Electronic Supplementary Information

Wet chemical epitaxial growth of cactus-like $CuFeO_2$/ZnO heterojunction for improved photocatalysis

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Experimental

1. Preparation of $CuFeO_2$ nanoflakes

$CuFeO_2$ nanoflakes were prepared by hydrothermal method and all chemicals were of analytic grade and used as received without further purification. A mixture of 1 mmol $CuSO_4 \cdot 5H_2O$, 1 mmol $FeSO_4 \cdot 7H_2O$, 10 ml sodium alginate (SA) of 5 g/L were dissolved into 10 ml deionized water by stirring for 10 min. The mixture were added in a Teflon-lined autoclave (50 ml), and then adding 10 ml NaOH of 10 M and stirring for 5 min and putting the autoclave into drying oven at 160 ^oC for 6 h. Finally, the synthesized nanoflakes were washed 3 times with water and 3 times with 75 % ethanol and dried at 60 ^oC for 10 h.

2. Wet chemical epitaxy growth of $CuFeO_2$/ZnO Heterojunction

A mixture of 50 mg $CuFeO_2$, 10 ml $Zn(NO_3)_2$ of 5 mol/L, 20 ml deionized water were dissolved into a three-necked flask (100 ml) by stirring for 10 min. And then put the three-necked flask on the hot plate and keep fluxing for 2 h. Immediately after, the mixture were added in a Teflon-lined autoclave (50 ml) and heat at 120 ^oC for different time in drying oven. Finally, the $CuFeO_2$/ZnO heterojunction sampleswere washed 3 times with water and 3 times with 75 % ethanol and dried at 60 ^oC for 10 h. The heterojunction samples are termed as $CuFeO_2$/ZnO-1, $CuFeO_2$/ZnO-2, and $CuFeO_2$/ZnO-3 for heat for 1h, 2h, and 3h, respectively.

3. Characterization

Scanning electron microscopy (SEM) images were obtained on a Zeiss-Supra55 electron microscope. High–resolution transmission electron microscopy (HRTEM) characterizations were performed with a Tecnai G2 F30 S-TWIN transmission electron microscope operated at 200 kV. X-ray diffraction (XRD) patterns of the products were recorded on a Bruker D8 Focus diffractometer by using Cu Kα radiation (λ= 1.54178 Å).

4. Photoelectrochemical Testing and Photocatalytic performance

Photoelectrochemical measurements were performed in a three electrodes system in 1 M NaOH. The $CuFeO_2$/ZnO heterojunction based work electrodes are fabricated by dip-coating method. Typically, 1 mg of the sample materials are added in 4 mL of glycol methyl ether solution, and ultra-sounded for 30 min. Then drop the sample suspension onto the FTO substrate and heated at 80 ^oC. The sintered the electrode in a tube furnace at 400 ^oC for 30 min in air. The reference electrode is saturated Ag/AgCl reference electrode and the counter electrode is Pt wire electrode. The light source is a 500 W xenon lamp and the lamp power was adjusted to 100 mW/cm^2. The photocatalytic reaction was carried out in a 30 mL quartz reactor with 20 mg $CuFeO_2$ or $CuFeO_2$/ZnO powder, 100 mmol benzaldehyde, and 10 mL isopropyl alcohol under N_2 atmosphere. The conversions were determined by gas chromatography-mass spectrometry (GC-MS) based on benzaldehyde consumption.

5. Computational methods.

The stable configuration of $CuFeO_2$/ZnO interface was studied by DFT calculation with the CASTEP program. Calculations were performed on heterojunction models composed of $CuFeO_2$ and ZnO epitaxial stacked along the (001) direction. Three possible interfaces, namely, Fe-O-Zn, Cu-O-Zn, Cu-O-Zn, were calculated as shown below. Every $CuFeO_2$ slab with eight atom layers where top two layers were allowed to relax and bottom six layers were frozen. Both structures were optimized at the generalized gradient approximation (GGA) level with Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional and the norm-conserving pseudopotentials. The vacuum layer of the interface models is set to be 10 Å to minimize the interaction between the periodic images. During the optimization, the lattice parameters were fixed and only the atoms were allowed to relax. The atomic positions were fully relaxed until a maximum energy difference and residual force on atoms, respectively, converged to 10^{-5} eV and 0.03 eV $Å^{-1}$ with a 520 eV plane-wave cutoff energy and a 4 × 4 × 1 k-point grid.

Results and discussion

Table S1. DFT calculated Zn-O bond length and E_{form} for different configuration.

