

Electronic Supplementary Information

Scalable one-step synthesis of TiO₂/WO₃ films on titanium plates with an efficient electron storage ability

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Materials

Ti plate (99.5% in purity) were obtained from Baoji Ronghao Ti Co. Ltd., Shanxi, China. Tungsten powder (W), sodium perchlorate (NaClO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) were procured from Sinopharm Chemical Reagent Co., Ltd., hydrogen peroxide (H_2O_2) and formic acid (HCOOH) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd., and sodium formate (HCOONa) was purchased from Aladdin Chemistry Co. Ltd. All chemicals used in this study without special states were of analytical grade and used as received. All solutions were prepared with deionized water.

Preparation of film electrodes

A peroxotungstic acid (PTA) solution was prepared by a modified procedure from Yagi et al.¹ Briefly, 1.0 g of tungsten powder was dissolved in a 10 ml hydrogen peroxide solution (30 wt%) with a water-ice bath to avoid overheat. The excess H_2O_2 was decomposed by irradiation under an infrared lamp. By diluting above solution with a water-ethanol mixture (V/V=4:1), a PTA aqueous ethanol solution (54 mmol/L respect to W) was finally obtained.

Cleansed Ti plates were pickled in a 10 wt% oxalic acid solution at 100 °C for 2 h, followed by rinsing with deionized water and drying in an air stream. Each piece of Ti plate ($1.5 \times 1.5 \text{ cm}^2$ for most tests, while $2 \times 2 \text{ cm}^2$ for photocatalytic degradation of phenol) was soaked in a mixture of 10 wt% H_2O_2 and desirable amounts of PTA solution in an airtight vial and maintained at 80 °C for 8 h. The treated Ti plate was rinsed gently with deionized water, dried and calcined at 400 °C for 2 h. The resulting samples are designated as T, TW1, TW2 and W under the synthetic conditions shown

in Table S1.

Characterizations

The crystal phases of the films were analyzed using a powder X-ray diffraction (XRD, XRD-6100, Shimadzu, Japan) with Cu K α radiation, operating at 40 kV 30 mA ($\lambda = 0.154$ nm). Raman spectra were obtained on a dispersive Raman microscope (Senterra R200-L, Bruker Optics, Germany) with a 532 nm laser source operating at 5 mW. X-ray photoelectron spectroscopy (XPS) experiments were taken on an AXIS Ultra DLD system (Shimadu-Kratos, Japan). To avoid the influence from the overlapping of Ti 3p and W 4f peaks, the high resolution XPS spectra of both W 4f and W 4d were obtained. The surface morphologies of the films were observed on a scanning electron microscopy (Nova NanoSEM 450, FEI, USA) equipped with an INCA energy dispersive spectrometer (EDS) system (Oxford Instrument, UK). A high resolution-transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan) was used to observe the morphology of nanocomposites.

Photoelectrochemical measurements

Photoelectrochemical test systems were composed of a CHI 660E Potentiostat/Galvanostat, a 300 W xenon lamp, and a homemade three-electrode cell. There is no filter used for the light source, which operated at 300 W. The synthetic film electrode on Ti plate was used as working electrode with an active surface area of 1.5 cm². A Pt wire and Ag/AgCl electrode were employed as counter electrode and reference electrode, respectively. The electrolyte solution was 0.1 M NaCOOH/0.1 M NaClO₄ aqueous solution with pH adjusted to 5.0, and bubbled with N₂ gas for 30 min

before tests. The time profiles of open circuit potentials (OCPs) were recorded under illumination for 400 seconds, then keep in dark for 30 seconds, and then galvanostatic discharge at $10 \mu\text{A}\cdot\text{cm}^{-2}$ for 5000 s. The photocurrent transients were taken in the same electrolyte at +0.2 V vs. Ag/AgCl bias.

To evaluate the stability of TW2 film electrode, continuous charge–discharge cycles were performed in a two-electrode configuration with Pt wire as both the counter electrode and reference electrode, and 0.2 V bias were applied on the working electrode.

Photocatalytic phenol degradation

Photocatalytic degradation of phenol were carried out to evaluate the photocatalytic activities of these films according to our previous method.² Two pieces of as-prepared Ti plates ($2 \times 2 \text{ cm}^2$) were applied in the degradation of 50 ml phenol solution at an initial concentration of 20 mg/L. A 1000 W xenon lamp operating at 500 W without any filter was employed as the light source. The Ti plate is placed on a net bracket. Before switching on the lamp to start the photocatalytic reaction, the solution was continuously stirred for 0.5 h to reach an adsorption balance. Samples were taken at regular time intervals, and the concentration of phenol in the filtered solution was monitored by a modified colorimetry with a UNICO UV-2102 spectrometer. A control test of phenol photodegradation was done over an original pickled Ti plate.

