

Polar Interface-Induced Improvement in High Photocatalytic Hydrogen Evolution over ZnO-CdS Heterostructures

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Experiment Section

Sample Preparation

Synthesis of Hexagonal ZnO disks. 40 mL of aqueous solution containing 0.5 M zinc acetate and 0.1 M (0.1 M and 0.05 M) sodium hydroxide in a Teflon-lined stainless autoclave with a volume of 80 mL were heated at 120 °C for 20 h. The resultant precipitate was washed with deionized water three times and dried at 80 °C for 24 h.

Synthesis of Hexagonal ZnO rods. ZnO rods were synthesized by a modified hydrothermal route, where 0.1 M zinc acetate and 0.6 M hexamethylene tetramine dissolved into 50 mL of deionized water were treated in a Teflon-lined stainless autoclave with a volume of 80 mL at 95 °C for 10 h. The precipitate was also washed with deionized water three times and dried at 80 °C for 24 h.

- 5 Preparation of ZnO-CdS Heterostructures. 200 mg of ZnO precursors in 20 mL of cadmium acetate aqueous solution were ultrasonically treated for 1 h. Then the suspension was evaporated at 80 °C under constant magnetic stirring. Cadmium acetate in the recovered powder was converted to CdO by heating the sample at 400 °C for 1 h in air. To obtain ZnO-CdS heterostructures, ZnO-CdO was heated in H₂S atmosphere at a flux of 50 mL·min⁻¹ at 350 °C for 0.5 h to convert CdO to CdS.
- 10 Synthesis of reference CdS. 500 mg of cadmium acetate was thermal-treated at 400 °C for 2 h in air. And then was heated in H₂S atmosphere at a flux of 50 mL·min⁻¹ at 400 °C for 2 h.

Characterization

- X-ray diffraction (XRD) patterns were recorded on Rigaku diffractometer using Cu K α irradiation. Scanning electron microscope (SEM) images were obtained on a SUPRA SEM 35. Transmission electron microscope (TEM) images were obtained by using Tecnai F30 (FEI). The UV-visible light absorption spectra were measured with a UV-visible spectrophotometer (JACSO-V550). The chemical compositions of the samples were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K α X-ray source). All binding energies were referenced to the C 1s peak

(284.6 eV) arising from adventitious carbon. Time-resolved fluorescence spectroscopy (HJY-FL3-221-TCSPC) with a light emission diode laser was used to monitor the emission decay of photoinduced carriers.

Photocatalytic water splitting measurements

5 Water splitting reactions were carried out in a gas-closed circulation in vacuum (the material of a reaction cell is quartz). Typically, 0.1 g of the photocatalyst powder was dispersed in 300 mL aqueous solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃. The light source was a 300 W Xe lamp, and the light intensity reaching the surface of the reaction solution was 135 mW·cm⁻². The amount of H₂ evolution was determined using a gas chromatography (Agilent Technologies: 6890N).

10 Computational Details

Our first-principles calculations were based on a density functional theory approach^{1,2} with exchange and correlation energy corrections included through a generalized gradient approximation.³ A plane wave basis was used with a cutoff kinetic energy of 450 eV, and the projector augmented wave method⁴ was used with the Monkhorst–Pack scheme⁵ to sample the Brillouin zone with a k-point mesh 15 of spacing $\leq 0.03 \text{ \AA}^{-1}$ for all phases. The Zn-3d4s and O-2s2p electrons were treated as valence electrons. As in Ref. 6, the residual internal electric field⁷ in these thin slabs was quenched by saturating the broken surface bonds on the one side of the slabs with hydrogen atoms to guarantee that the surface band of this side was always fully occupied and that ideal charge neutralization for this side

of the slab was enforced. All atomic configurations were fully relaxed by minimizing the atomic forces.

With this setting the calculated lattice parameters of ZnO were found to be $a = 3.277 \text{ \AA}$, $c = 5.291 \text{ \AA}$, in good agreement with the previous experimental ($a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$) and theoretical studies ($a = 3.282 \text{ \AA}$ and $c = 5.291 \text{ \AA}$)⁷ and references therein).

