

Supporting information

Enhanced Photocatalytic Hydrogen Evolution by Prolonging Lifetime of Carriers in ZnO/CdS heterostructures

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Experimental sections and characterizations

Experimental sections

Sample Preparation

ZnO/CdS heterostructures were prepared by a wet chemistry method. 0.02 M NH₃·H₂O solution was dropwise added into 20 mL aqueous solution containing 20 mmol Zn(CHCOO)₂·2H₂O at room temperature. When pH value of the solution reached 7, white Zn(OH)₂ was precipitated and then washed with de-ionized water for three times. After that, 2-36 mmol CdCl₂·2.5H₂O was dissolved into 30 mL aqueous water containing all the above white Zn(OH)₂ precipitate. Afterwards, 0.2 M Na₂S solution was dropwise added into the suspension until pH=7. The final precipitate was washed for three times and dried at 60 °C for 24 h in air, resulting in ZnO/CdS heterostructure samples.

Photoanode Film Preparation

A doctor-blade technique was employed to prepare ZnO)₁/(CdS)_{0.2} heterostructure, ZnO and CdS films on indium-doped tin oxide (ITO) coated glass substrates. The slurries consisted of 0.1 g sample, 1 mL de-ionized water, 3 drops of Triton X-100 and 1 drops of acetylacetone. The slurries were deposited on the substrate by the doctor-blade method with adhesive type as the spacer and the substrates were coated twice. After each coating, the film was calcined at 380 °C for 1 h.

Co-catalyst Loading

Pt loading on the ZnO/CdS heterostructures was conducted by impregnation using an aqueous solution of H₂PtCl₆·6H₂O. A sample of ZnO/CdS heterostructure was added into aqueous solution

containing a desirable amount of $\text{HPtCl}_6 \cdot 6\text{H}_2\text{O}$ ($1 \text{ mg} \cdot \text{mL}^{-1}$ Pt) in an evaporating dish at $60 \text{ }^\circ\text{C}$. The suspension was evaporated under constant stirring with a glass rod, and the resulting powder was collected and heated in air at $180 \text{ }^\circ\text{C}$ for 1 h.

Hydrogen Evolution Tests

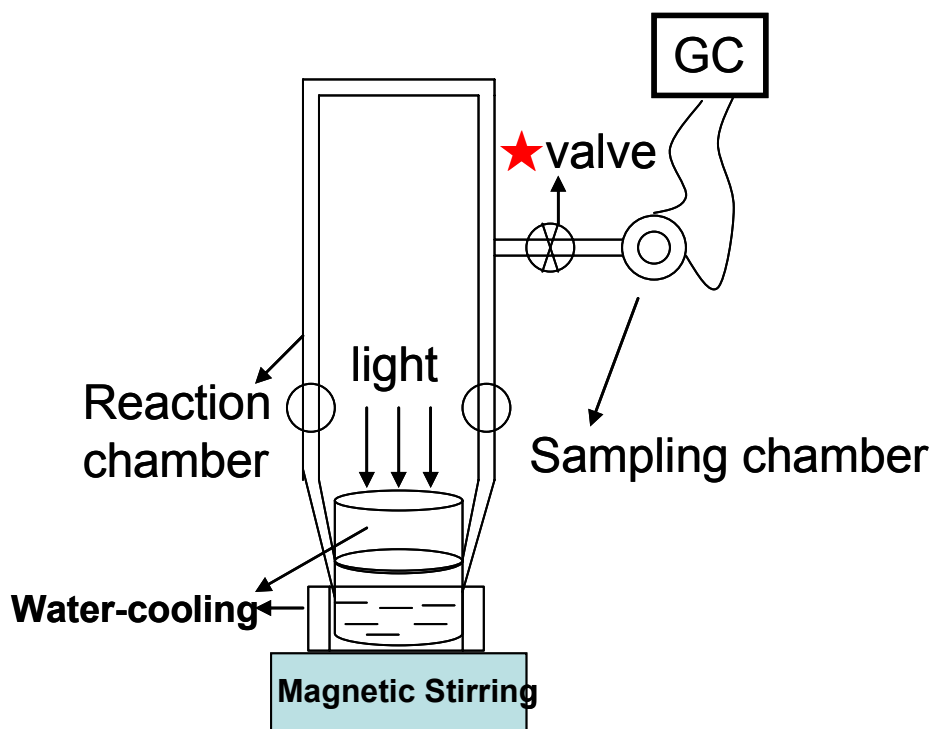
Water splitting reactions were carried out in a top-irradiation vessel connected to a closed gas circulation system made of glass. 0.2 g photocatalyst powder was dispersed in a 300 mL aqueous solution with 0.1 M Na_2S and 0.1 M Na_2SO_3 . The whole reaction process was cooled between $4 \text{ }^\circ\text{C}$ and $9 \text{ }^\circ\text{C}$. The light source was a 300 W Xe lamp. The amount of H_2 evolution was determined using a gas chromatography (Agilent Technologies: 6890N). The average apparent quantum efficiency (Φ) was estimated by the following equation.