1 M. Yagi and S. Umemiya, *J. Phys. Chem. B*, 2002, **106**, 6355.

2 Y. H. Wu, M. C. Long, W. M. Cai, S. D. Dai, C. Chen, D. Y. Wu and J. Bai, *Nanotechnol.* 2009, **20**, 185703.

Table S1.

Table S1. Synthetic conditions for various films

| Film | T | TW1 | TW2 | W |
|-------------------------------------|------|------|------|------|
| PTA (mmol/L respect to W) | 0 | 2.7 | 13.5 | 54 |
| H ₂ O ₂ (wt%) | 5 | 5 | 5 | 0 |
| Initial pH | 5.67 | 2.93 | 2.07 | 1.45 |

Table S2

Table S2. Elementary contents on the surface of TW1 and TW2 (wt%) by XPS analyses

| Element | TW1 | TW2 |
|---------|-------|-------|
| O | 38.98 | 37.20 |
| Ti | 48.63 | 41.71 |
| W | 0.35 | 7.78 |

Figure S1.

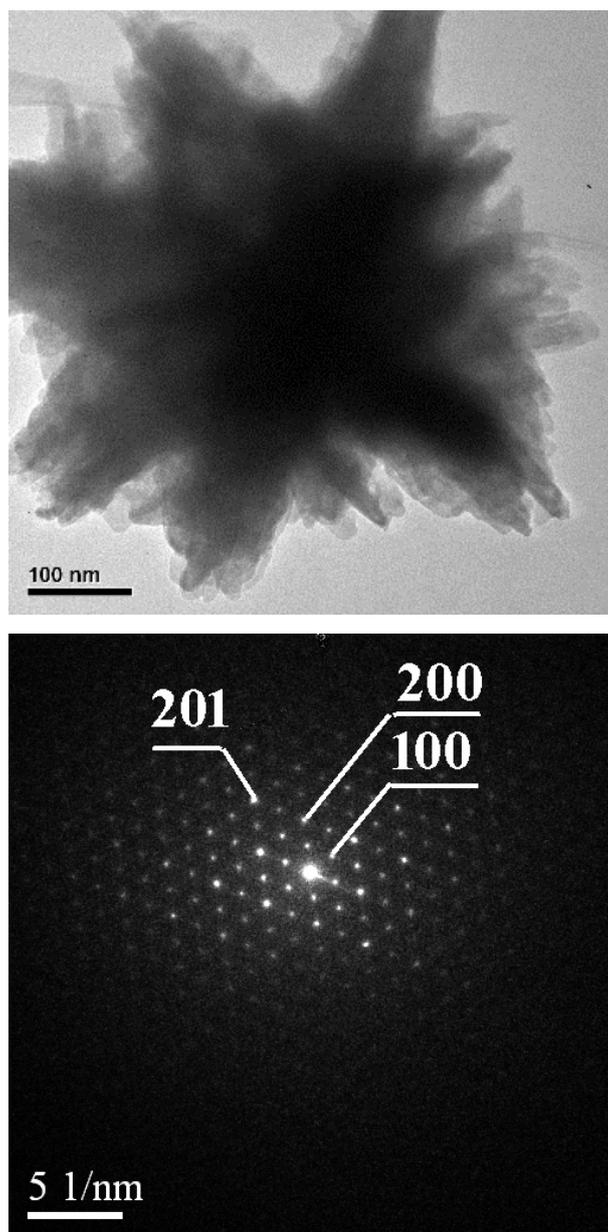


Fig. S1. TEM image and ED pattern of WO_3 nanostructures in W film (obtained by sonicating W film in ethanol)

Figure S2.

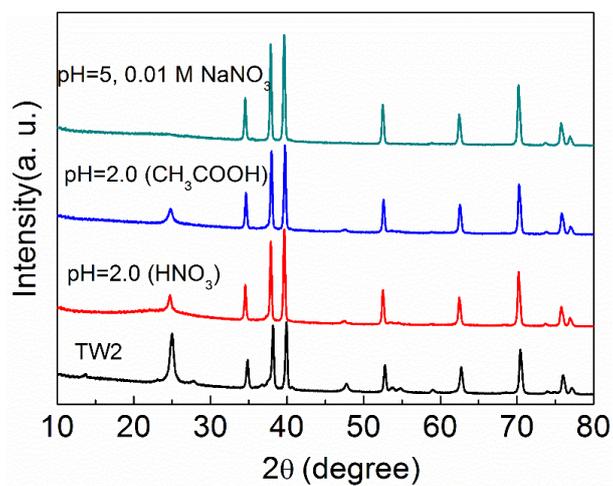


Fig. S2. A comparison of XRD patterns of TW2 with TiO₂ films prepared with the addition of HNO₃, CH₃COOH, and NaNO₃

Figure S3.

