

Supporting Information

Photoelectrochemical Water Oxidation on Photoanodes Fabricated with Hexagonal Nanoflower and Nanoblock WO₃

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Experimental Section

Preparation

All chemical reagents were analytical grade and were used without further purification. High purity water (PURELAB Ultra, resistivity = 18.2 M Ω ·cm) was used for the preparation of all solutions. WO₃ electrodes were fabricated by a microwave-assisted hydrothermal method and post annealing similar to that reported by Demir et al.²⁸ HCl was added into 10mM Na₂WO₄·2H₂O solution until no more precipitate was formed. Then the precipitate was collected and washed with high purity water several times by centrifugation before redispersion in water to form a final suspension. 50mM oxalic acid was added into the above suspension under intensely stirring and the capping agent, such as CH₃COOK, CH₃COONH₄, HCOOK or C₁₇H₃₅COOK was added when the suspension became transparent. For comparison, the solutions contained no capping agent were also prepared. The pH value of the solution was adjusted at about 0.8 by adding HCl into the above solution with stirring. The FTO (fluorine-doped tin oxide) substrate (NSG, Japan) was placed in the 30 mL solution and then transferred into a fluoropolymer lined vessel, sealed, and heated in a microwave oven (Mars-5, CEM). The substrates were ultrasonic cleaned beforehand by acetone, isopropanol, ethanol, and deionized water in sequence and then cleaned by the oxygen plasma treatment using a Diener Plasma Cleaner at

180W under 0.6 Pa for 10min. The solution was heated from room temperature to the designated temperature with 8 °C / minute under a microwave irradiation power of 400 W and then kept at 180 °C for 60min under autogenous pressure. After the hydrothermal reaction, the thin film deposited on FTO substrates and the powders dispersed in the reactant solution were washed and then dried naturally in air. To obtain WO₃ thin films with vertical array, the FTO substrates should be coated with a thin layer of seed by spin coating at first. In brief, 5mL HCl was added into 50 mM Na₂WO₄·2H₂O. After filtrating and washing, 80 mM of oxalic acid was added into the suspension under intense stirring. The precipitate was dissolved and used as a seed precursor. The spin coating processes were performed at 1500 rpm for 30 s. The samples were then annealed in air at 400 °C for 30 min, and then cooled down to room temperature. This process was repeated for 3 times. To test their photocatalytic and photoelectrocatalytic activities for oxidization of water, the as-prepared samples were calcined in air at 500 °C for 60 min to remove the organic residues.

Characterization

The crystal structure of the products was characterized by X-ray powder diffraction (XRD, Rigaku D/Max-2500/PC powder diffractometer) using Cu K α ($\lambda = 0.15406$ nm) radiation with an operating voltage of 40 kV and an operating current of 200 mA. The scan rate is 5 °/ min in the range of

10° – 60°. The morphologies of the as-prepared samples were observed by scanning electron microscopy (SEM, Quanta 200 FEG). High-resolution transmission electron microscopy (HRTEM) images were obtained by a JEM-2000eX transmission electron microscope. Raman scattering spectra were recorded on an Acton Raman spectrometer by 532 nm semiconductor laser as the excitation source with the power of 60 mW. The UV-vis absorption spectra were measured using a UV-Vis spectrophotometer (Cary 5000, Varian, Inc.). X-ray photoelectron spectroscopy (XPS) were recorded on a Thermo ESCALAB 250Xi spectrometer (Thermo Fisher, UK) with a Al K α ($h\nu = 1486.6\text{eV}$) radiation source, using C 1s (284.8 eV) as reference.

