Electronic Supplementary Information (ESI)

Self-assembled CdS/Au/ZnO heterostructure induced by surface polar charges for efficient photocatalytic hydrogen evolution

Sample synthesis. *Preparation of flower-like ZnO crystals by hydrothermal process*. 0.55 g Zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$) powder was added in 60 mL aqueous solution containing 0.74 g trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) and 0.36 g sodium hydroxide (NaOH). The suspension was then transferred to a Teflon-lined autoclave, and treated at 200 ^oC for 4 h. After reaction, the ZnO product was collected by centrifugation and washed with de-ionized water several times to remove dissolvable ionic impurities. The sample was finally dried at 80 ^oC in air.

Preparation of Au/ZnO by photodeposition. 300 mg ZnO powder was suspended in 30 mL water/methanol solution (2/1 in volume) containing targeted auric trichloride ($AuCl_3 \cdot HCl \cdot 4H_2O$, 1 wt% Au *vs*. ZnO). The suspension was stirred for 24 h in dark to achieve the preferential adsorption of Au based complex ions on $(000\bar{1})$ facets of ZnO, and then exposed to ultraviolet light (450 W high-pressure Hg lamp) for 6 h to reduce Au based complex ions to Au nanoparticles. After the photodeposition, the dark purple Au/ZnO product was collected by centrifugation and washed with de-ionized water several times to remove dissolvable ionic impurities. The sample was dried at 80 ^oC in air.

Preparation of CdS/ZnO or CdS/Au/ZnO by chemical bath deposition. 200 mg of ZnO or Au/ZnO sample was added in 20 mL water containing 74 mg cadmium acetate dihydrate ($Cd(CH_3CO_2)_2 \cdot 2H_2O$), which was stirred for 0.5 h in dark to achieve the preferential adsorption of Cd based complex ions on $(000\bar{1})$ facets of ZnO. 40 mg thiourea (CH_4N_2S) was then added to the suspension. After the chemical bath depostion at 80 ^oC for 0.5 h, the CdS/ZnO (or CdS/Au/ZnO) product was collected by centrifugation and washed with de-ionized water several times to remove dissolvable

ionic impurities. The sample was dried at 80 ^{o}C in air. In addition, the pure CdS can be obtained through the similar chemical bath process without introducing ZnO.

Preparation of Au/CdS/ZnO by photodeposition. 300 mg of CdS/ZnO powder was suspended in 30 mL water/methanol solution (2/1 in volume) containing targeted auric trichloride ($AuCl_3 \cdot HCl \cdot 4H_2O$, 1 wt% Au *vs*. ZnO). The suspension was stirred for 1 h and then exposed to ultraviolet light for 6 h. After the photodeposition, the Au/CdS/ZnO product was collected by centrifugation and washed with de-ionized water several times to remove dissolvable ionic impurities. The sample was dried at 80 ^{o}C in air.

Characterization. X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu Kα irradiation. Their morphology was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) performed on Nova NanoSEM 430 (equipped with an X-ray energy dispersive spectrometer (EDS)) and JEOL2010 electron microscopes. The chemical compositions of CdS/Au/ZnO were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al Kα X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. Fluorescence emission spectra were recorded at room temperature by excitation wavelength of 270 nm with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920).

Photoreactivity measurements. Photocatalytic hydrogen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. 100 mg of the photocatalyst powder was dispersed in 270 mL aqueous solution with0.1 M Na_2SO_3 and 0.1 M Na_2S as sacrificial agent. The reaction temperature was maintained around 10 ^{o}C. The amount of H_2 evolved was determined by using a Shimadzu gas chromatography system (GC-2014).The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV).

