# Electronic Supplementary Information

## Enhanced photocatalytic $H_2$ evolution on CdS with cobalt polyoxotungstosilic and $MoS_2$/graphene as noble-metal-free dual co-catalysts

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### Experimental details

**Synthesis of $SiW_{11}Co/MoS_2$/graphene-CdS photocatalyst.** The composite samples were synthesized by a hydrothermal method. CdS was synthesized according to the literature method[1] except being kept at 60 ºC for 12 h. Graphene oxide (GO) was synthesized from natural graphite powder (>99.8%, Alfa Aesar) by a modified Hummers, method[2]. Layered $MoS_2$/graphene was synthesized according to the literature method[3]. $SiW_{11}O_{39}Co(II)(H2O)^{6-}$($SiW_{11}Co$) was synthesized according to the literature method[4]. In a typical synthesis of $SiW_{11}Co/MoS_2$/graphene-CdS ($SiW_{11}Co$/M/G-CdS) photocatalyst, 0.2g of CdS , 0.1g $MoS_2$/graphene and a certain amount of $SiW_{11}Co$ were dispersed in 30mL of deionized water and 10ml ethanol. After ultrasonication for 1 h, the mixture was transferred into a 50 mL Teflon-lined autoclave followed by hydrothermal treatment at 160 ºC 6 h. The dark green solids were collected by filtrated and washed with deionized water for several times, followed by drying overnight at 80 ºC. Similarly, a series of the $SiW_{11}Co$/M/G-CdS composites was prepared by changing the ratio of $SiW_{11}Co$, $MoS_2$ and graphene in co-catalyst under the same conditions but replacing 95M-5.0G with (100-x)M-xG or GO. Moreover, in order to further investigate the effect of the content of the $MoS_2$/graphene (95M-5.0G) co-catalyst on the photocatalytic hydrogen activity of CdS, the mass ratio of 95M-5.0G/CdS was changed from 0% to 10.0% (0, 1.0, 5.0 and

10.0wt%) by varying the amount of 95M-5.0G. $SiW_{11}Co$ was changed from 0% to 2.0% (0, 0.5, 1.0, 1.5, and 2.0 wt%).

**Photocatalytic testing.** In a typical photocatalytic experiment, 0.1 g photocatalyst was well suspended with constant stirring in a 160 mL of aqueous solution containing 30 vol% of lactic acid (85-90% aqueous solution, Alfa Aesar). Prior to irradiation, the suspension of the catalyst was bubbled with nitrogen through the reactor for 30 min to completely remove the dissolved oxygen and to assure anaerobic conditions. After thoroughly degassed, the suspension was irradiated by a 300 W Xe lamp (25 cm far away from the photocatalytic reactor) which is equipped with an optical filter ($\lambda > 400$ nm) to cut off the light in the ultraviolet region. The temperature of the reaction solution was maintained at 20 ºC by a flow of cooling water.

**Characterization**

Elemental analyses were determined by a Leaman inductively coupled plasma (ICP) spectrometer. Powder X-ray diffraction (XRD) measurements were recorded ranging from 5 to 80° at room temperature on a Siemens D5005 diffractometer with Cu-Kα ( $\lambda$ = 1.5418 Å) radiation. The ultraviolet-visible diffuse reflectance spectra were obtained using a CARY 500 scan UV-vis-NIR spectrophotometer. Morphology and composition analyses were carried out on a FEI quanta 250 field emission scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analysis accessory. Transmission electron microscopy (TEM) images were obtained on a JEM-2100F microscope with an accelerating voltage of 200 kV. The hydrogen evolved was analyzed with a gas chromatograph (Agilent 6890GC, thermal conductivity detector, Ar carrier). Photocurrents were measured using a CHI660C electrochemical analyzer with a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 1.0 $cm^2$, a Pt foil as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode and 0.1 M $Na_2SO_4$ electrolyte.

**References:**

[1] H. J. Yan, J. H. Yang, G. J. Ma, G. P. Wu, X. Zong, Z. B. Lei, J. Y. Shi and C. Li, *J. Catal.*, 2009, **266**, 165.

[2] L. J. Cote, F. Kim and J. X. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 1043.

