

**Work Function Engineering Derived All-solid-state Z-scheme
Semiconductor-Metal-Semiconductor System towards High-efficiency
Photocatalytic H₂ Evolution**

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Supporting Information

Chemicals

ethanol (99.8+%, Sinoreagent), acetone (99.5+%, Sinoreagent), chloroauric acid tetrahydrate ($\text{Au} \geq 47.8$, Sinoreagent), chloroplatinic acid hexahydrate (ACS, $\text{Pt} \geq 37.5\%$, Sinoreagent), tungsten trioxide (99.8+%, Aladdin), cadmium sulfide (98+%, Aladdin), PEG 20000 (Tianjin tiantai chemical), sodium tungstate dehydrate (99.5+%, Aladdin), Sodium chloride (99.5+%, Sinoreagent), hydrochloric acid (36+%, Beijing chemical works), sodium borohydride (98+%, Sinoreagent), cadmium nitrate tetrahydrate (99+%, Aladdin), sodium sulfide nonahydrate (98+%, Sinoreagent)

Experimental section

Fabrication of Au and Pt films: FTO glass were cut into 1×2 cm pieces and ultrasonically degreased in distilled water, ethanol and acetone in turn for 5 min, and then dried in a nitrogen flow. FTO/Au or FTO/Pt films were prepared by a cyclic voltammetry methods in a solution of 20 mM chloroauric acid or chloroplatinic acid aqueous solution from - 0.7 V to 0.2 V vs. Ag/AgCl (3M) reference for 30 segments with a scan rate of 0.05V/s. The obtained FTO/Au or FTO/Pt films were washed with ethanol and then dried in a nitrogen flow. The light transmittance of the metal films are about 20%.

Fabrication of CdS and WO_3 films: The commercial WO_3 or CdS power were thoroughly mixed with PEG 20000 as a binder material and then cast on FTO glass. The film was dried at room temperature and calcined in air at 380 °C for 2 h to remove the binder.

Fabrication of FTO/metal/semiconductor films: The commercial WO_3 or CdS power were thoroughly mixed with PEG 20000 and cast on FTO/Au or FTO/Pt films.

Fabrication of Au/CdS and Pt/CdS photocatalyst: 0.3 g CdS were dispersed into 30 ml deionized water and 2.4 ml 18 mM HAuCl_4 or H_2PtCl_6 aqueous solution were added into the solution. Finally, 4 ml 165 mM NaBH_4 aqueous solution was slowly added into the mixture under strong stirring. The product was filtered and washed several times with deionized water and absolute ethanol and dried at 50 °C for 10 h.

Fabrication of CdS/Au/WO₃ and CdS/Pt/WO₃ photocatalyst: WO₃ nanorods were synthesized by a hydrothermal method. Typically, 1 g of Na₂WO₄·2H₂O and 0.2 g of NaCl were added in 30 mL of deionized water and then stirred for 6 h. The pH values of the solution were adjusted to around 2 with concentrated hydrochloric acid and stirred for another 3 h. Then, the solution was transferred into a 50 mL Teflon-lined autoclave. The autoclave was maintained at 180 °C and 24 h. The product was filtered and washed several times with deionized water and absolute ethanol and dried at 50 °C for 10h.

The Au/WO₃ and Pt/WO₃ were prepared by a NaBH₄ reduction method. 0.3 g WO₃ nanorods were dispersed into 30 ml deionized water and 2.4ml 18 mM HAuCl₄ or H₂PtCl₆ aqueous solution were added into the solution. Finally, 4 ml 165 mM NaBH₄ aqueous solution was slowly added into the mixture under strong stirring. The product was filtered and washed several times with deionized water and absolute ethanol and dried at 50 °C for 10 h.

The CdS/Au/WO₃ or CdS/Pt/WO₃ were prepared by an uncomplicated precipitation method. 0.2 g of Au/WO₃ or Pt/WO₃ was scattered into 20 mL of deionized water. Subsequently, 85 mg Cd(NO₃)₂·5H₂O was put in the above solution, and then 2 ml 165 mM Na₂S aqueous solution was added dropwise. After stirring 1 h, the precipitation was washed several times with deionized water, absolute ethanol and dried at 50 °C for 10 h.

