

SUPPLEMENTARY INFORMATION

Transforming Anodized WO₃ Films into Bi₂WO₆ Electrodes for Photoelectrochemical Water Splitting under Visible-Light Irradiation

*Charlene Ng, Akihide Iwase, Yun Hau Ng and Rose Amal**

*ARC Centre of Excellence for Functional Nanomaterials,
School of Chemical Engineering, The University of New South Wales,
Sydney New South Wales 2052, Australia*

Experimental Section

Synthesis of the samples Tungsten (W) foil (Alfa Aesar, 99.95% , 0.05 mm thick) was anodized in 120 mL of electrolyte solution consisting of 1 M of sulphuric acid (H₂SO₄, Univar, 98%) and 0.5 wt % sodium fluoride (NaF, Analar, 99%). The samples were then contacted with a Cu spring and pressed against an o-ring in an anodization cell, leaving 4.15 cm² exposed to the electrolyte solution. The anodization cell consists of a two-electrode configuration with a platinum foil as the counter electrode (cathode) and the tungsten foil as the working electrode (anode); the distance between the cathode and the anode was kept constantly at 2 cm. The sample was anodized at an applied voltage of 50 V for 60 minutes under un-stirred condition. Prior to the hydrothermal treatment, 10 mmol of bismuth nitrate solution (Bi(NO₃)₃·5H₂O, Sigma-Aldrich, 99%) was prepared by mixing solid Bi(NO₃)₃·5H₂O with deionized water. White precipitates appeared and the mixture was placed under sonication for 10 minutes followed by vigorous magnetic stirring for 30 minutes to complete the precipitation. Subsequently, the as-anodized film and prepared bismuth nitrate solution was added to a Teflon-lined hydrothermal reactor and the hydrothermal reaction proceeds for 24 h at 160 °C. The reactor was then allowed to cool down to room temperature naturally and the resulting film was collected and washed with deionized water and dried in air. Subsequently, thermal treatment of the Bi₂WO₆ films was carried out at 400 °C for 4 h with a ramping rate of 2 °C/min in an air environment. The film was then allowed to cool down by natural convection in the furnace back to ambient condition. Pure WO₃ film (Sample C) was synthesized without any hydrothermal treatment with similar anodization condition and calcination at 400 °C for 4 h performed on the as-anodized film, while amorphous porous WO₃ (Sample A) was synthesized under homogenous anodization condition without any thermal treatment.

Material characterization A scanning electron microscope (SEM, Hitachi S900, operating accelerating voltage of 4 kV) was used to analyze the morphology of the films. XRD and GAXRD measurements were collected at room temperature using Cu K α radiation ($\lambda=1.54 \text{ \AA}$) with a potential of 40 kV and a current of 30 mA (Philips PW1830). Diffuse reflectance ultraviolet and visible (DRUV-Vis) spectra of the films were recorded in a range of 200-800 nm to investigate the light harvesting properties of WO₃ /Bi₂WO₆ thin films using a UV-Vis spectrophotometer (Cary 5 UV-VIS-NIR). The reflectance of the sample was measured and the corresponding absorbance (F(R)) was calculated using the Kubelka-Munk theory. Cyclic voltammetry measurements were taken in 0.1 M H₂SO₄ at room temperature using Autolab potentiostat/galvanostat (Model PGSTAT302N) in a standard three-electrode configuration with platinum wire as counter electrode, Ag/AgCl as the reference electrode, and WO₃ film as the working electrode. Cyclic voltammetry (CV) measurements were taken from -1.0 V to 0 V versus Ag/AgCl reference electrodes and scan rates were fixed at 0.05 V/s for all measurements. Wavelength dependency photocurrent measurements of the samples were taken in 0.1 M H₂SO₄ at room temperature using Autolab potentiostat/galvanostat (Model PGSTAT302N) at 1.0 V and $\lambda \geq 320, 395, 420, 435$ and 515 nm cut-off filters with 300 W Xenon lamp (Perkin Elmer, Cerman, PE300BF).

Water splitting reaction PEC water splitting experiments were carried out by applying external bias of 1.0 V in a two-electrode cell with Bi₂WO₆ as the working electrode and Pt as the counter electrode placed separately in each compartment with both electrodes being immersed in 0.1 M H₂SO₄ electrolyte solution. Argon gas was being employed as the main carrier gas in the whole system and a cut-off filter was used to obtain visible light of wavelength $\lambda \geq 420$ nm from a 300 W Xe lamp. The evolved H₂ and O₂ were determined with gas chromatography (Shimadzu, GC-8A).