[3] Q. J. Xiang, J. G. Yu and M. Jaroniec, *J. Am. Chem. Soc.*, 2012, **134**, 6575.

[4] J. L. Samonte and M. T. Pope, *Can. J. Chem.*, 2001, **79**, 802.

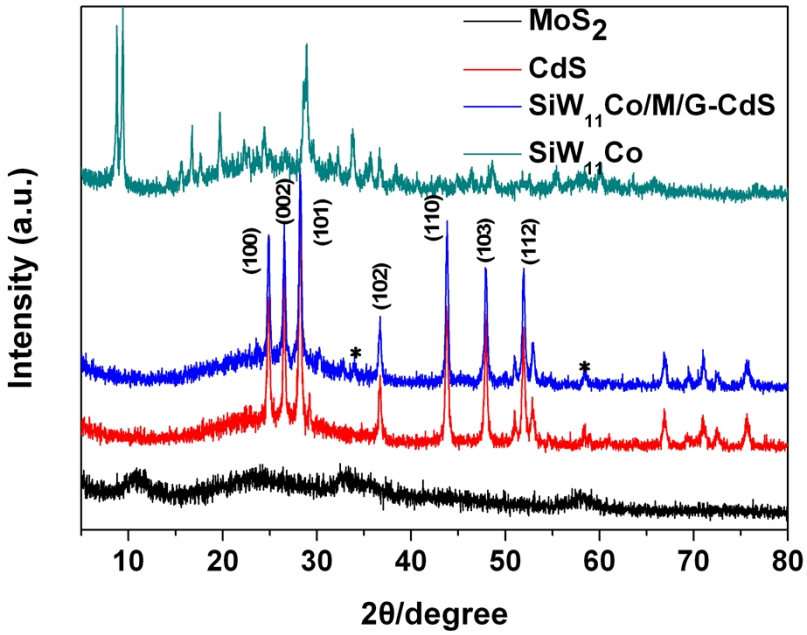


**Fig. S1** The XRD patterns of $MoS_2$, CdS, $SiW_{11}Co$/M/G-CdS and $SiW_{11}Co$. The star-labeled peaks correspond to the (100) and (110) planes of $MoS_2$.