$$\begin{aligned}\Phi(\%) &= \frac{\text{no. of reacted electrons}}{\text{no. of incident photons}} \times 100 \\ &= \frac{\text{no. of evolved H}_2 \text{ molecules} \times 2}{\text{no. of incident photons}} \times 100\end{aligned}$$

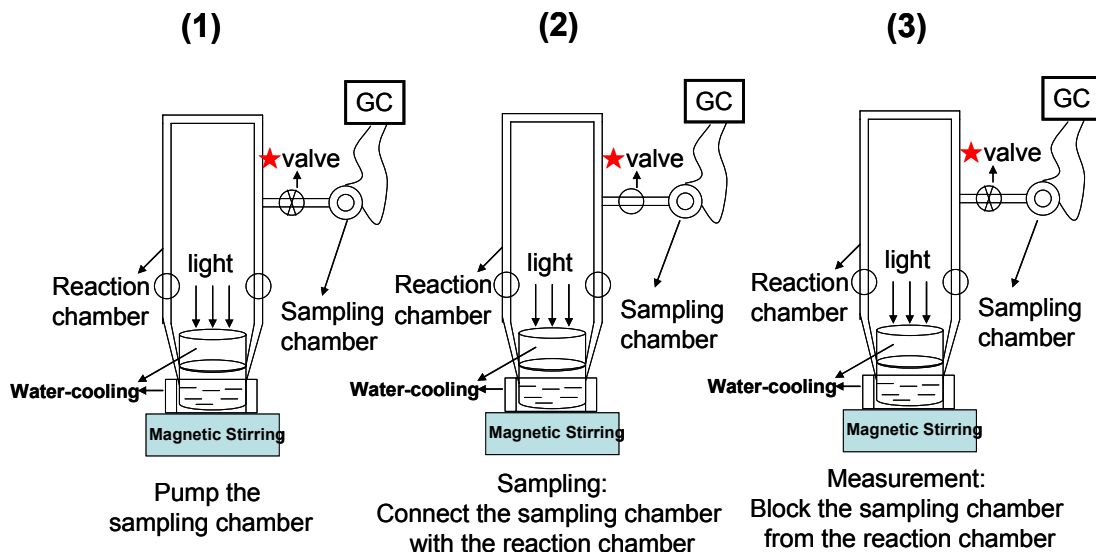
Where Φ is the apparent quantum efficiency, and it is assumed that all incident photons are absorbed by the reaction system.

