

Supplemental information for

Construction of p-Bi₂O₃/n-ZnO Nanowire Heterojunctions with Enhanced Photoelectrochemical Properties

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Experimental Section

Synthesis of Bi₂O₃/ZnO Nanowire Heterostructures

ZnO nanowire (NW) arrays were first grown on FTO-coated glass substrates using a hydrothermal method adapted from our previous work [12]. Prior to growth, a seed layer was deposited by spin-coating 80 μ L of 15 mM zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) in ethanol onto the FTO substrate, followed by thermal decomposition at 350 $^\circ\text{C}$ for 5 min to form nanocrystalline ZnO seeds. The seeded substrate was then immersed in an aqueous growth solution containing 5 mM zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), 5 mM hexamethylenetetramine (HMTA), 5 mM polyethyleneimine (PEI), and 0.25 M ammonium hydroxide (NH_4OH). The reaction was conducted at 65 $^\circ\text{C}$ for 24 h to yield vertically aligned ZnO NWs. The as-grown NWs were subsequently annealed in air at 550 $^\circ\text{C}$ for 5 h to enhance crystallinity and remove organic residues.

For Bi₂O₃ deposition, the ZnO NW/FTO substrates were immersed in an ethylene glycol solution containing 10 mM bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$) and heated to 190 $^\circ\text{C}$ under reflux for 3 h. The resulting samples were then annealed in air at 300, 400, or 500 $^\circ\text{C}$ for 1 h to form the final Bi₂O₃/ZnO heterostructures.

Materials Characterization

Surface morphology was examined using scanning electron microscopy (SEM, JEM-4000EX). Crystal structure and phase purity were analyzed by X-ray diffraction (XRD) and Raman spectroscopy. Chemical states were investigated by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 1600). High-resolution microstructural and compositional analyses were performed using scanning transmission electron microscopy (HR-STEM, JEM2010F and JEM2200FS, JEOL) operating at 200 kV. Optical properties were characterized by UV-Vis absorption spectroscopy.

Photoelectrochemical Measurements

Photoelectrochemical (PEC) measurements were conducted in a three-electrode configuration using a potentiostat/galvanostat (CHI 6273D). The Bi₂O₃/ZnO NW electrode served as the working electrode, with a Pt sheet (4 cm²) as the counter electrode and an Ag/AgCl (3 M KCl) reference electrode. A 0.5 M Na₂SO₄ solution was used as the electrolyte. All potentials are reported relative to Ag/AgCl.

Illumination was provided by a 150 W Xe lamp equipped with an AM 1.5G filter, calibrated to 100 mW·cm⁻² at the sample surface. Linear sweep voltammetry (LSV) was performed under both

continuous and chopped illumination at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. The illuminated area for all PEC measurements was precisely defined using a circular mask with an area of 1 cm^2 . Incident photon-to-current conversion efficiency (IPCE) was measured using a monochromator coupled to the Xe lamp, with light incident from the front side through a quartz window and the electrolyte. Electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 10 mV at an applied potential of 0.3 V under illumination. Mott–Schottky analysis was performed in the dark at a frequency of 1 kHz.

