

Supporting Information

1 Experiment

1.1 Fabrication of WO₃ working electrodes

All chemicals were analytical grade. AISI 316L stainless steel foil (composition of Cr: 17-19, Ni: 11-13, Mn: 2, C: 0.015, and Fe balanced, in wt.%) was cut into specimens of 1×3.5×0.05 cm. All stainless steel specimens were mechanically polished with abrasive papers (grade 1000, 1500 and 2000) and diamond pastes (from 3.5 to 0.25 μm). All specimens were ultrasonically cleaned in acetone, ethanol, and double distilled water (DDW) for 20 min, and then dried in a nitrogen stream.

The WO₃ films were prepared on the surface of stainless steel by hydrothermal method according to the reported literature [19]. A total of 0.231 g of sodium tungstate dihydrate powder (Na₂WO₄·2H₂O) was dissolved in 30 mL of DDW under magnetic stirring. Then, 4 mL hydrochloric acid (HCl, 3 M) was added to the solution drop by drop. Yellow-white precipitate was generated. 0.189 g of sodium oxalate (Na₂C₂O₄) was added to the above mixture. After stirring for 30 min, as-prepared precursor was transferred into a 50 mL Teflon-lined stainless autoclave. The Teflon-vessel was sealed by a stainless autoclave, and put in an oven at 120 °C for 1 h, 2 h, 2.5 h, 3 h and 4 h, respectively. After the reaction, the autoclaves were cooled down to room temperature naturally. Subsequently, the specimens were rinsed repeatedly with DDW and dried at 50 °C in air. The prepared films were calcined in air at 450 °C for 1 h. The resulting samples were designed as WNPs-1, WNPs-2, WNPs-2.5, WNPs-3 and WNPs-4, respectively.

1.2 Materials characterization

The field emission scanning electron microscopy (FESEM, FEINova 400 Nano) and the transmission electron microscopy (TEM, JEM-2100UHR STEM/EDS, JEOL, Japan) was utilized to investigate the morphologies of the as-prepared thin films. X-ray diffraction (XRD) patterns of the products were collected using a XRD-7000S diffractometer (Shimadzu). The UV-vis absorption spectra measurements were carried out by using a UV-vis spectrophotometer (TU 1901, Beijing Purkinje General Instrument Co., China).

1.3 Photoelectrochemical performance

Photoelectrochemical measurements were carried out in a conventional three-electrode configuration with a CHI 660E potentiostat (CH Instruments, Shanghai, China). The WO_3 photoelectrodes served as working electrodes. Ag/AgCl in saturated KCl solution and platinum foil served as reference electrode and counter electrode, respectively. 0.1 M of Na_2SO_4 aqueous solution was used as the electrolyte. 0.8 V of bias voltage was employed to impel the photo-generated electrons transfer from the working electrode to the counter electrode. A 500 W Xe lamp (CHF-XM35, Beijing Trusttech Go. Ltd.) equipped with 400-800 nm cut-off optical filter ($400 < \lambda < 800$ nm) was used as the visible light source and located at 5 cm away from the photoelectrochemical reaction cell.

1.4 Photoelectrocatalytic degradation experiments

The PEC degradation properties of the WO_3 photoelectrodes were measured by degrading methylene blue (MB) solution. An aqueous solution containing 10 mg/L MB and 0.1 M Na_2SO_4 was used as the model pollutants. Magnetic stirring was

applied to improve the mass transfer during PEC degradation. The mixed solutions containing WO_3 photoelectrode was kept in the dark for 30 min to ensure that the adsorption equilibrium was achieved. The concentration change of MB was analyzed by colorimetrically monitoring the changes of absorption ($\lambda_{\text{max}} = 664 \text{ nm}$) using a UV-vis spectrophotometer at 20 min intervals for 120 min. The kinetic behavior can be explained by Langmuir-Hinshelwood mechanism as follows: $\ln(C_0 / C) = kt$, where k is the apparent rate constant, C_0 and C are the initial concentration and the residual concentration of MB, respectively, t is the reaction time.

