

Supporting Information

Toward enhanced photocatalytic activity of NiO-porous NiO homojunction derived from the in-situ templated metal-organic framework

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1. Experimental section

1.1 Chemicals and synthesis.

All of the reagents and solvents were commercially available and could be used without further purification.

Synthesis of spherical Ni(OH)₂: appropriate amount of NiCl · 6H₂O, ammonium chloride, PVP, dissolved in 10 mL water and 10 mL ethanol into the beaker, and then ultrasound treatment, dissolve and add 10 mL urea. Then put the mixed solution into a 50 mL reaction kettle, put the kettle into the oven, set the reaction temperature at 120 °C, and the reaction time for 24 h. The reaction mixture was centrifuged, washed twice with water and twice with ethanol, and the spherical nickel hydroxide prepared was dried in a 60 °C, oven.

Synthesis of NiO@Ni-MOF: NiO@Ni-MOF was prepared by dissolving appropriate spherical nickel hydroxide and 1,4-benzenedicarboxylic acid in 15 mL dimethylformamide (DMF), four identical solutions were prepared and placed in a 50 mL high temperature reactor at 120 °C, at 24 h, 48 h, 72 h and 96 h, respectively. After the reaction, wash with DMF and ethanol three times each, and then dry in a 60 °C oven.

Synthesis of NiO@PNiO homojunction: 0.5 g NiO@Ni-MOF was put into a high temperature furnace, which was heated to 500 °C every 2 minutes by 2 degrees, and the holding time was 2 h.

1.2 Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$). Corresponding work voltage and current is 40 kV and 100 mA, respectively. The morphologies and compositions of samples were observed on field emission scanning electron microscope (SEM, Gemini300) and transmission electron microscopy (TEM, JEM-2100Plus). The UV–Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Viarian, USA) with BaSO₄ as a reflectance standard. Steady photoluminescence (PL) emission spectra were tested by luminescence spectrophotometer (QM-400, PTI) with 380 nm excitation wavelength.

1.3 Photocatalytic hydrogen production.

The photocatalytic H₂ production experiments were performed in a 100 mL Pyrex flask at

ambient temperature and atmospheric pressure, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp through a UV-cutoff filter with a wavelength range of 360-800 nm, which was positioned 13 cm away from the reaction solution, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was about $200 \text{ mW}\cdot\text{cm}^{-2}$, which was measured by a FZ-A visible-light radiometer (CEAU-Light, China). In a typical photocatalytic H_2 -production experiment, 20 mg of the as-prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing 5 mL $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEOA, AR,98%). Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles in suspension during the experiments. H_2 content was analyzed by gas chromatography (GC-7900, CEAU-Light, China). All glass wares were carefully rinsed with DI water prior to usage. The photocatalytic stability was performed in the same processing parameters.

1.4 Photocatalytic degradation performance.

The photocatalytic activity of the samples was evaluated by degrading the aqueous solution of methylene blue (MB) under the visible light irradiation with 300 W Xe lamp. Normally, 30 mg of the sample was suspended in the dye aqueous solution (50 mL, 20 mg/L) for 30 min in the dark to achieve the adsorption-desorption equilibrium. Then, 2 mL of the suspension was collected and centrifuged every 10 min after illumination. The concentration of the residual dye was measured with an ultraviolet-visible spectrophotometer.

1.5 Electrochemical measurements.

All the electrochemical measurements were conducted by Bio-Logic SP150 electrochemical station using three-electrode system at room temperature with a glassy carbon electrode (3 mm in diameter), (sheet resistance $20\text{-}25 \ \Omega\text{-}2$) as the working electrode, a carbon rod as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. For the electrochemical measurements, 4 mg of the catalysts were dispersed in 2 mL of 9:1 v/v water/Nafion by sonication to form a homogeneous ink. Typically, 5 μL well-dispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrocatalyst was prepared with a catalyst loading of 0.14 mg cm^{-2} . The electrolyte of transient photocurrent

responses experiments, electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) was in 0.5 M Na₂SO₄ aqueous solution, and the electrolyte of linear sweep voltammetry (LSV) was in 1 M KOH solution for the OER results, respectively. EIS was performed at an impressed voltage of -0.3 eV, for voltage ranging from -2.5 V to 2.5 V. M-S was measured for a scan voltage ranging from -1 V to 0.5 V at 500-2000 Hz. The transient photocurrent responses measurement was performed under full light irradiation, and the LSV obtained at a scan rate of 1 mV/s.