Structural characterizations

A Quanta 400 FEG field-emission scanning electron micro-scope (FESEM; FEI Company) was used to characterize the morphologies of the samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were carried out on a transmission electron microscope (TECNAIG2, FEI company) working at 200 kV. The crystal structure of the as-prepared samples were characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 X-ray diffractometer with Cu–K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 50 kV and 200 mA in the 2θ range of 20–80° with a scanning rate of 5° min⁻¹. The optical absorption spectra of the samples were measured using a UV-vis-NIR spectrophotometer (Shimadzu UV-3600) to detect absorption over the range of 300–700 nm.

The work function measurement was carried out on a Kelvin Probe instrument (SKP 5050, KP Technology Ltd, Scotland, UK). The lock-in amplifier-based surface photovoltage (SPV) spectroscopy measurement system is constituted of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell, and a computer. Monochromatic light was provided by passing light from a 500 W xenon lamp (CHF-XM-500 W, Global Xenon Lamp Power) through a grating monochromator (Omni-5007, Zolix). A low chopping frequency of 23 Hz was used in the conventional testing. The SPV transient measurement was carried out on a home-made system. The samples were excited with a laser radiation pulse (wavelength of 355/532 nm and pulse width of 5 ns) from a third-harmonic Nd:YAG laser (Polaris II, New Wave Research, Inc.). The SPV transient signal was recorded by a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix). The SPV and SPV transient measurements were finished in air atmosphere at room temperature.

Photocatalytic H₂ evolution

The photocatalytic H₂ evolution reactions were examined in a quartz cell which is connected to an airtight gas circulation system. Typically, 50 mg photocatalyst was added into 100 ml mixed solution contain 5 mL lactic acid and 95 ml deionized water and dispersed by sonication treatment for 5 min. The reaction system was evacuated to vacuum before light irradiation and then irradiated with a 300 W xenon lamp. The amount of H₂ was obtained with an online gas chromatography (GC-2014C TCD, Shimadzu, Japan, with nitrogen as a carrier gas and 5 Å molecular sieve column).