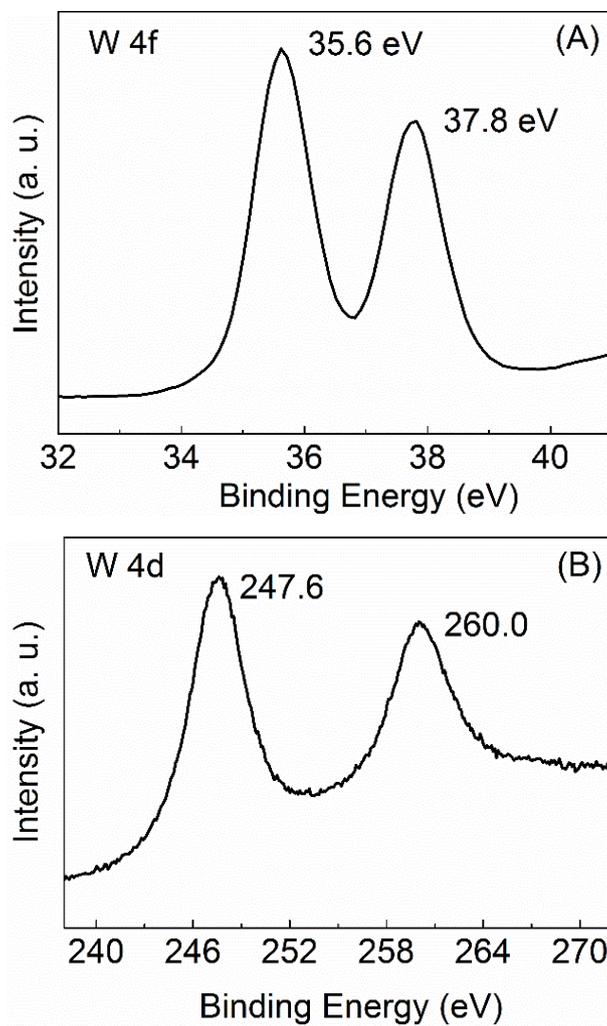


Fig. S3. XPS spectrum of W 4d and W 4f for the film W.

Figure S4.

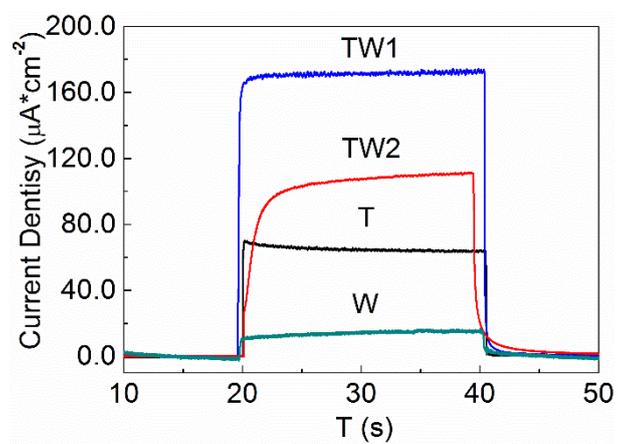


Fig. S4. Photocurrent transients of various film electrodes (+0.2 V vs. Ag/AgCl bias).

Figure S5.

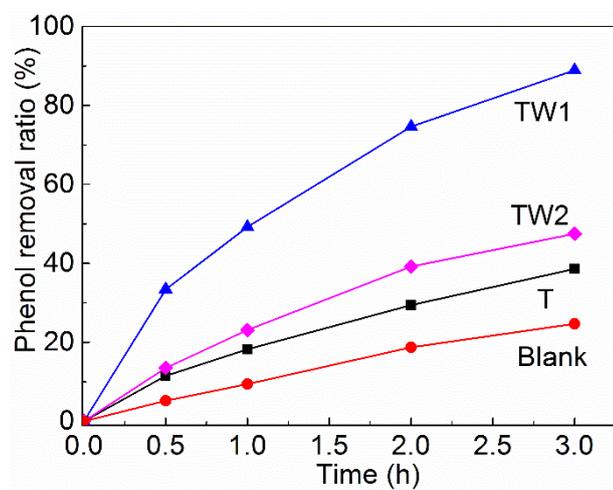


Fig. S5. Photocatalytic degradation of phenol degradation in the presence of as prepared films.