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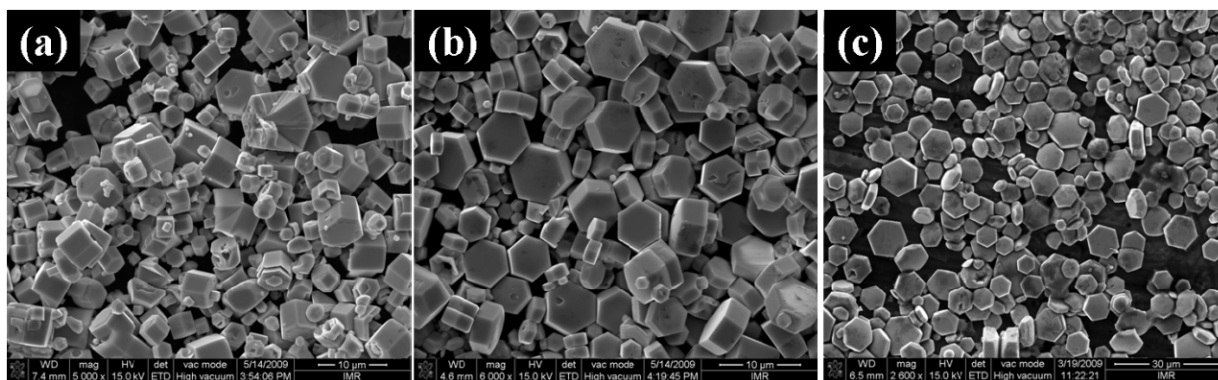


Figure S1. SEM images of ZnO disks with different ratios of (0001) and (000 $\bar{1}$) facets, the ratio increases from a to c with decrease of NaOH concentration (a: 0.2 M, b: 0.1 M, c: 0.05 M).

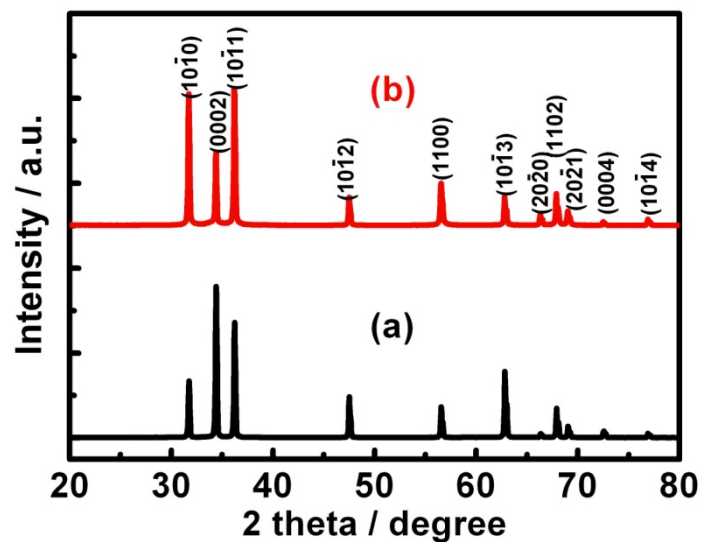
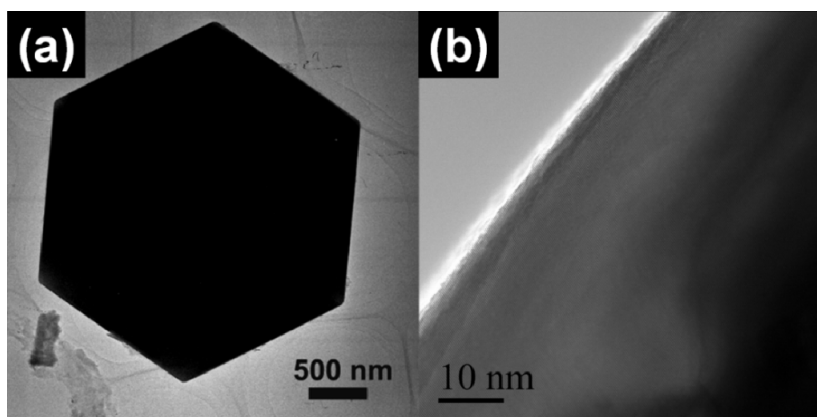


Figure S2. X-ray diffraction patterns of hexagonal ZnO (a) disks and (b) rods.