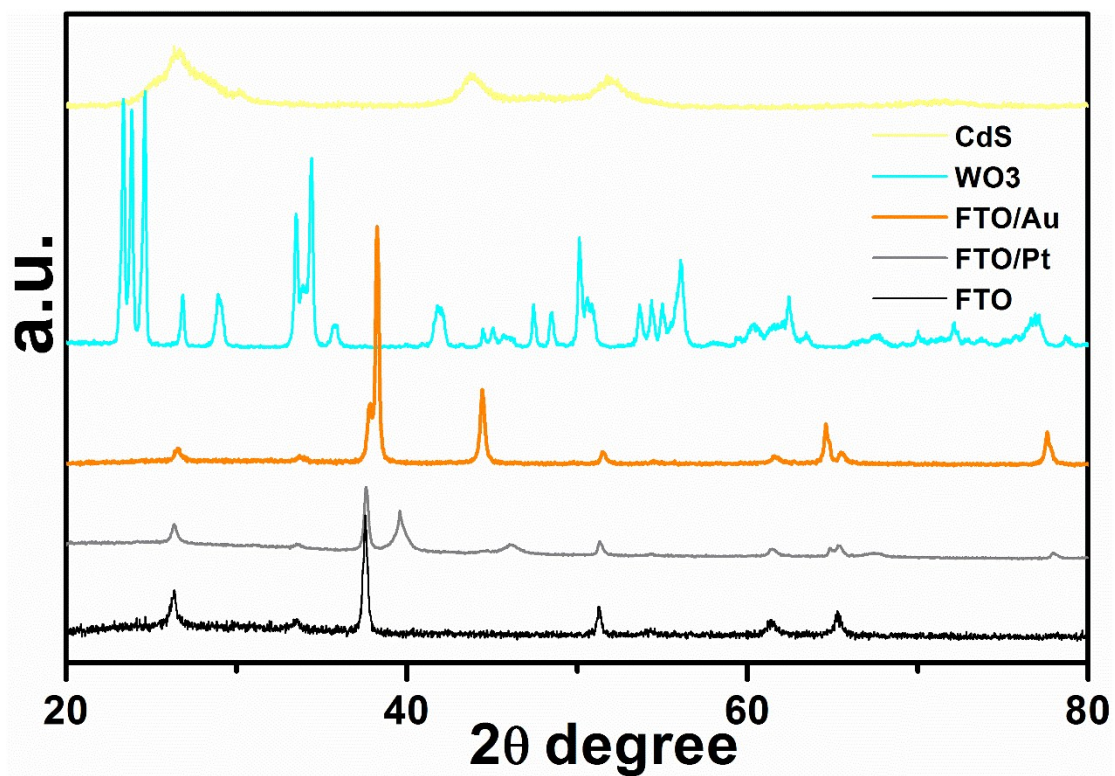


Figure S1. XRD patterns of the Au, Pt, CdS and WO₃ films.

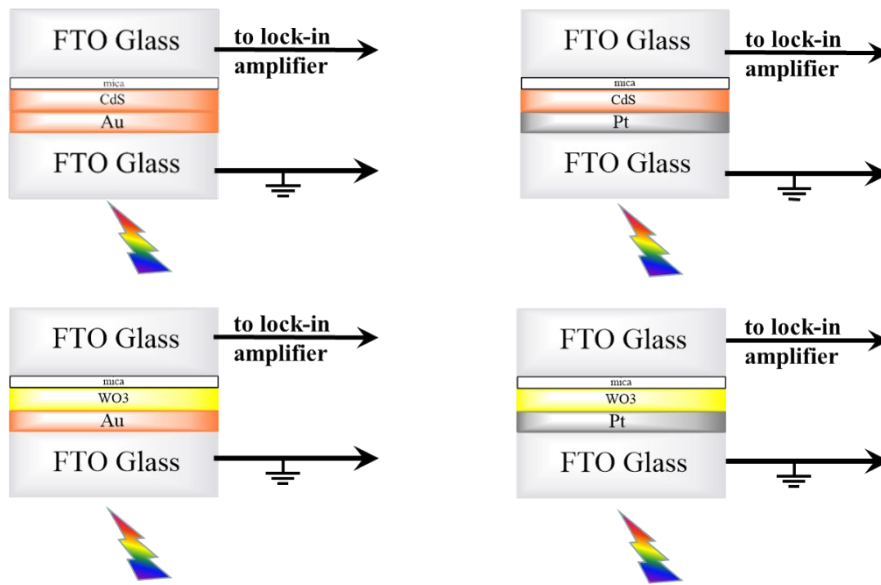


Figure S2. SPV measurement configurations of FTO/Au/CdS, FTO/Au/WO₃, FTO/Pt/CdS, FTO/Pt/WO₃ films.