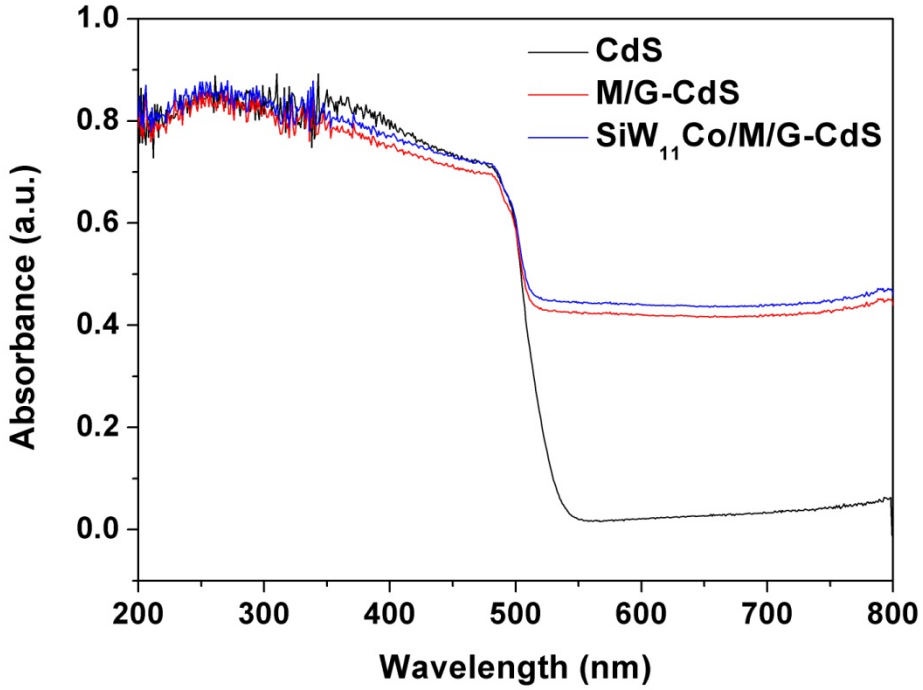


**Fig. S2** UV-vis diffuse reflectance spectra of CdS，M/G-CdS and $SiW_{11}Co$/M/G-CdS.

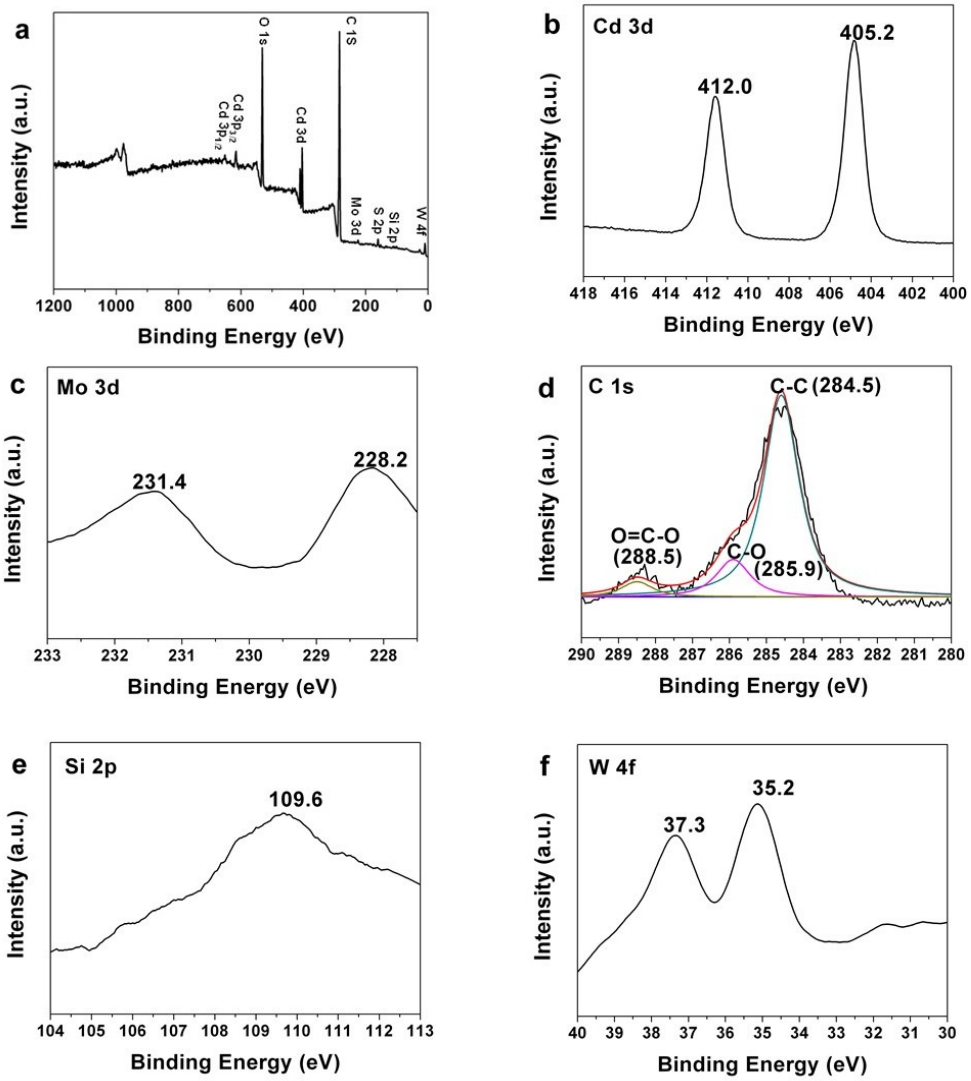


**Fig. S3** (a) XPS survey spectrum of $SiW_{11}Co$ /M/G-CdS. (b) The high-resolution XPS spectra of Cd 3d, (c) Mo 3d, (d) C 1s, (e) Si 2p and (f) W 4f in $SiW_{11}Co$ /M/G-CdS.

