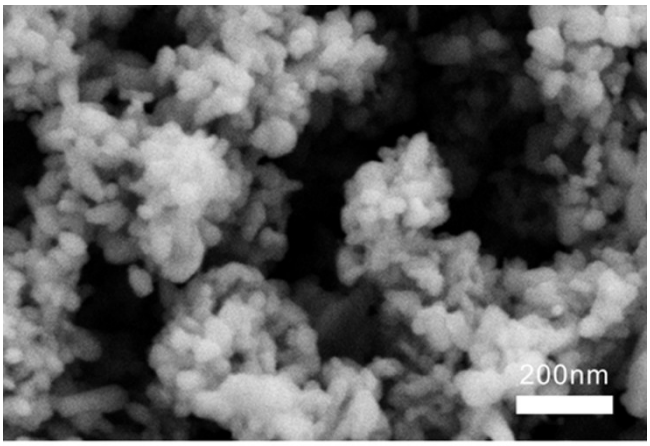

Fig. S1. SEM image of WO_3 nanoparticle.

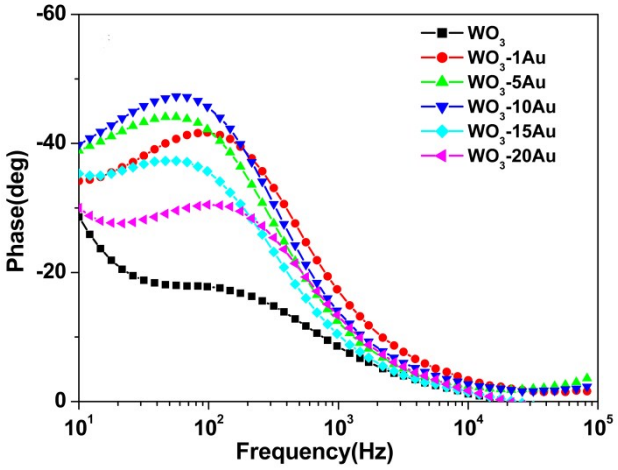

Fig. S2. Bode phase diagram for WO_3 and WO_3-Au electrode.

Tab. S1. Elemental ration of WO_3-10Au

element	Quality percent	Atomic percent
O K	23.95	78.37
W M	74.85	21.31
Au M	1.20	0.32
total	100.00	

Tab. S2. The exact contents (wt %) of Au in the Au decorated WO_3 with different cycles

Sample	WO_3-1Au	WO_3-5Au	WO_3-10Au	WO_3-15Au	WO_3-20Au
Contents (wt%)	0.47	0.65	1.20	1.40	2.01