The detailed process of H_2 evolution measurements is described below. To better show how to measure the amount of hydrogen, we also give the following two schemes (I. The measurement setup, and II. The process of H_2 evolution measurements). In the measurement system, 0.2 g sample was suspended in a 300 mL aqueous solution with 0.1 M Na_2S and 0.1 M Na_2SO_3 . The reaction chamber with a large volume and the sampling chamber with a small volume were separated. Prior to light irradiation, these two chambers were vacuumed to remove the air in the whole system. When the pressure of the system was lower than 20 Pa, the two sections were isolated. During reaction, the pressure in the reaction chamber increased with the H_2 evolution. For each H_2 evolution measurement, the sampling chamber was vacuumed to the pressure of 20 Pa, and then opened to the reaction chamber until the pressure equilibrium between two sections was established. The sampling chamber was blocked from the reaction chamber and the hydrogen gas in the sampling chamber was sent to a gas chromatography (GC) with argon as a carrier gas to determine the amount of hydrogen. The standard calibration curve used for determining the amount of hydrogen with GC was measured by injecting a series of different amounts of hydrogen gas into the GC.

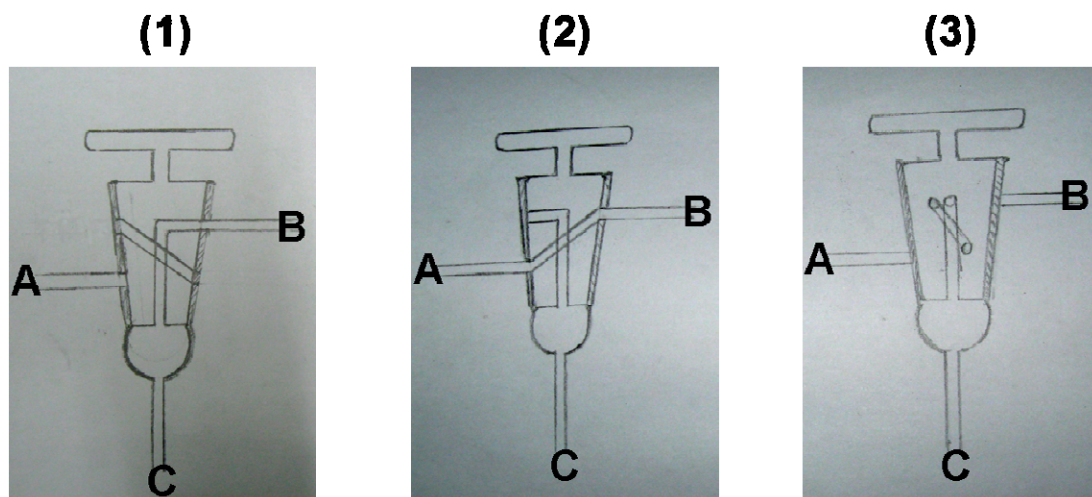
I .The measurement setup of H₂ evolution



II. The process of H₂ evolution measurements



★: The inner structure of the valve at different stages



A: To the reaction chamber
B: To the sampling chamber
C: To the pumping system

Characterization

X-ray diffraction patterns of the samples were recorded on Rigaku diffractometer using Cu irradiation ($\lambda = 1.54056 \text{ \AA}$). UV-visible spectrophotometer was used to collect the UV-visible absorption spectra (JACSO-550). Transmission electron microscopy (TEM) performed on Tecnai F30. Chemical compositions and states of the ZnO/CdS heterostructures were analyzed using X-ray photoelectron spectroscopy (XPS) (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 (The range of measured spectrum: 200 nm~1700 nm; the highest wavelength resolution: 0.1 nm; the measured lifetime of fluorescence signal: 100 ps~100 μ s) was employed to monitor the emission decay of photoexcited carriers. The instrument works on the principle of the time correlated single photon counting (TCSPC) technique. The powder samples of the $(\text{ZnO})_1/(\text{CdS})_{0.2}$ heterostructure, ZnO and CdS in a quartz cell were excited by the laser of 340 nm, and their fluorescence emission decay spectra was monitored at 575 nm by time-correlated single photon counting. The emission decay spectrum acquisition was not stopped until the counting number of fluorescence signal reached 5000. The size of the quartz cell used was 1 mm in depth and 8 mm in diameter. All the measurements were conducted at room temperature in air.