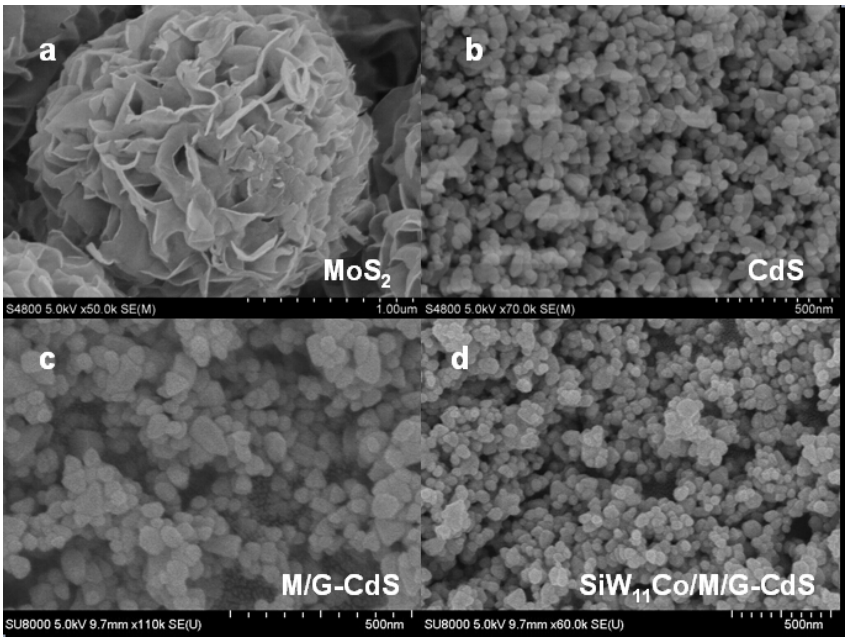


**Fig. S4** SEM images of $MoS_2$ (a), CdS (b), M/G-CdS (c) and $SiW_{11}Co$/M/G-CdS.

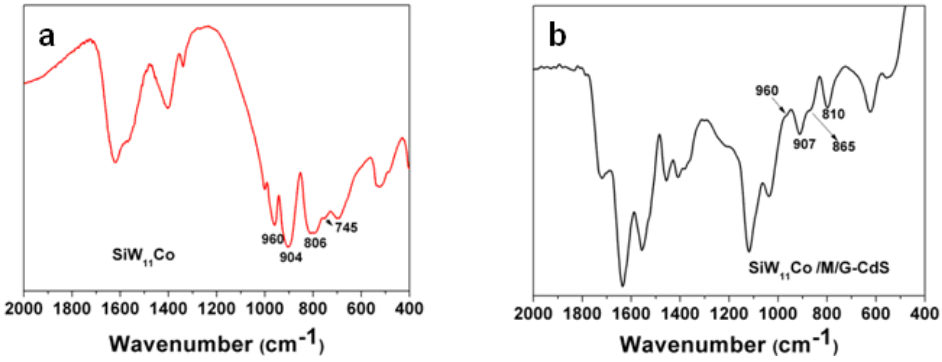


**Fig. S5** The IR spectra of $SiW_{11}Co$ (a) and $SiW_{11}Co$/M/G-CdS (b).

As shown in Fig. S4b, the peaks observed at 960, 907, 865 and 810 $cm^{-1}$ are assigned to $\nu_{as}(W{=}O_d)$, $\nu_{as}(Si{-}O_a)$,$\nu_{as}(W{-}O_b{-}W)$ and $\nu_{as}(W{-}O_c{-}W)$, respectively ($O_d$, terminal oxygen; $O_a$, central tetrahedral oxygen; $O_b$, bridging oxygen of two octahedral sharing a corner; $O_c$, bridging oxygen sharing an edge). Compared with pure $SiW_{11}Co$ (Fig. S4a), blue shifts occurred in the IR spectrum of $SiW_{11}Co$/M/G-CdS owing to the weak interactions between $SiW_{11}Co$ and other components. These results suggest that $SiW_{11}Co$ has been introduced into the composite photocatalysts $SiW_{11}Co$/M/G-CdS.