Additional Supporting Data

Figures

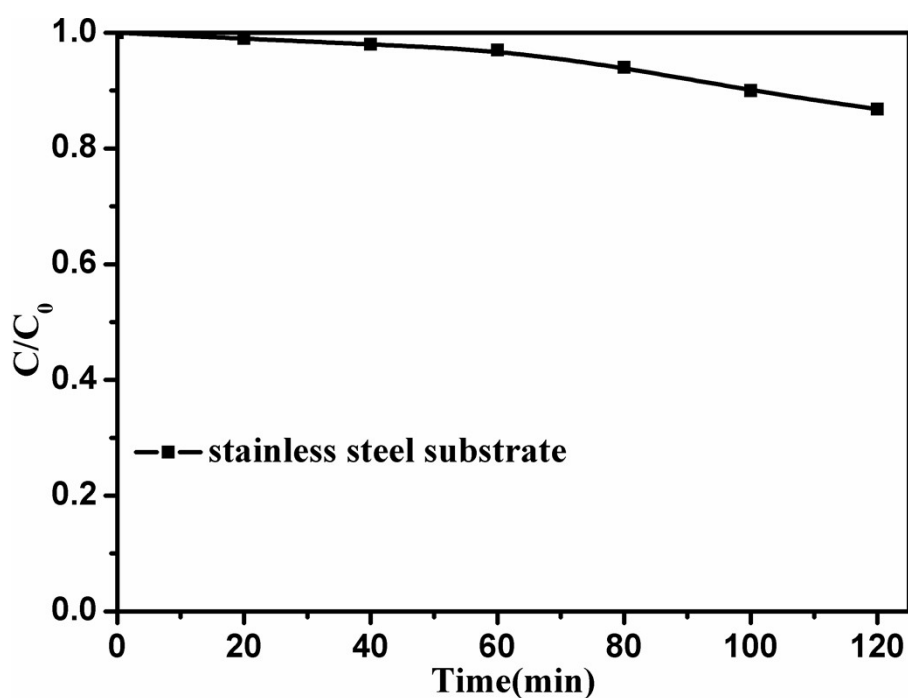


Figure S1 Curves of MB degradation ratios of the stainless steel substrate alone as a comparison through the photoelectrocatalysis process

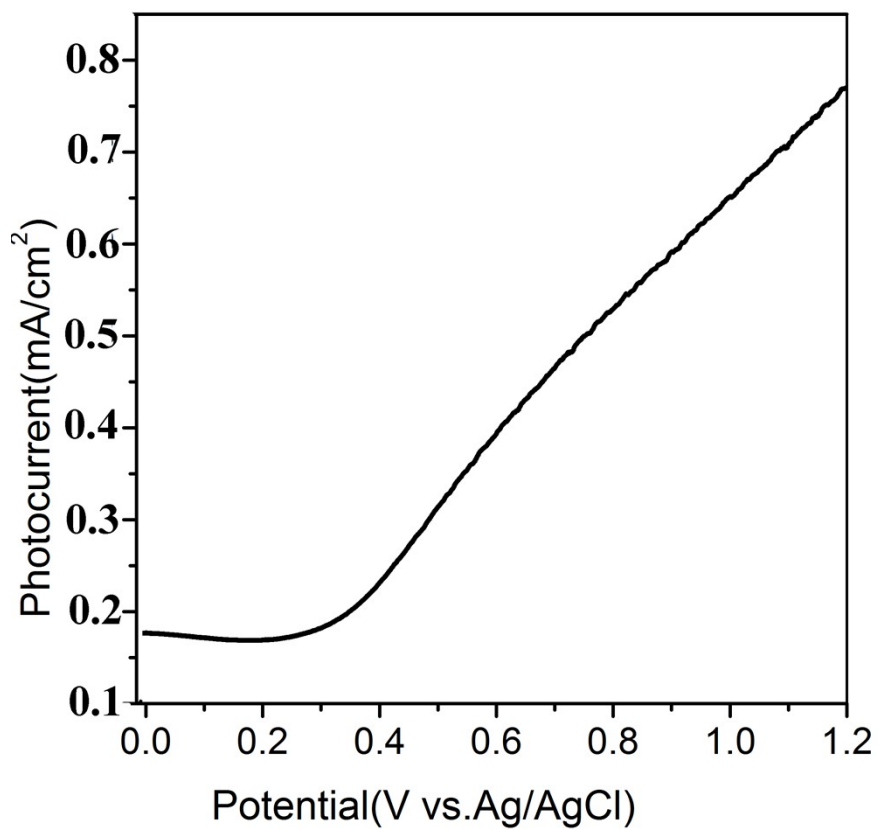


Figure S2 liner sweep voltammogram of the WNPs-2.5 electrode