Configuration	Zn-O bond length (Å)	E_{form} (eV)
O1 ($CuFeO_2$)-Zn1 (ZnO)	2.044	-4.26
O1 ($CuFeO_2$)-Zn2 (ZnO)	1.836	-2.21
O2 ($CuFeO_2$)-Zn2 (ZnO)	2.152	-1.79
O2 ($CuFeO_2$)-Zn1 (ZnO)	1.961	-1.21

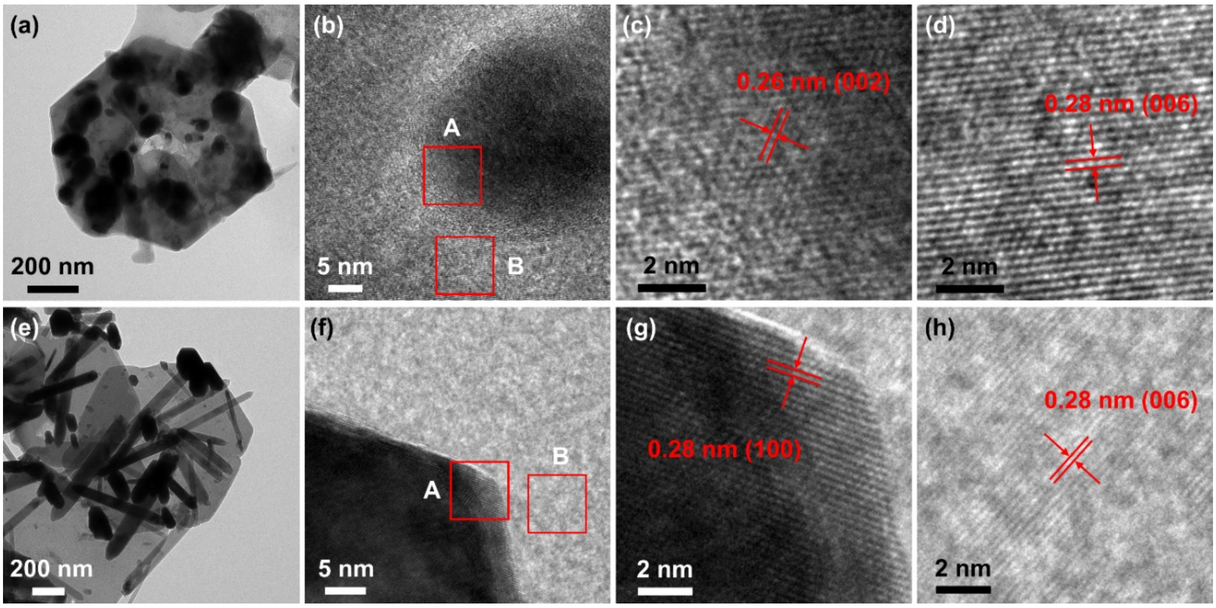

Fig. S1. TEM (a) and HRTEM (b) images of $CuFeO_2$/ZnO-2, HRTEM image of area A (c) and B (d) in (b); TEM (e) and HRTEM (f) images of $CuFeO_2$/ZnO-3, HRTEM image of area A (g) and B (h) in (f).

Table S2. The phase composition of $CuFeO_2$/ZnO heterojunction from Rietveld refinement.

Sample	Phase composition (%)		
	$CuFeO_2$-2H	$CuFeO_2$-3R	ZnO
$CuFeO_2$	56.01	43.99	0
$CuFeO_2$-ZnO-1	45.17	40.70	14.13
$CuFeO_2$-ZnO-2	37.38	33.31	29.31
$CuFeO_2$-ZnO-3	26.88	24.31	48.81

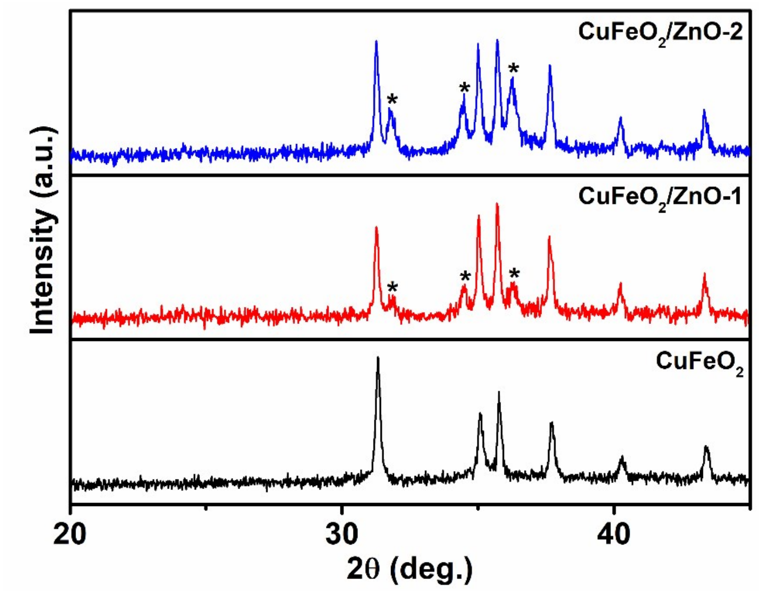

Fig. S2. XRD patterns of the CuFeO$_2$/ZnO-1, CuFeO$_2$/ZnO-2 and pure CuFeO$_2$. The diffraction peaks of ZnO are marked with an asterisk (*).

