Electronic Supplementary Information

Self-Sacrificed Construction of Defect-Rich ZnO@ZIF-8 Nanocomposites for Enhanced Photocurrent Property

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Materials. All chemicals were used without further purification. Zinc nitrate hexahydrate (> 99.0%) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ascorbic acid (AA, >99.0%), methanol and ethanol were obtained from Beijing Chemical Co. Inc. Cetyltrimethylammonium bromide (CTAB) was obtained from Huishi Biochemical Reagent Company of China. Hexamethylenetetramine (HMTA, > 99.0%) was obtained from Tianjin Guangfu Technology Development Co., Ltd. 2-methylimidazole (H-MeIM) was purchased from Aladdin. Deionized water was used for the synthesis.

Synthesis of mesoporous ZnO nanoparticles. The synthetic procedure of mesoporous ZnO nanoparticles was similar to the previously reported method with some minor modifications.¹ Typically, 35 mg of AA and 146 mg of CTAB were added into the mixture of ethanol (20 mL) and deionized water (180 mL) in a beakerflask (250 mL) under vigorous stirring at room temperature to form a clear solution. Then 238 mg of Zn(NO₃)₂·6H₂O and 56 mg of HMTA were introduced the solution under stirring, and a clear solution was obtained. Finally, the beakerflask was sealed and then heated in the oven of 85°C for 8 h without stirring. The product was collected by centrifugation at 8000 rpm for 5 min and dried at room temperature for 12 h. The dried powder was calcined at 400 °C to obtain mesoporous ZnO nanoparticles.

Synthesis of $ZnO@SiO_2$ particles. The synthesized ZnO nanoparticles of 80 mg were firstly dispersed into the mixture of 6 mL water and 18.9 mL ethanol to form a uniform suspension under strong stirring. After a few minutes, 0.84 mL ammonia solution was then added into the solution. 1.2 mL tetraethoxysilane dispersed in 10 mL ethanol was quickly dropped into the above solution under stirring. Finally, the solution was kept stirring for 12 h under room temperature. The product were collected by centrifugation (4000 rpm for 3 min) and washed with water for 2 times and ethanol for 2 times. The photocurrent response of the sample was tested under the same condition with the ZnO@ZIF-8 nanoparticles.

Synthesis of ZIF-8 crystals. $Zn(NO_3)_2 \cdot 6H_2O(0.2389 \text{ g}, 0.8 \text{ mmol})$ and H-MeIM (0.06 g, 0.7 mmol) were introduced into 12 mL N,N-dimethylformamide to form a clear solution. The clear solution was settled into an oven of 120 °C for 24 h. the obtained product was washed with N,N-dimethylformamide for 3 times and dried at 65 °C for 12 h. The photocurrent response of the sample was tested under the same condition with the ZnO@ZIF-8 nanoparticles.

Characterization. Scanning electron microscopy (SEM) images were obtained on a HITACHI SU8020 scanning electron microscopy with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained on an FEI Tecnai G2 F20 S-Twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max 2550diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) operated at 50 kV and 200 mA. N₂ adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2420 surface area analyzer. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear part of the BET plot. CO₂ adsorption-desorption isotherms were obtained at 0 °C and 25 °C on a Micromeritics 3-Flex. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ under a flow of air from 50 °C to 600 °C. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectroscopy (XPS) was performed with a three-

electrode system using a CH Instrument (Model 660E), in which the as-synthesized materials were used directly as the working electrode. The hydrodynamic diameters were measured by photon correlation spectroscopy employing a Nano ZS90 laser particle analyzer (Malvern Instruments, UK) at 25°C. UV absorption of the samples was measured with a Shimadzu UV-2450 spectrometer. The FT-IR spectra were recorded on a Brüker IFS 66 V/S FTIR spectrometer with KBr pellets as the background.

Calculation. The mathematical form of pore size distribution (PSD) data presentation in this work: differential pore volume versus diameter (DV/Dd) was used to analyze pore structures of the obtained nanocomposites through Density functional theory (DFT) method. The differential pore volume curves could represent the pore ranges. According to the PSD data, the peak area percentage of the 1.5 nm micropores was calculated and fitted by the Gaussian formula, which was provided in the software of OriginPro 8.5.

As observed in the high-resolution TEM image (Fig. S1), it allows the resolution of lattice fringes with a spacing of 0.26 nm to be correlated to the (002) planes of wurtzite ZnO.



Fig. S1 High-resolution TEM image of mesoporous ZnO nanoparticles before being coated with ZIF-8 shells.



Fig. S2 SEM and TEM images of ZnO@ZIF-8 nanoparticles with H_2O/CH_3OH volume ratio of (A) 0; (B) 0.5; (C, D) 2.0; (E) 3.0; (F) 5.0.



Fig. S3 N_2 adsorption-desorption isotherm and pore size distribution of mesoporous ZnO nanoparticles.



Fig. S4 FT-IR spectra of the ZIF-8 crystals and ZnO@ZIF-8 nanocomposites.



Fig. S5 CO_2 adsorption isotherms of (A) ZZNCs-0.7 and (B) ZIF-8 crystal at 273, 283 and 298 K.



Fig. S6 XPS of ZIF-8 crystals (green line), ZZNCs-0 (orange line), ZZNCs-0.5 (magenta line), ZZNCs-0.7 (red line), ZZNCs-2.0 (navy line), ZZNCs-3.0 (cyan line), and ZZNCs-5.0 (olive line).



Fig. S7 Energy dispersive X-ray spectroscopy (EDS) of the synthesized ZZNcs-0.7.



Fig. S8 Hydrodynamic diameters of ZnO and ZnO@ZIF-8 nanoparticles with different H₂O/CH₃OH volume ratio.



Fig. S9 SEM images of the product separated from the reactants at the 2nd h.



Fig. S10 Ultraviolet-visible spectra of H-MeIM left in the solution along with reaction time.



Fig. S11 SEM images of ZnO@ZIF-8 nanocomposites synthesized with addition concentration of H-MeIM at (A) 0.04 M; (B) 0.03 M.



Fig. S12 Electrochemical impedance spectroscopy (EIS) of the synthesized ZnO@ZIF-8 nanocomposites.



Fig. S13 SEM and TEM images of the synthesized $ZnO@SiO_2$ (A, B) and ZIF-8 single crystal (C).



Fig. S14 Photocurrent response of the synthesized (a) ZnO, (b) ZIF-8 single crystal and (c) $ZnO@SiO_2$ materials.

Material	H ₂ O/CH ₃ OH volume ratio	^a BET (m ² /g)	N ₂ maximum adsorption amount (cm ³ /g)	^b Pore size (nm)
ZnO@ZIF-8	0	632	158	1.0, 1.4
ZnO@ZIF-8	0.5	1024	245	1.0, 1.4
ZnO@ZIF-8	0.7	1175	267	1.0, 1.4
ZnO@ZIF-8	2	1305	308	1.0, 1.4
ZnO@ZIF-8	3	1353	317	1.0, 1.4
ZnO@ZIF-8	5	500	125	1.0, 1.4

 Table S1 Properties of the as-synthesized ZnO@ZIF-8 nanocomposites.

^a **BET** is the BET surface area.

 $^{\text{b}}$ Pore size is calculated from adsorption branch of N_2 isotherm.