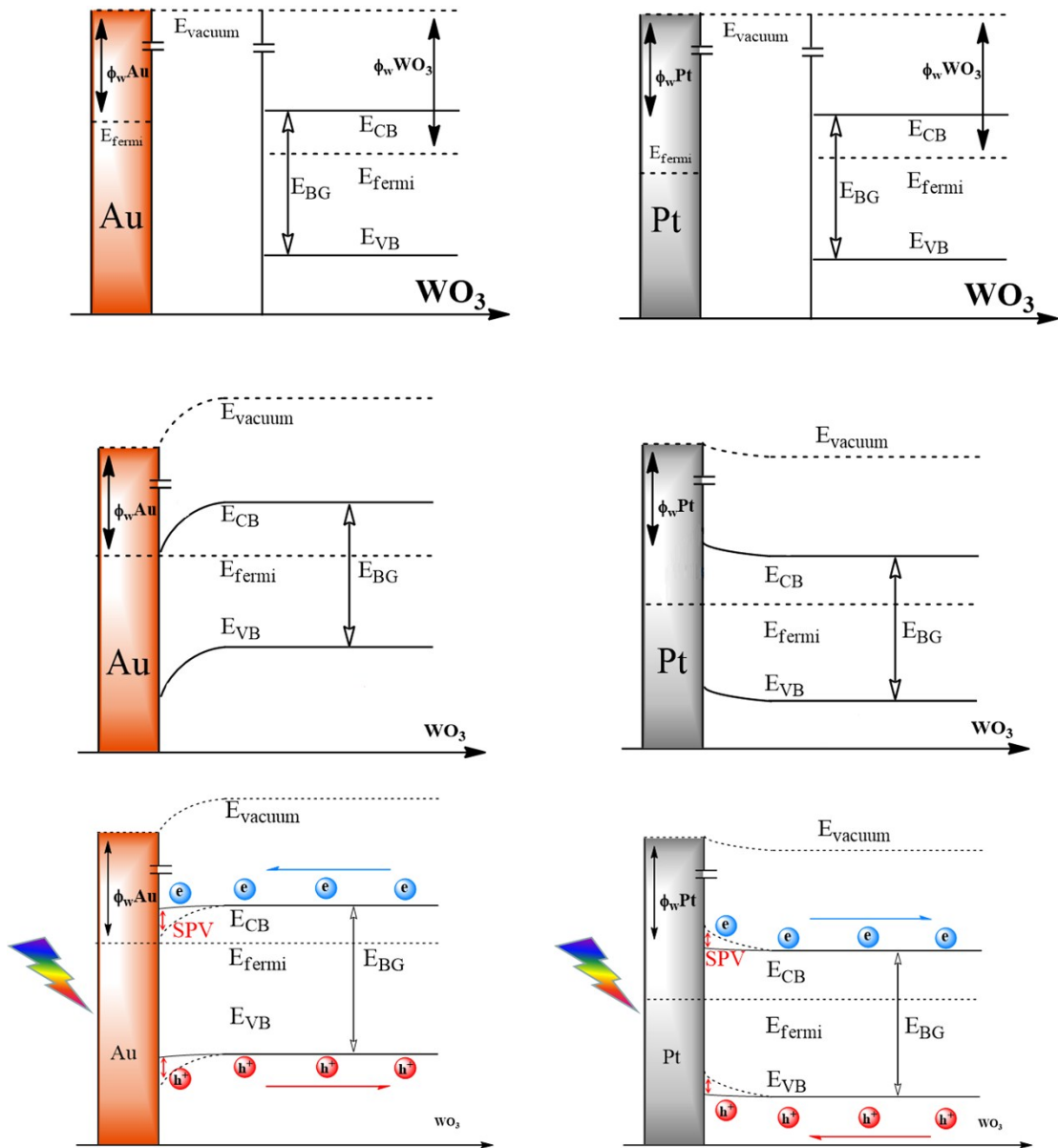


Figure S3. Energy band diagrams of metal Au, Pt and semiconductor WO₃ before contacts, in contacts under equilibrium and in contacts under irradiation according to the data of work function mapping, respectively.