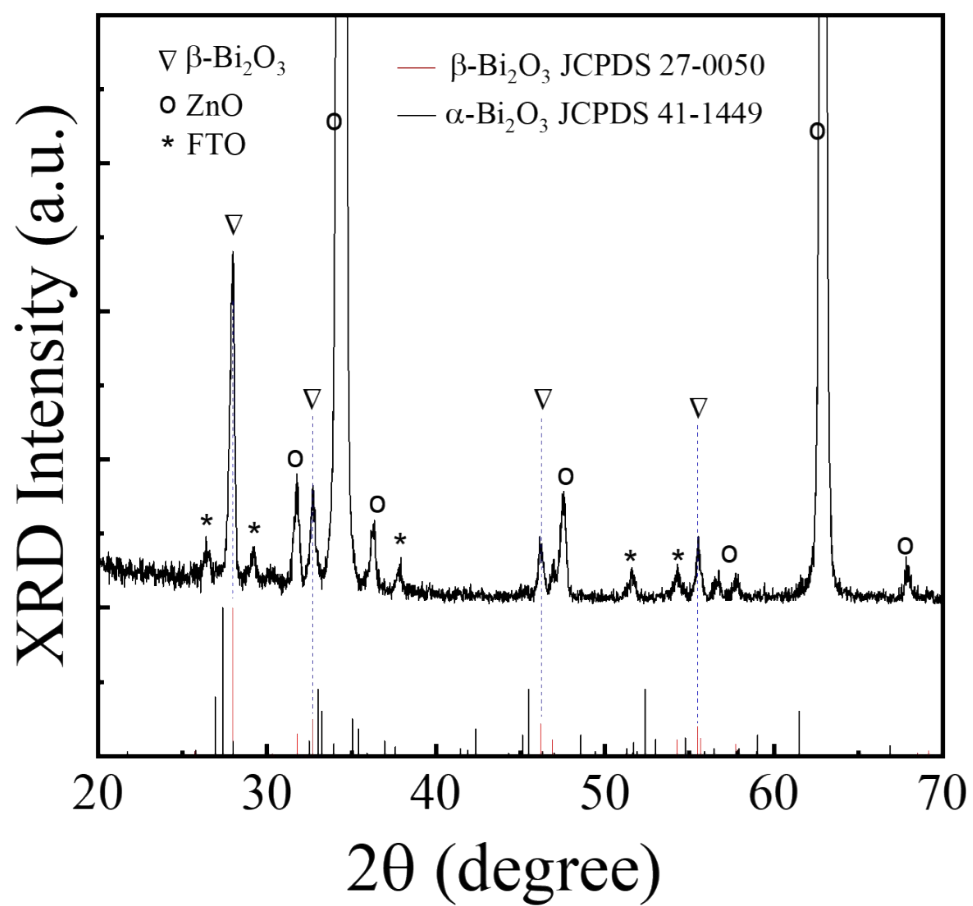


Figure S1. XRD pattern with peak indexing and standard reference overlays.

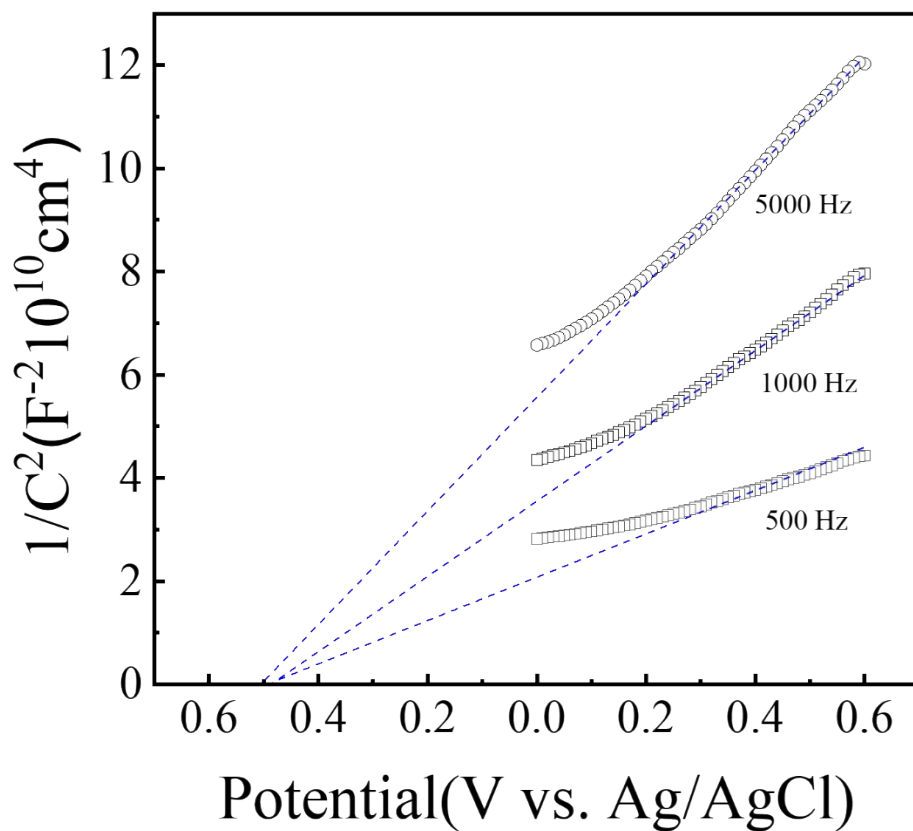


Figure S2. Frequency-dependent Mott–Schottky measurements at 500 Hz, 1 kHz, and 5 kHz.

