**Supporting information**

# One-step Electrochemical Synthesis of $Bi_{3.84}W_{0.16}O_{6.24}$ with Superior Photocatalytic Activities

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## 1. Experimental details.

An electrochemical method to prepare bismuth tungstates with different phases at room temperature was described below. The experiment was performed in a double cell bath with cooling system, using two pieces of bismuth sheets (100mm×20mm×2mm, 99.9% purity) as the cathode and the anode, where the active species containing Bi resulted from the oxidation of anode. The bismuth sheets were carefully polished with 1μm alumina powders until a mirror surface obtained and then were rinsed by acetone, ethanol and distilled water for several times and ultrasonically cleaned. The typical electrolyte is prepared as follows: 10.6 g $Na_2WO_4 \cdot 2H_2O$ and 3.2g KOH were dissolved in 74mL mixed solvent composed of distilled water and ethanol under magnetic stirring for 10min, followed by the addition of 6mL $H_2O_2$ (30 vol%) acted as oxygen supplier in the anodic oxidation process. In order to study the effect of ethanol amount, the volume ratio of ethanol/water (R) was adjusted to 0, 0.1, 0.3, 0.5, 0.7 and 1.0, respectively. After that, the pretreated bismuth sheets were parallelly dipped into the electrolyte for 4cm keeping a horizontal distance of 2cm and connected with the outer DC supply. Then the electrochemical process was carried out at a designated electric current value (EC = 0.5, 1, 2, 3, 4 and 5A), companied with vigorously magnetic stirring. After 10min, the precipitate generated in the electrolyte was harvested by centrifugation and washed by deionized water for several times, and finally dried at 60°C.

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## 2. Characterization.

The crystalline phases of the obtained samples were investigated by X-ray diffractometer (Bruker D8 ADVANCE) using Cu Ka radiation (λ = 1.5406 Å) radiation. The XRD data for indexing were collected in a scan mode with a scanning speed of 3°/min in the 2θ range between 10° and 80°. The morphology of samples was studied with a field emission scanning electron microscope (FE-SEM, JSM-7500, Japan), a transmission electron microscope (TEM, HT7700, Japan) and a high-resolution transmission electron microscopy (HRTEM, JEOL-2010, Japan) with an accelerating voltage of 200 kV. The light absorption ability was analyzed by UV-vis diffuse reflectance spectra (DRS, TU1901, China) equipped with an integrating sphere attachment, where $BaSO_4$ was used as a reflectance standard. The Brunauer-Emmett-Teller (BET) surface area of samples was measured by means of $N_2$ adsorption over a NOVA 2200e (Quantachrome) equipment.

Photocatalytic activities of the materials were evaluated in the degradation of RhB ($1.0 \times 10^{-5}$ M) under visible-light irradiation. A 150 W Xe lamp was used as visible-light source, and a 420 nm cutoff filter was placed above the reactor to cut off UV light. In each experiment, the quantity of the photocatalyst is 2.0 g $L^{-1}$. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure adsorption/desorption equilibrium. During the experiment, 5 mL aliquots were collected at intervals of 30min from the suspension and immediately centrifuged and analyzed by UV-Vis spectroscopy (TU1901, China) at the characteristic wavelength of 554 nm for the determination of RhB concentration.

## 3. BET surface area of $Bi_{3.84}W_{0.16}O_{6.24}$, $Bi_{3.84}W_{0.16}O_{6.24}/Bi_2WO_6$ and bulk $Bi_{3.84}W_{0.16}O_{6.24}$.

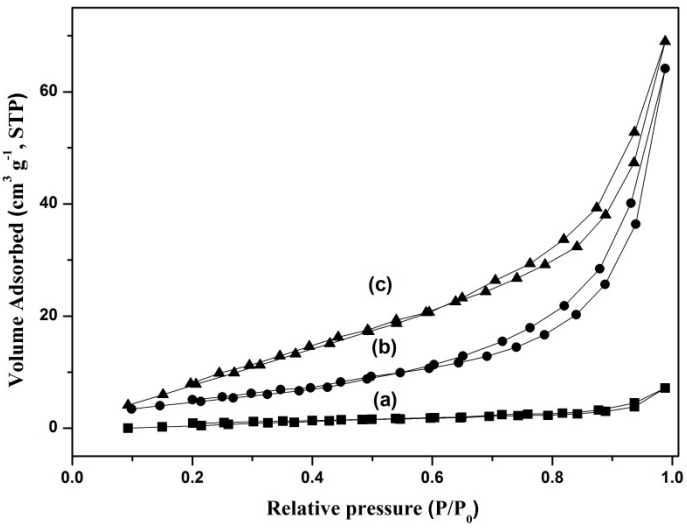


Fig. S1 $N_2$ adsorption-desorption isotherms and pore diameter distributions of the samples: (a) the bulk $Bi_{3.84}W_{0.16}O_{6.24}$, (b) $Bi_{3.84}W_{0.16}O_{6.24}$-$Bi_2WO_6$ (c) $Bi_{3.84}W_{0.16}O_{6.24}$.