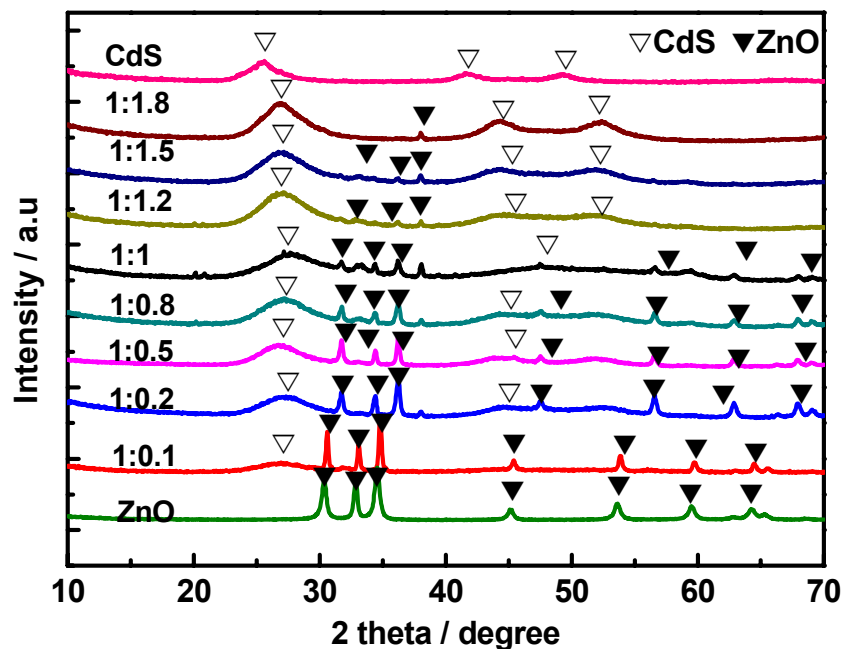


Figure S1. XRD patterns of the $(\text{ZnO})_x/(\text{CdS})_y$ heterostructures, where x and y denote the molar ratios of Zn and Cd precursors.