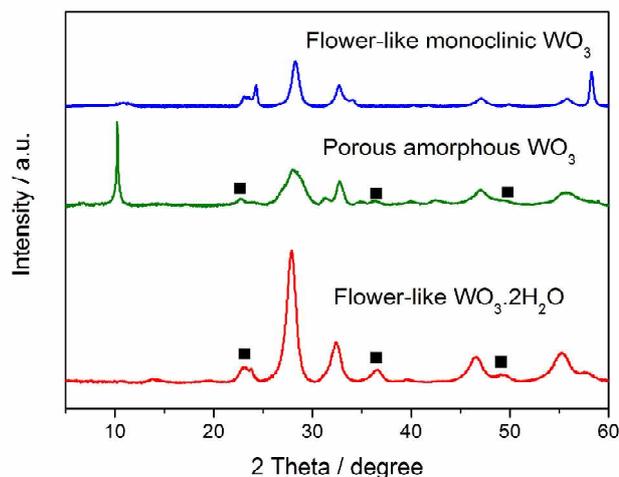
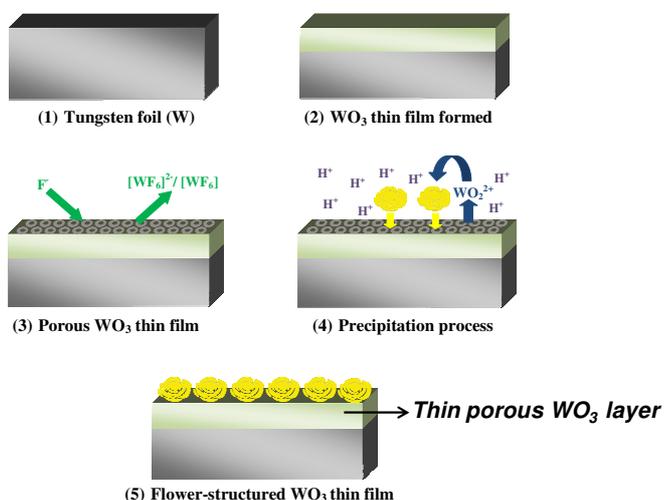


Figure S1. XRD patterns of three different tungsten precursors for the hydrothermal reaction. The porous amorphous WO_3 and flower-like monoclinic WO_3 did not result in orthorhombic Bi_2WO_6 illustrates the importance of the layered structure in $\text{WO}_3 \cdot 2\text{H}_2\text{O}$.



Scheme S1. Schematic Illustration of the Formation Process of Flower-Structured WO_3 Thin Film (1) Tungsten foil as the starting material and substrate. (2) Compact WO_3 film growth. (3) Nanoporous structure formed in the presence of fluoride ions (F^-) to form soluble fluoride complexes. (4) WO_2^{2+} Is generated due to the low pH and supersaturation condition and leads to the precipitation and growth of sparingly soluble products ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$) as represented by the light gray particle. (5) Flower-structured WO_3 thin film formed as a result of anodic growth of oxide later and the successive precipitation and crystal growth process.

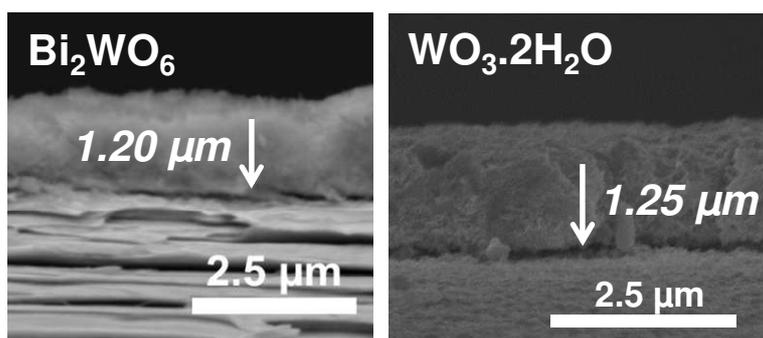


Figure S2. Side profile of Bi_2WO_6 and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ to depict the same thickness attained before and after hydrothermal treatment.

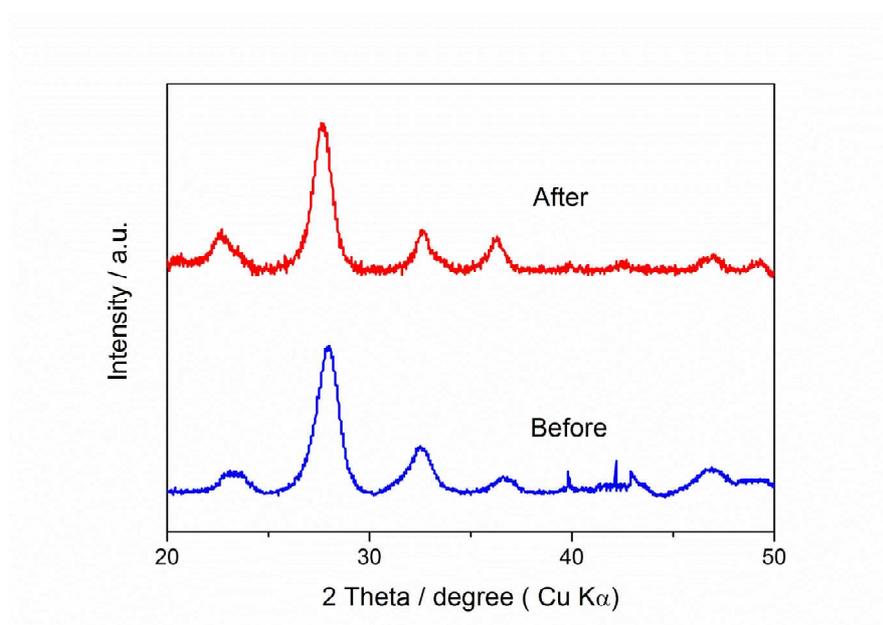


Figure S3. XRD spectra of the film before and after the PEC measurements.