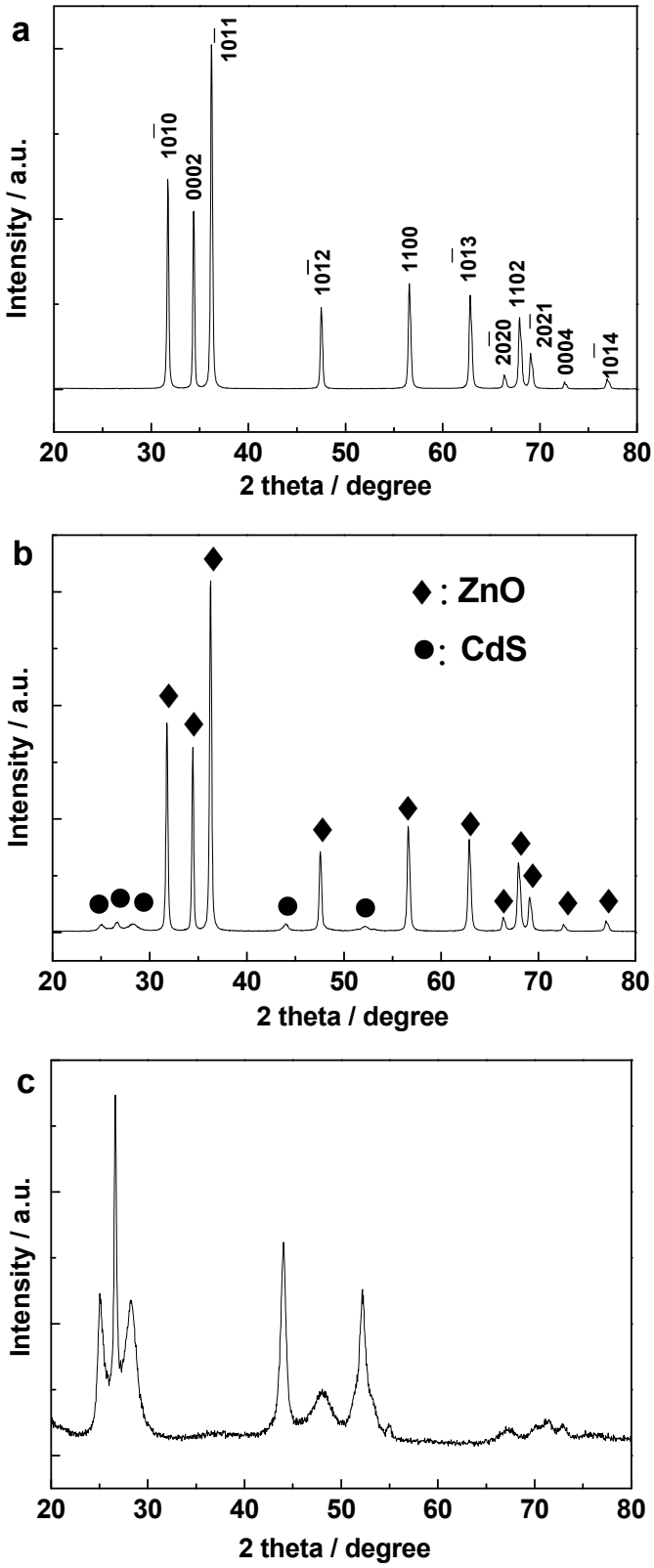

Fig. S1 XRD patterns of (a) ZnO (Hexagonal phase, JCPDS Card No. 65-3411), (b) CdS/ZnO and (c) CdS (Hexagonal phase, JCPDS Card No. 41-1049).