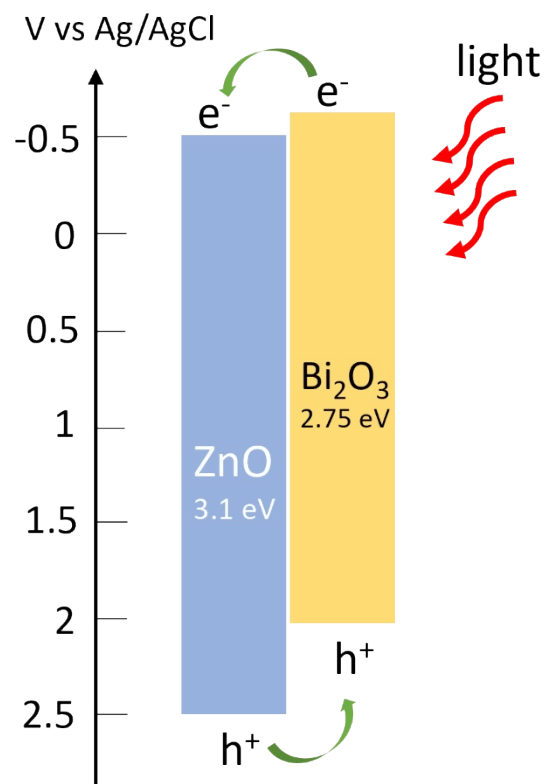


Figure S3. Schematic band structure diagram for the Bi₂O₃/ZnO heterojunction.

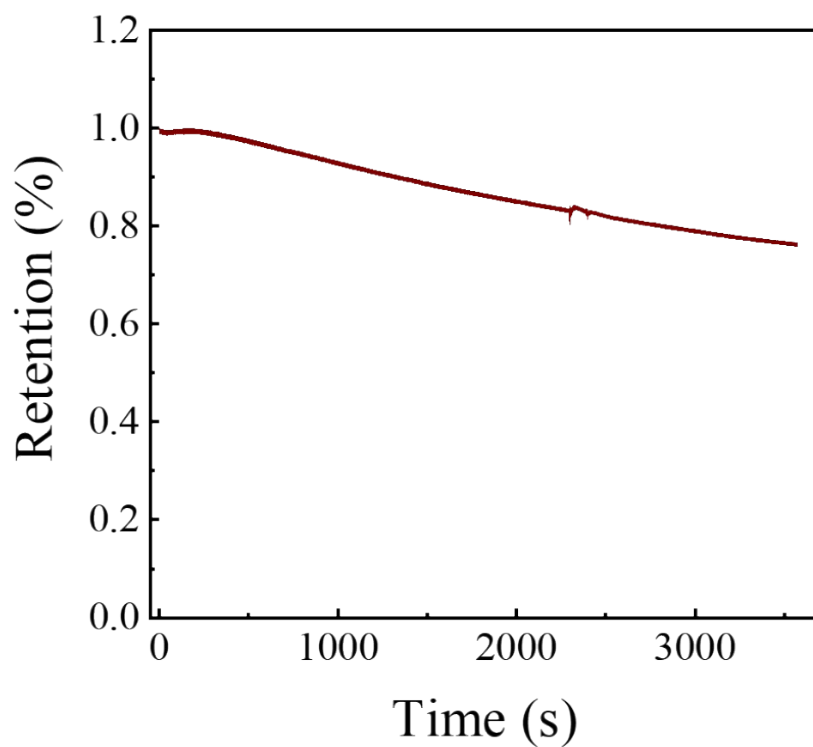


Figure S4. Chronoamperometric (*i*-*t*) measurements on the Bi₂O₃/ZnO (400 °C) electrodes at a constant applied potential of 0.3 V vs. Ag/AgCl under AM 1.5G illumination for 3600 s.