Sample synthesis. Preparation of flower-like ZnO crystals by hydrothermal process. 0.55 g Zinc acetate dihydrate (Zn(CH3CO2)2·2H2O) powder was added in 60 mL aqueous solution containing 0.74 g trisodium citrate dihydrate (Na3C6H5O7·2H2O) and 0.36 g sodium hydroxide (NaOH). The suspension was then transferred to a Teflon-lined autoclave, and treated at 200 °C 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 °C 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 (AuCl3·HCl·4H2O, 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 (0001) 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 °C 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(CH3CO2)2·2H2O), which was stirred for 0.5 h in dark to achieve the preferential adsorption of Cd based complex ions on (0001) facets of ZnO. 40 mg thiourea (CH4N2S) was then added to the suspension. After the chemical bath deposition at 80 °C 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 °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 (AuCl₃·HCl·4H₂O, 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 °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 with 0.1 M Na₂SO₃ and 0.1 M Na₂S as sacrificial agent. The reaction temperature was maintained around 10 °C. The amount of H₂ 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.