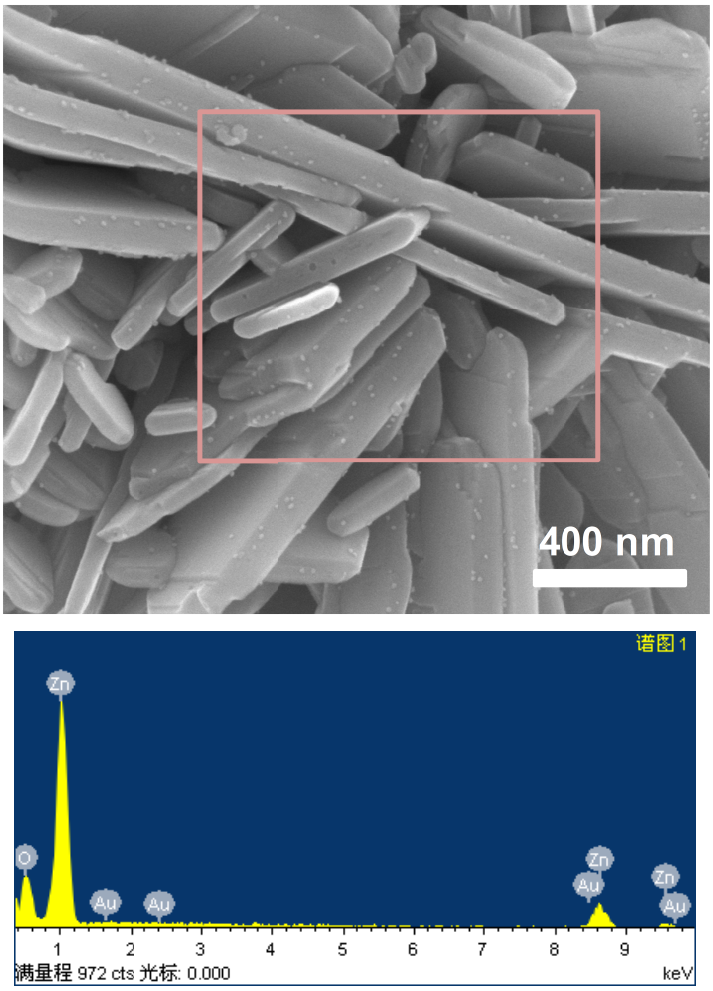

Fig. S2 SEM image of Au/ZnO and the EDS image recorded from the region marked by the square in the top SEM image.

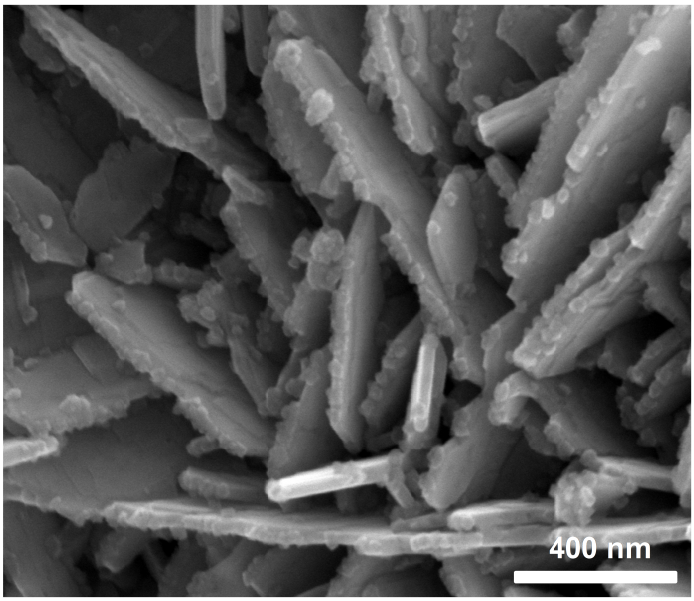

Fig.S3 SEM image of CdS/ZnO.