Photoelectrochemical and Photocatalytic Measurements

The photoelectrochemical properties were measured by a CHI electrochemical analyzer (CHI 440B, CH Instruments, Inc.). Chopped I-V curves of the as-prepared thin films were performed under simulated AM 1.5 solar illumination (100 mW/cm^2) using three electrode setup which the as-prepared WO₃ films as working electrode, platinum foil as counter electrode, saturated calomel electrode (SCE) as reference electrode in 1 M H₂SO₄ with scan rate of 20 mV/s. Electrochemical impedance spectra (EIS) was measured at 0.8 V vs. SCE with frequency range of 100 kHz-100 mHz and AC amplitude of 10 mV using an electrochemical workstation (IM6 Zahner, Germany). Incident photon-to-electron

conversion efficiency (IPCE) was performed on QTest Station 2000ADI system (Crowntech. Inc.). The light intensity at monochromatic light irradiation was calibrated with a standard silicon detector. The electrode potential was set at 0.8V vs. SCE. The photocatalytic O₂ evolution reactions were carried out using a 300 W Xe lamp (Ushio-CERMAX LX300) with a filter ($\lambda > 420$ nm) and a water filter to prevent passing of the ultraviolet and infrared light. The photocatalyst (0.2 g) was dispersed in 200 mL aqueous solution using AgNO₃ (0.02 M) as an electron acceptor. The temperature of the reaction mixture was maintained at 288 K by a continuous flow of cooling water. The amount of evolved O₂ was determined by an on-line gas chromatograph (Shimadzu GC-8 A, TCD, Ar carrier).

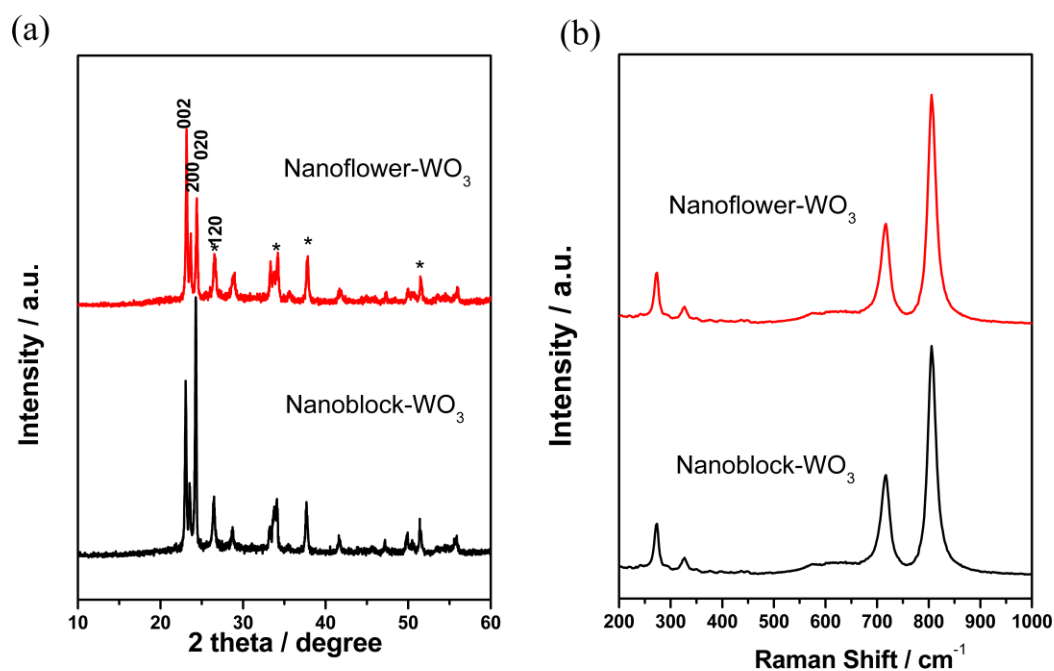


Figure S1 (a) XRD patterns (The peaks marked with * are signals from FTO substrate.) and (b) Raman spectra of nanoflower and nanoblock WO₃ photoelectrodes.