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Figure S3. (a) Transmission electron microscope (TEM) and (b) magnified TEM images of a hexagonal ZnO disk.

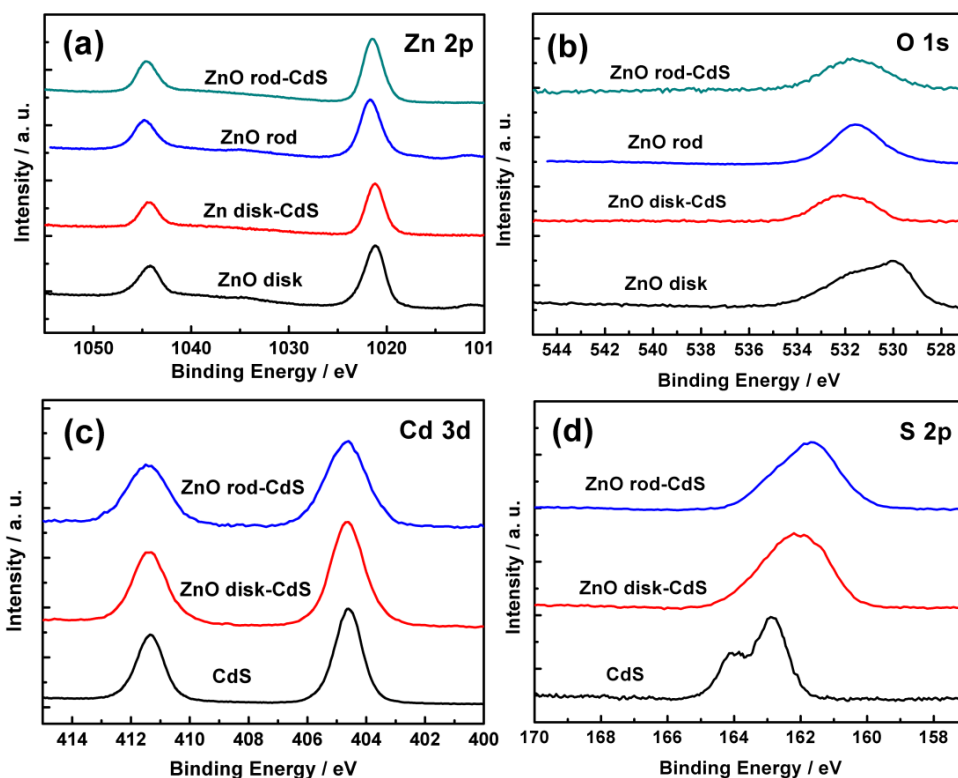


Figure S4. X-ray photoelectron spectra (XPS) of (a) Zn 2p, (b) O 1s, (c) Cd 3d and (d) S 2p in the ZnO disk-CdS NP and ZnO rod-CdS NP heterostructures compared to those in the sole ZnO disks, ZnO rods and CdS.

5 Table S1. Photocatalytic hydrogen evolution of ZnO disks with different ratio of (0001) and (000 $\bar{1}$) polar facets.

Samples	NaOH Concentration	Hydrogen Evolution*
	(mol L ⁻¹)	(μ mol h ⁻¹)
ZnO disk-a	0.2	11.7
ZnO disk-b	0.1	15.6
ZnO disk-c	0.05	16.2

*Measurement conditions: 0.1 g of sample, 300 mL of aqueous solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃, and light source of 300 W Xe lamp.

Table S2. Photocatalytic hydrogen evolution* of ZnO disk and rod loaded different amount of CdS NPs (1 wt%, 2.5 wt% and 5 wt%), respectively.

CdS loading	ZnO disk	ZnO rod
1 wt%	46	19.7
2.5 wt%	72.3	22.3
5 wt%	88.6	31.2

*Measurement conditions: 0.1 g of sample, 300 mL of aqueous solution containing 0.1 M Na₂S and 5 0.1 M Na₂SO₃, and light source of 300 W Xe lamp; Unit: $\mu\text{mol h}^{-1}$.