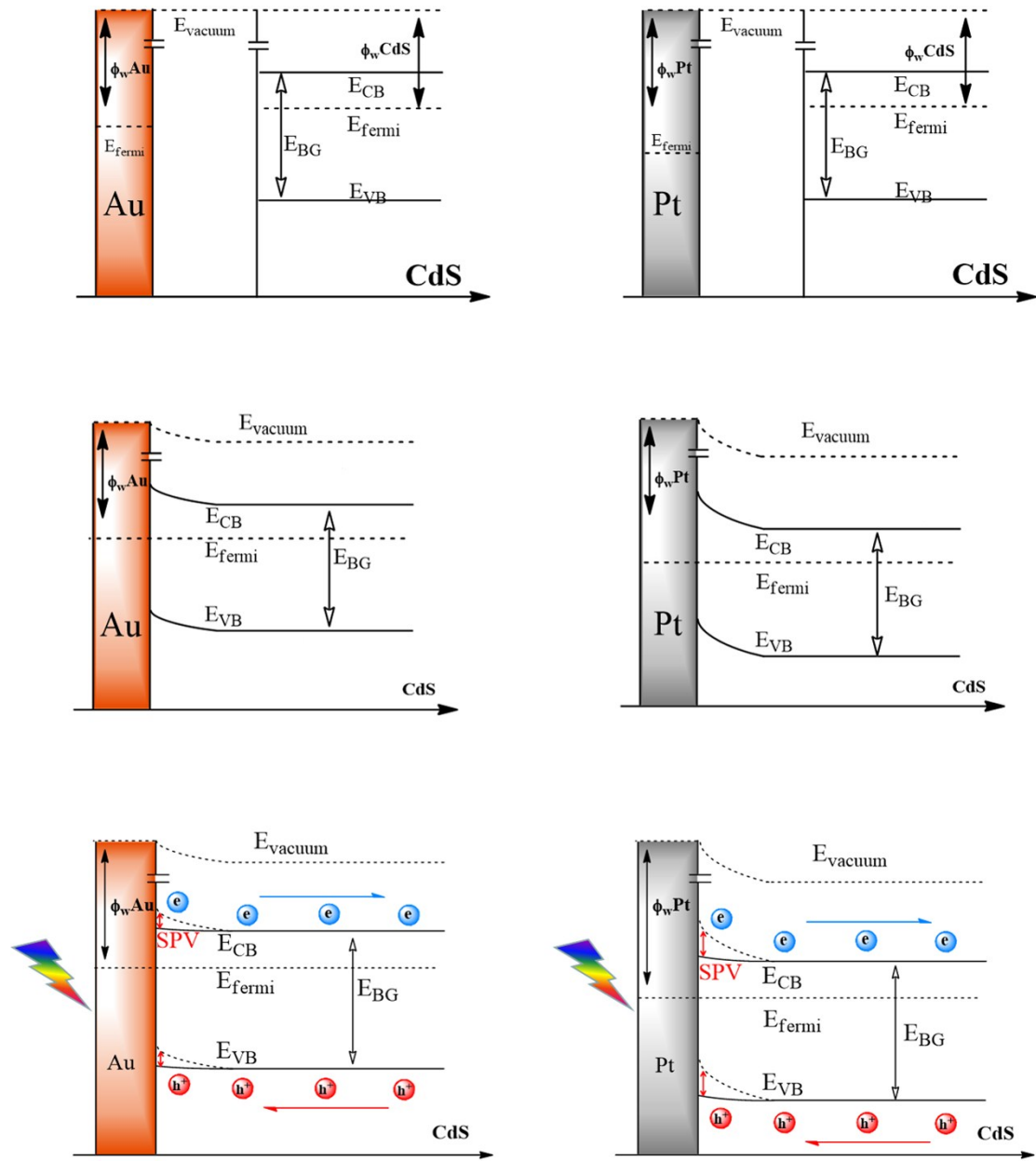


Figure S4. Energy band diagrams of metal Au, Pt and CdS semiconductor before contacts, in contacts under equilibrium and in contacts under irradiation according to the data of work function mapping, respectively.