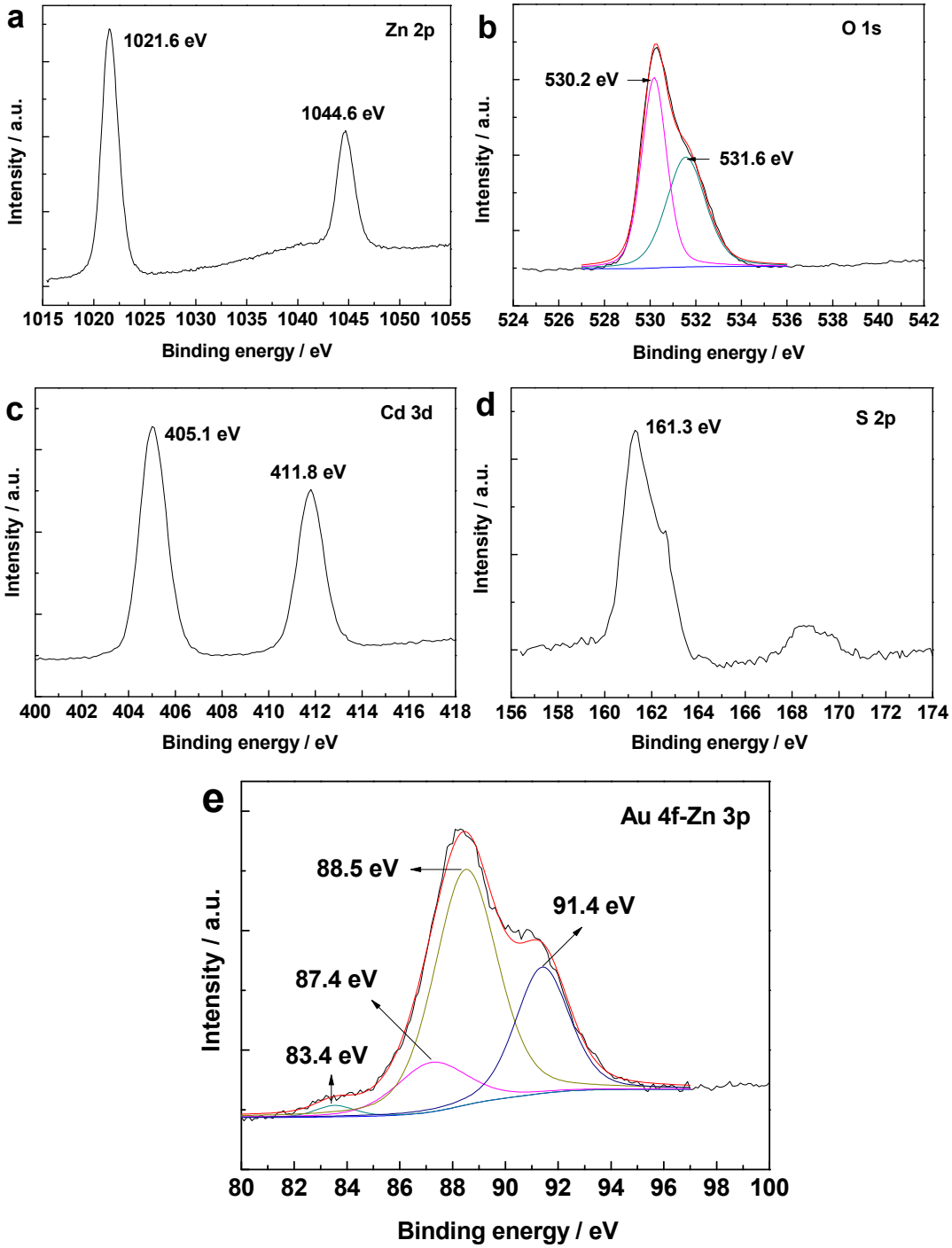

Fig. S4 XPS spectra of (a) Zn 2p, (b) O 1s, (c) Cd 3d, (d) S 2p and (e) Au 4f-Zn 3p (Binding energy: Au $4f_{7/2}$ and Au $4f_{5/2}$, 83.4 eV and 87.4 eV; Zn $3p_{3/2}$ and Zn $3p_{1/2}$, 88.5 eV and 91.4 eV) in CdS/Au/ZnO.