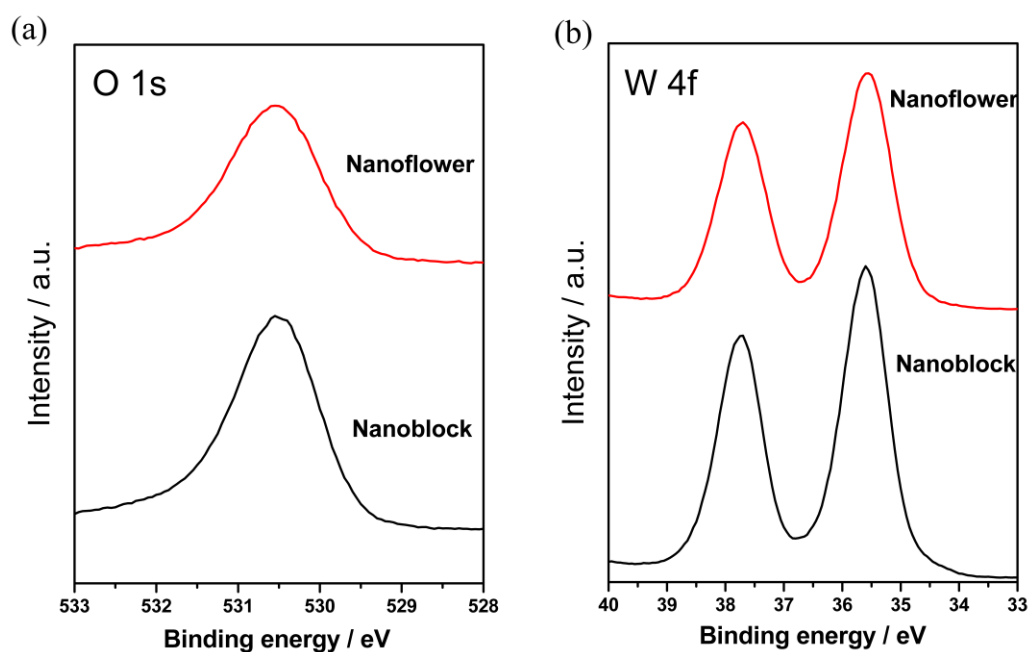


Figure S2 XPS of calcinated nanoflower and nanoblock WO₃ samples (a) O 1s and (b) W 4f. (The O 1s spectra show the main peak at 530.5 eV. A couple of bands located at 37.7 eV and 35.6 eV correspond to the W 4f_{5/2} and W 4f_{7/2} signals.)

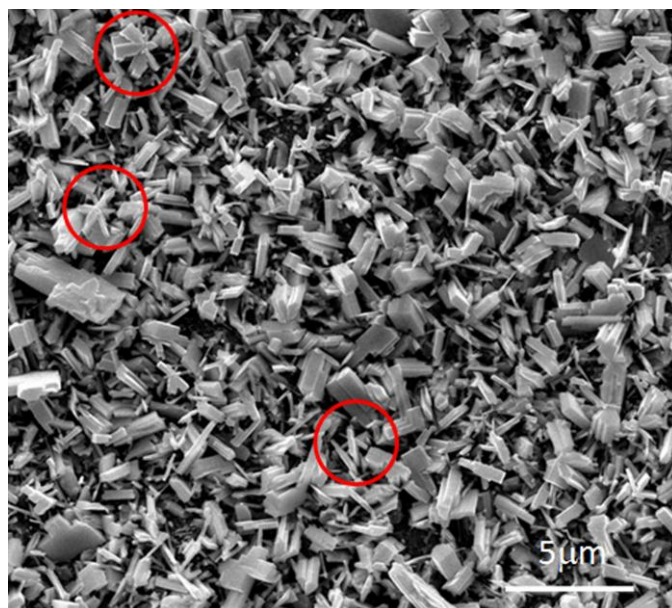


Figure S3 SEM images of WO_3 thin films synthesized by hydrothermal synthesis with CH_3COOK as directing agent.