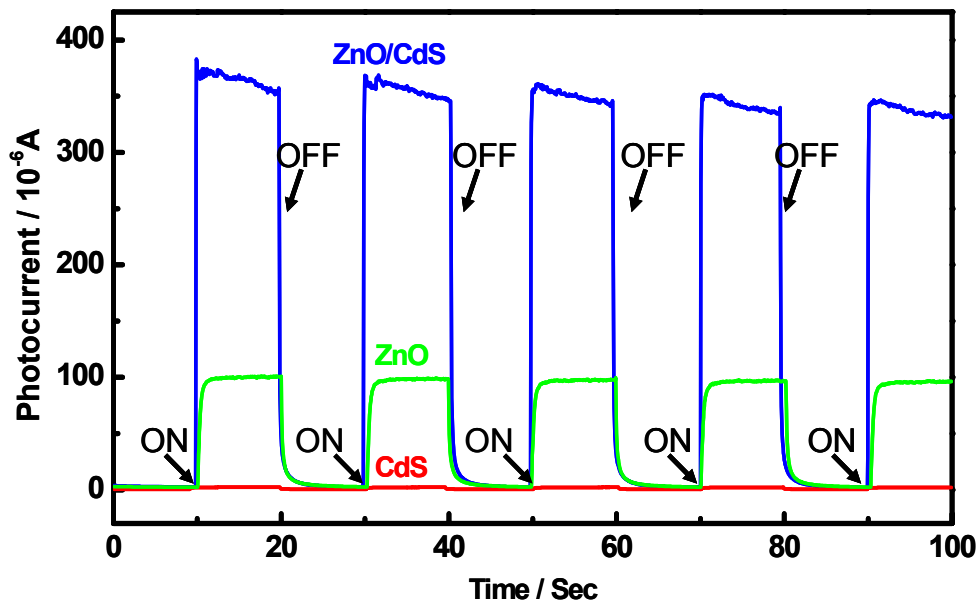


Figure S2. Photocurrent response to light-on and light-off of the photoanodes prepared from ZnO, CdS and $(\text{ZnO})_1/(\text{CdS})_{0.2}$ on ITO substrate versus Hg/HgCl reference electrode at 0.4 V under simulated solar irradiation. The thickness of photoactive films was around 10 μm . Measurement conditions: 0.1 M NaOH electrolyte, scanning rate of $5 \text{ mV}\cdot\text{s}^{-1}$. The illuminated photoanode surface area was 1 cm^2 . Light source: 300 W Xe lamp.

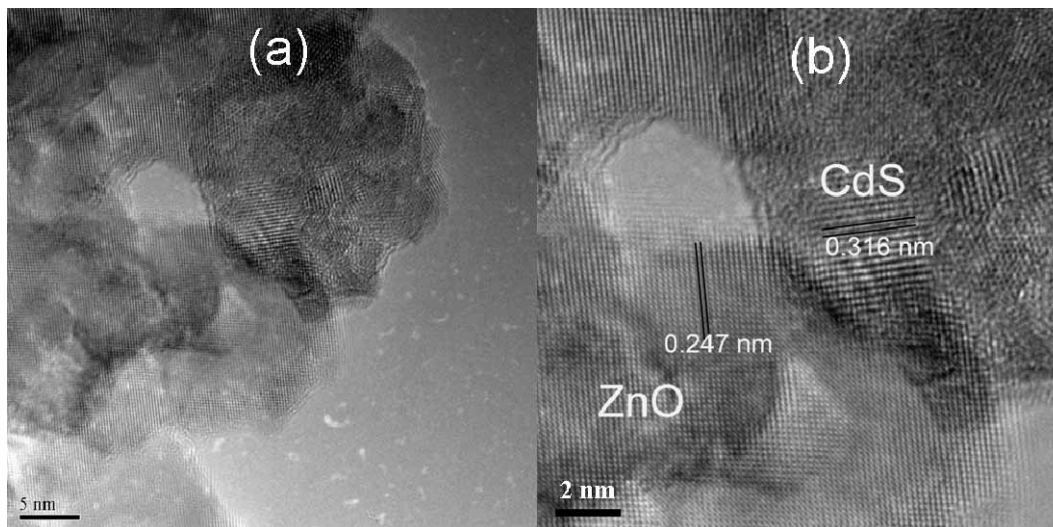


Figure S3. Typical TEM (a) and high resolution TEM (b) images of $(\text{ZnO})_1/(\text{CdS})_{0.2}$ heterostructure.