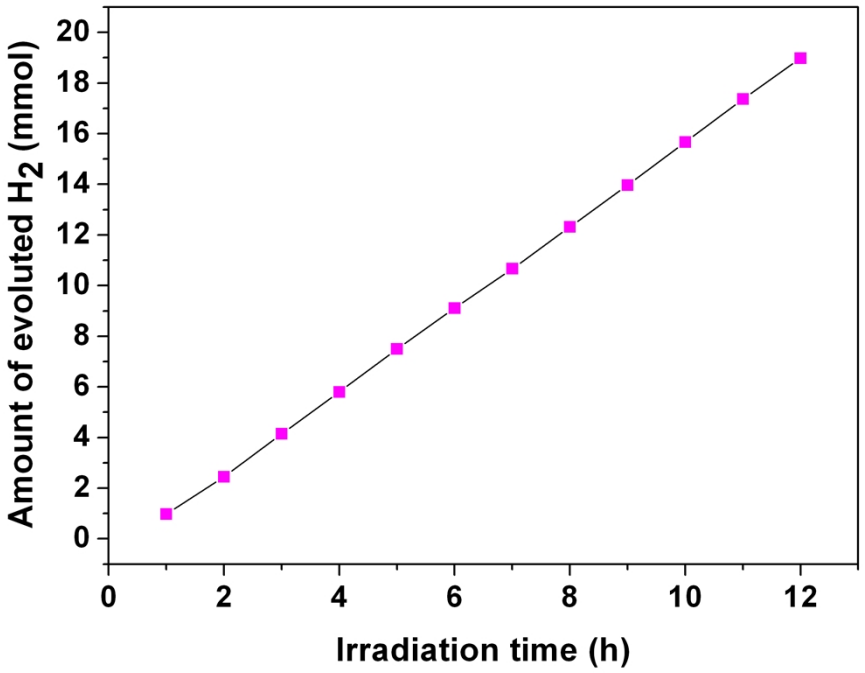


**Fig. S6** The amount of $H_2$ evolved on $SiW_{11}Co$/M/G-CdS in 12 h of continuous reaction.

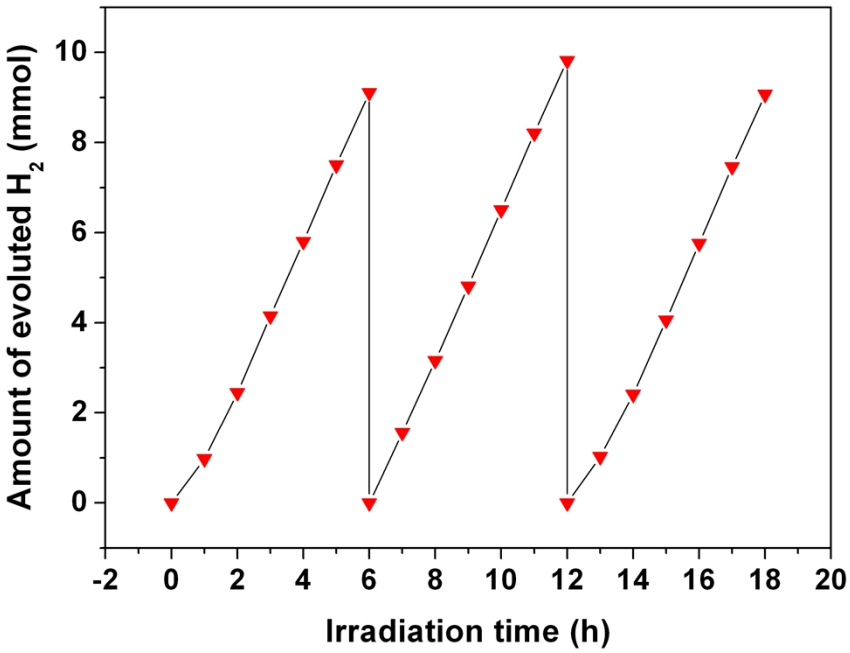


**Fig. S7** Long-time stability test of $SiW_{11}Co$/M/G-CdS for hydrogen evolution. Reaction condition: 0.1 g catalyst; 1 wt% $SiW_{11}Co$ loaded; 160 ml 30 vol% lactic acid aqueous solution; light source: 300 W Xe lamp ($\lambda > 400$ nm). The reaction solution was replaced by a new one after 6 h of the reaction.