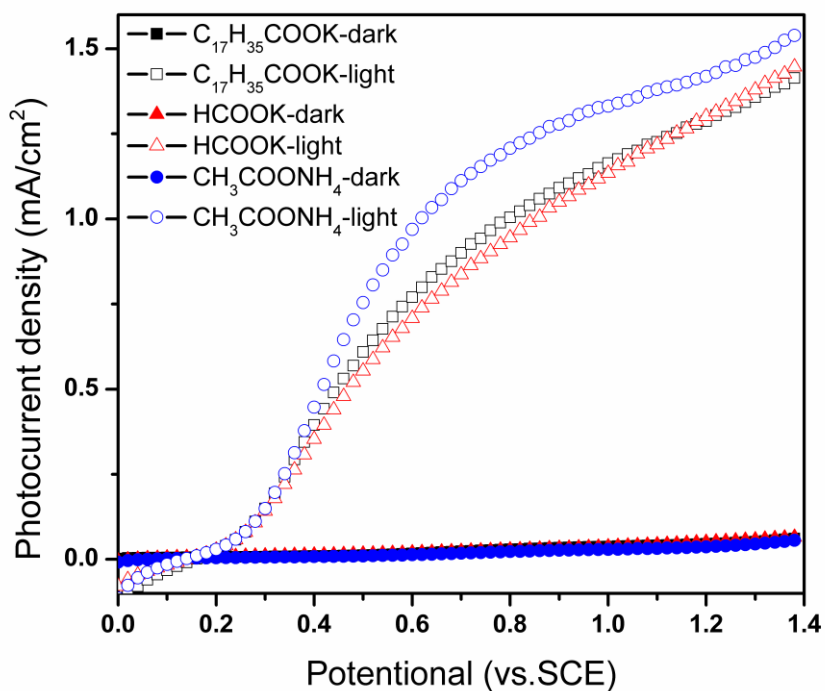


Figure S4 Linear sweep voltammetric scans of nanoflower WO_3 photoanodes prepared by different directing agents in 1 M H_2SO_4 .

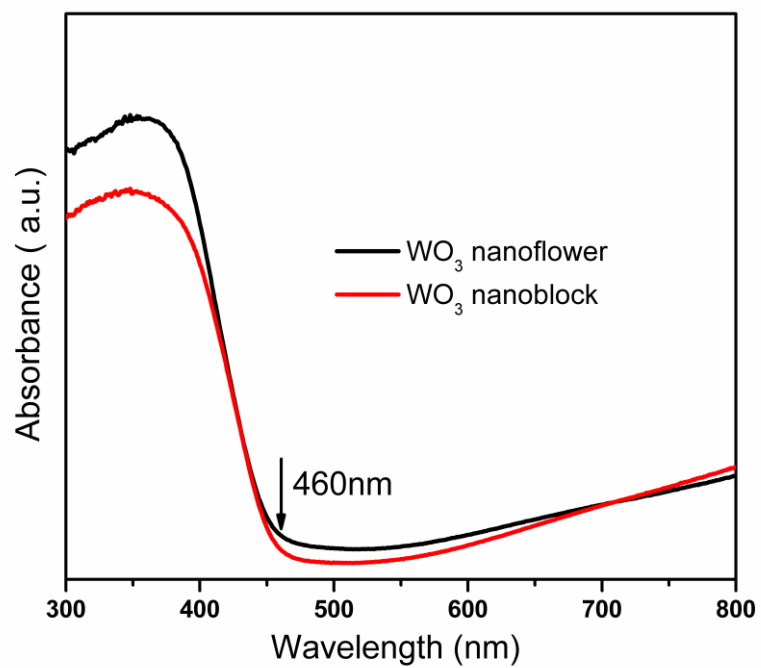


Figure S5 UV-visible diffusion spectra of naoflower and nanoblock WO₃ electrodes.