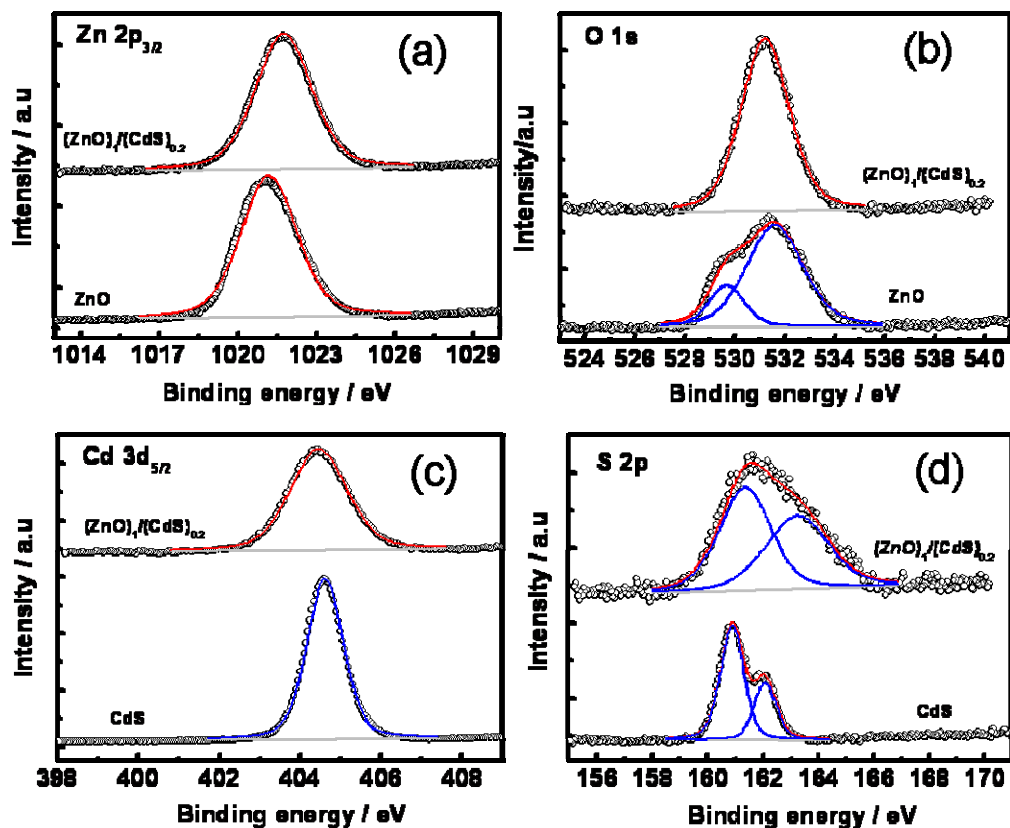


Figure S4. XPS spectra of Zn $2p_{3/2}$ (a), O $1s$ (b), Cd $3d_{5/2}$ (c) and S $2p$ (d) in $(\text{ZnO})_1/(\text{CdS})_{0.2}$ heterostructure, ZnO and CdS.

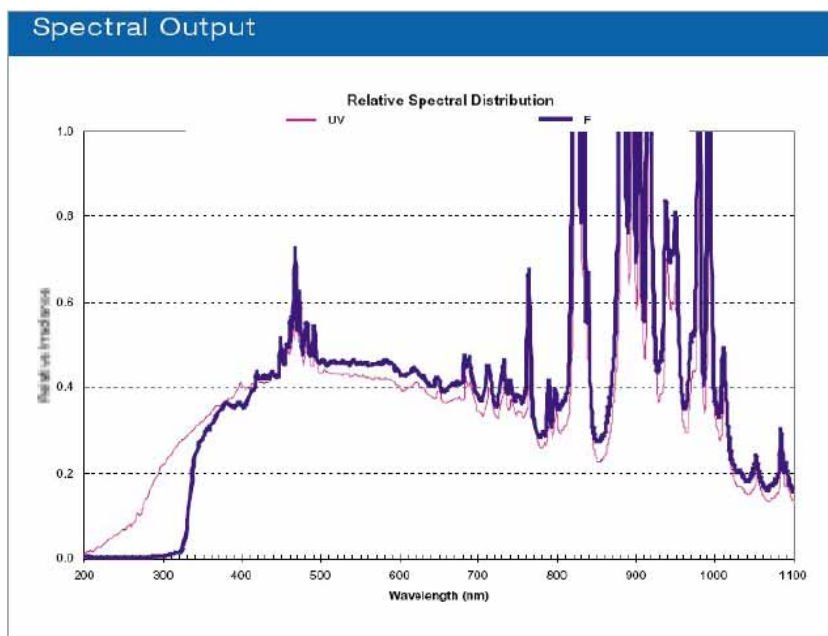


Figure S5. The emission spectrum (dark blue one) of the Xe lamp employed in the hydrogen evolution measurement.