2. Supporting Figures

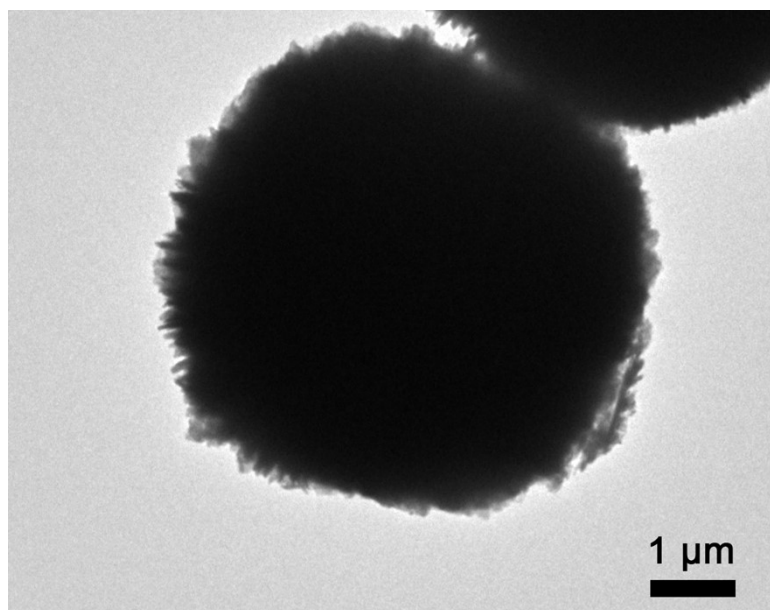


Fig. S1 The TEM image of NiO@PNiO-48.

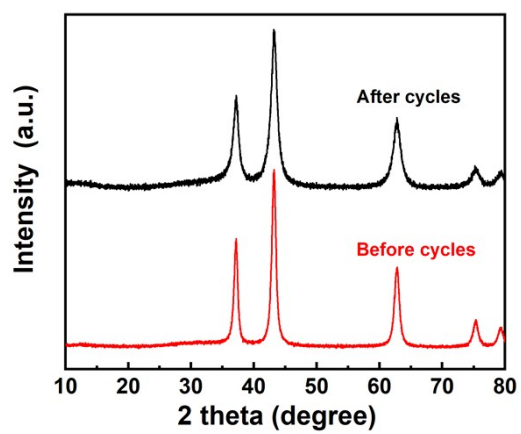


Fig. S2 The XRD patterns of NiO@PNiO-48 before and after photocatalysis.

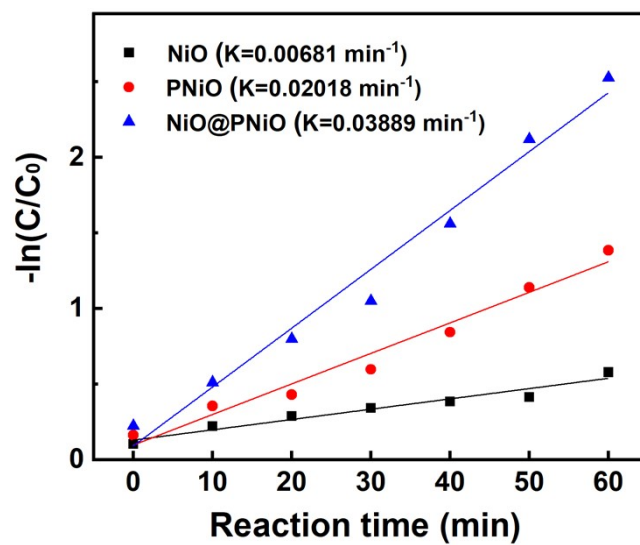


Fig. S3 Kinetic fits corresponding to the degradation of NiO, PNiO and NiO@PNiO.

3. Supporting Tables

Table S1 Resistance value (R_s and R_c) of NiO, PNiO, NiO@PNiO homojunction samples.

Sample	R_s (Ω)	R_c (Ω)
NiO	7.95	12.68
PNiO	5.31	8.94
NiO@PNiO-24	2.87	4.92
NiO@PNiO-48	1.16	1.97
NiO@PNiO-72	1.38	2.48
NiO@PNiO-96	1.68	2.75