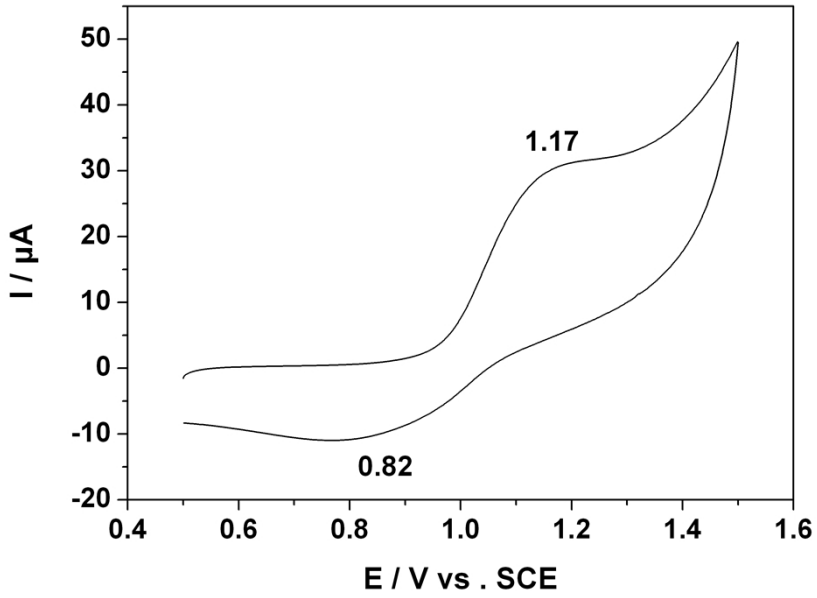


**Fig. S8** Cyclic voltammogram of $SiW_{11}Co$ in 0.1 M $Na_2SO_4$-$NaHSO_4$ solution (pH = 1.0) at a scan rate of 10 mV/s.

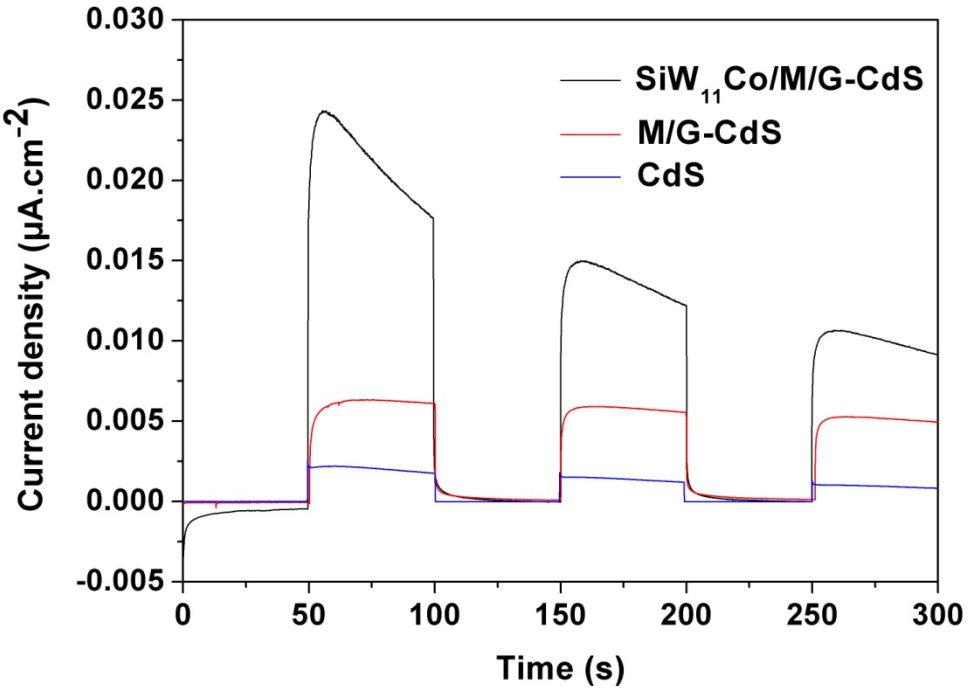


**Fig. S9** Transient photocurrent responses of the films of $SiW_{11}Co$/M/G-CdS， M/G-

CdS and CdS. A three-electrode system was employed in a quartz cell with a Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum foil as the counter electrode, the film assembled ITO glass as the working electrode and 0.1 M $Na_2SO_4$ electrolyte.