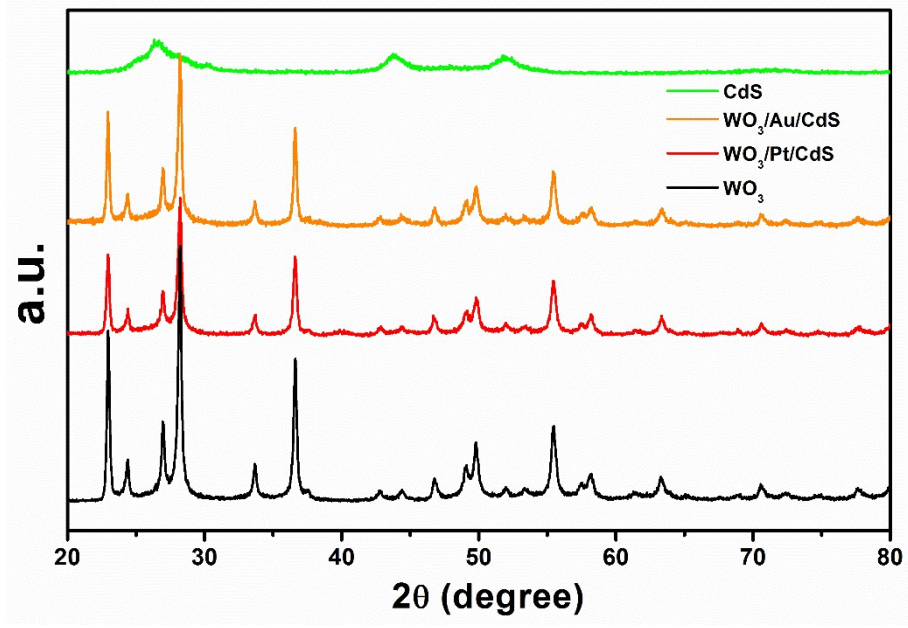


Figure S5. XRD patterns of CdS, WO₃, WO₃/Au/CdS and WO₃/Pt/CdS powder samples.

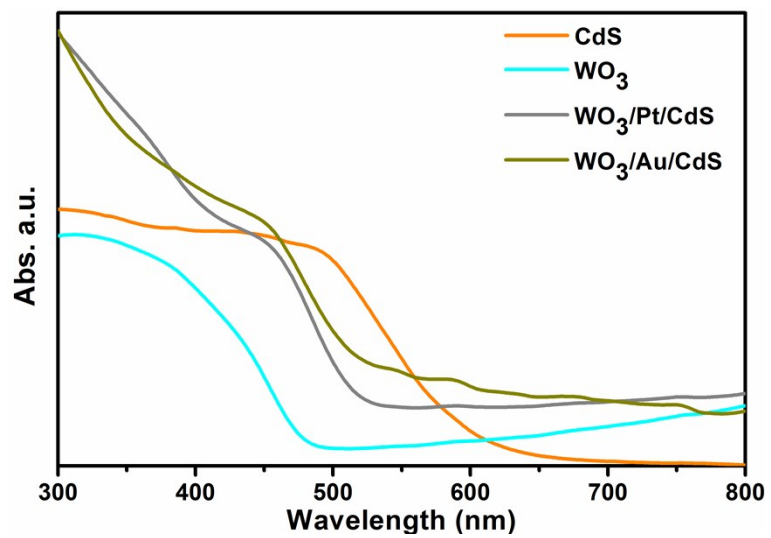


Figure S6. UV–visible diffuse reflectance spectra of CdS, WO₃, WO₃/Au/CdS, and WO₃/Pt/CdS powder samples.

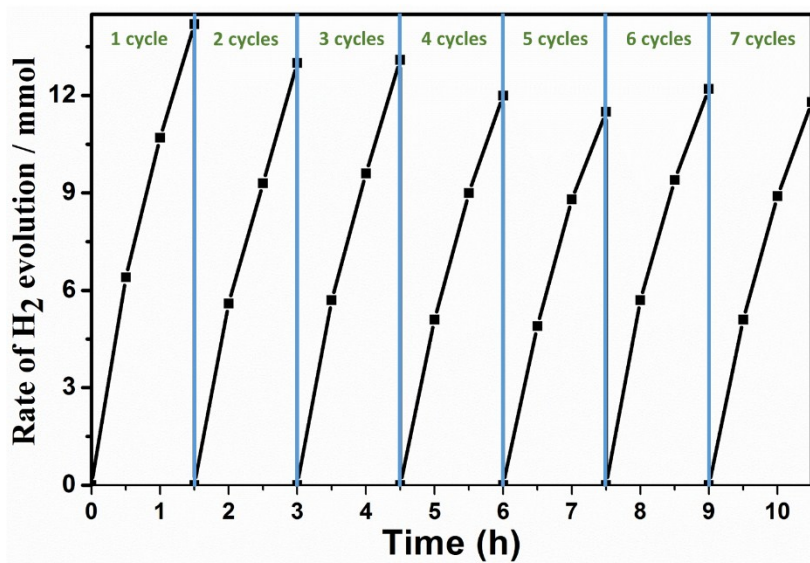


Figure S7. The time course of photocatalytic H₂ evolution over WO₃/Au/CdS sample.