The diffraction peaks are indexed to 3R (JCPDS 39–0246) and 2H (JCPDS 79–1546) delafossite CuFeO$_2$, which proves all of the products are composed of mixture crystal phases. After epitaxial growth, the appeared diffraction peaks can be indexed as ZnO crystals with a hexagonal wurtzite structure (JCPDS 36–1451). No impurities were observed in these patterns.

Table S3. The decay lifetime of the photoinduced carriers of CuFeO$_2$/ZnO heterojunction.

Sample	τ_1 (s)	τ_2 (s)	τ_{av} (s)
CuFeO$_2$	1.53 (98.27%)	13.30 (1.73%)	1.73
CuFeO$_2$/ZnO-1	0.32 (99.18%)	5.42(0.82%)	0.36
CuFeO$_2$/ZnO-2	0.95(99.99%)	14.25(0.01%)	0.95
CuFeO$_2$/ZnO-3	2.02(95.28%)	15.56 (4.72%)	2.66

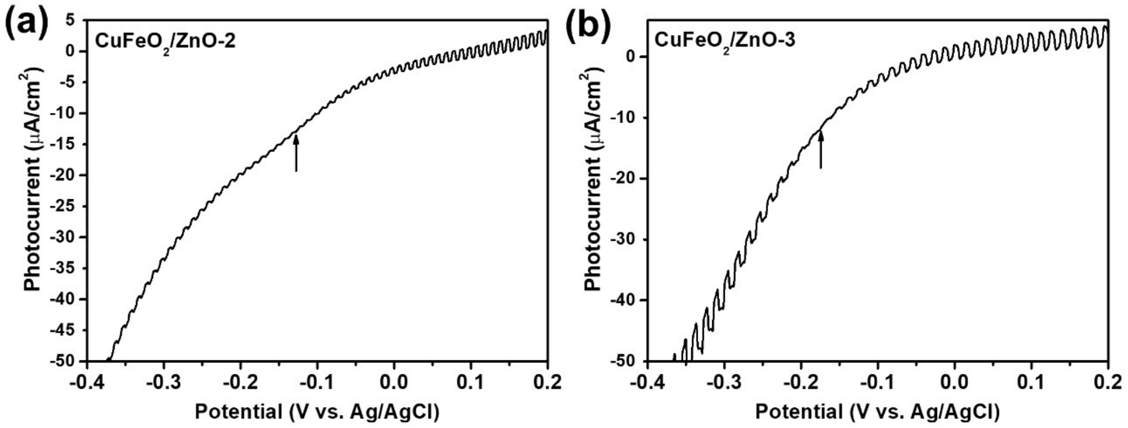

Fig. S3. The LSV curves of $CuFeO_2$/ZnO-2 and $CuFeO_2$/ZnO-3 photoelectrodes.

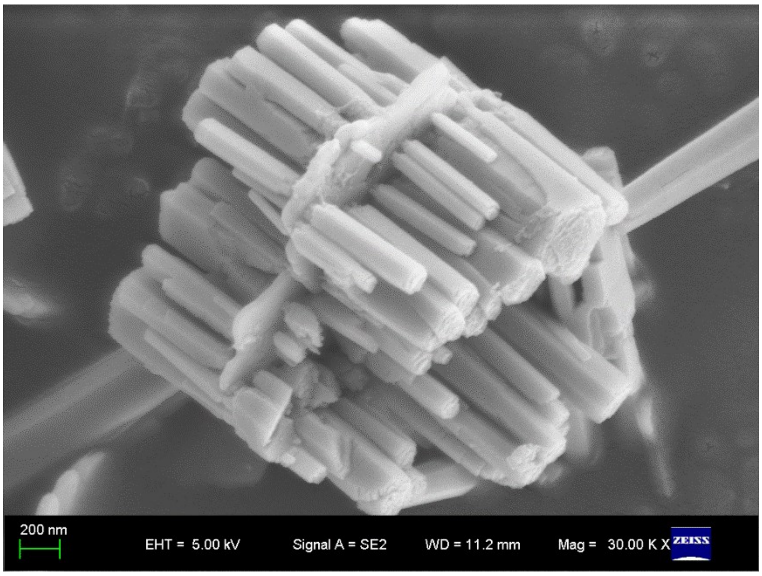

Fig. S4. SEM image of $CuFeO_2$/ZnO heterojunction with reaction time of 4 h.