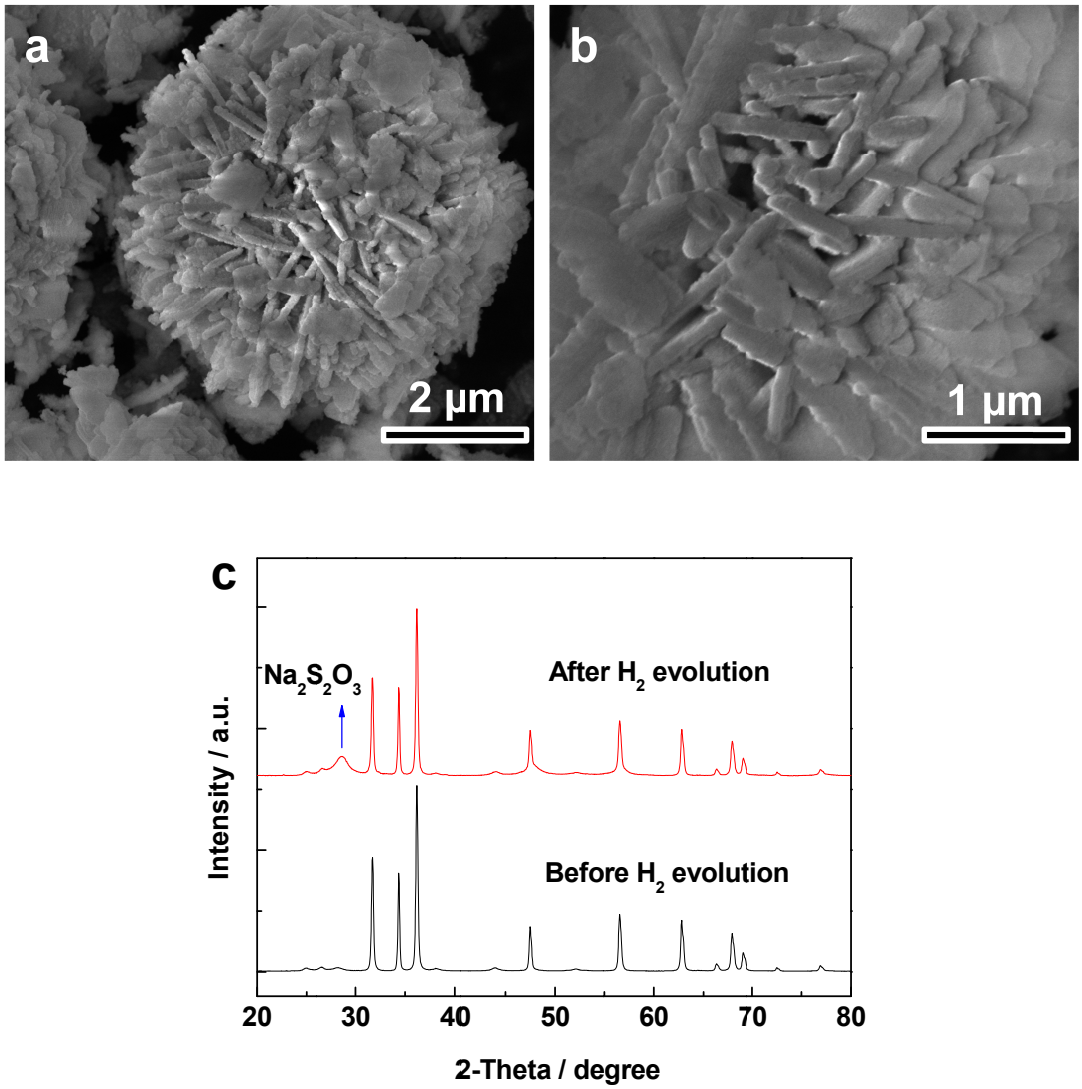

Fig. S5 a) and b), SEM images of CdS/Au/ZnO collected after photocatalytic reactions; c) XRD patterns of CdS/Au/ZnO before and after photocatalytic reactions.