Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

Enhanced photocatalytic hydrogen production activity via dual modification of MOF and graphene on CdS

Rui Lin,[ab] Lijuan Shen,[a] Zhuyun Ren,[c] Weiming Wu,[a] Yanxi Tan,[b] Hongru Fu,[b] Jian Zhang,[*b] and Ling Wu[*ab]

a. State Key Laboratory of Photocatalysis on energy and environment, Fuzhou University, Fuzhou 350002, P. R. China E-mail: wuling@fzu.edu.cn; Tel: +86-591-83779105
b. State Key Laboratory of structural chemistry, Fujian Institute of research on the structure of matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China E-mail: zhj@fjirsm.ac.cn; Fax: +86-591-83715030; Tel: +86-591-83715030
c. Instrumental measurement and analysis center, Fuzhou University, Fuzhou 350002, P. R. China

Materials and Reagents: Zirconium chloride ($ZrCl_4$), terephthalic acid (H_2bdc) were purchased from Alfa Aesar China Co., Ltd. (Tianjin, China); Cadmium Chloride ($CdCl_2 \cdot 2.5H_2O$), elemental sulfur (S_8), *N,N*-dimethylformamide(DMF), methanol (CH_3OH) and ethanol (CH_3CH_2OH) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); Graphite powder, nitric acid (HNO3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), phosphorous pentoxide (P_2O_5), potassium persulfate ($K_2S_2O_8$), hydrogen peroxide (30% H_2O_2), potassium permanganate ($KMnO_4$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Preparations:

The synthesis of graphene oxide (GO): GO was synthesized from natural graphite powder by a modified Hummers method.[S1] 2 g of graphite powder was put into a mixture of 12 mL of concentrated H_2SO_4, 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5. The solution was heated to 80℃ in a oil bath kept stirring for 24 h. The mixture was carefully diluted with 500 mL deionized water, filtered and washed until the pH of rinse water became neutral. The product was dried under ambient condition overnight. This preoxidized graphite was added to a mixture of 120 mL of concentrated H_2SO_4 and 30 mL HNO_3 under vigorous stirring, and the solution was cooled to 0℃. Then 15 g of $KMnO_4$ was added gradually under stirring, and the temperature of the mixture was kept to be below 20℃. Then this mixture was stirred at room temperature for 96 h and diluted with 1L deionized water in a ice bath to keep the temperature below 50℃ for 2h. After the dilution with 1 L of DI water, 20 mL of 30% H_2O_2 was then added to the mixture, and a yellow product was formed along with bubble. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove the metal ions followed by DI water to remove the acid. The filter cake was then dispersed in water by a mechanical agitation. After centrifugation with 1000 rpm for 2 min, the supernatant then underwent two more high speed centrifugation steps at 8000 rpm for 15min to remove small GO pieces and water soluble by-product. The final sediment was redispersed in water with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, giving a solution of exfoliated GO. The GO separated and dried is in the form of a brown powder.

The preparation of UiO-66: 700mg $ZrCl_4$ and 500mg terephthalic acid were added in 50ml DMF under vigorous stirring for 30min, and then this clear solution was transferred to a 100ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120℃ for 36h. After cooled naturally, the as-synthesized solid was rinsed by DMF and centrifuged for several times, and then the product was purified with anhydrous methanol to exchange the guests-DMF molecules for 5 days. The activated UiO-66 was dried at 80℃ for 12h.

The synthesis of UiO-66/CdS: 85 mg $CdCl_2 \cdot 2.5H_2O$ and 10.7 mg sulfur powder were added to 25ml anhydrous ethanol and then sonication for 30 min until these solids were completely dissolved. 96mg UiO-66 was dispersed in this clear solution with vigorous stirring, meanwhile, nitrogen gas was bubbled into the suspension for 30min. And then, the suspension was irradiated under a 300W Xe lamp without optical filter for 1h. The as-prepared product was centrifuged and washed by ethanol for 3 times, then dried at 80℃ for 12h.

The synthesis of UiO-66/GR/CdS: 85 mg $CdCl_2 \cdot 2.5H_2O$ and 10.7 mg sulfur powder were added to 25ml anhydrous ethanol and then sonication for 30 min until these solids were completely dissolved. 96mg UiO-66 powder and the corresponding portion of graphene oxide suspension were added to the 50ml ethanol and stirred for 30 min. Then the suspension was transferred to a 100ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120℃ for 12h. After cooled naturally, the product were washed with ethanol and centrifuged for several times. Then the as-synthesized UiO-66/GR was transferred to the bottle contained the ethanol solution of $CdCl_2$ and S_8. This suspension was stirred vigorously and bubbled N_2 for 30 min, then under illuminated under a 300W Xe lamp without optical filter for 1h. The as-prepared UiO-66/GR/CdS solids were washed with ethanol and centrifuged for several times and then dried at 80℃ for 12h.

The synthesis of P25/GR/CdS: 85 mg $CdCl_2 \cdot 2.5H_2O$ and 10.7 mg sulfur powder were added to 25ml anhydrous ethanol and then sonication for 30 min until these solids were completely dissolved. 96mg P25 powder and the corresponding portion of graphene oxide suspension were added to the 50ml ethanol and stirred for 30 min. Then the suspension was transferred to a 100ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120℃ for 12h. After cooled naturally, the product were washed with ethanol and centrifuged for several times. Then the as-synthesized P25/GR was transferred to the bottle contained the ethanol solution of $CdCl_2$ and S_8. This suspension was stirred vigorously and bubbled N_2 for 30 min, then illuminated under a 300W Xe lamp without optical filter for 1h. The as-prepared P25/GR/CdS solids were washed with ethanol and centrifuged for several times and then dried at 80℃ for 12h.

Characterization: Powder X-ray diffraction analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056$Å) in the 2θ range from 5° to 80° with a scan rate of 5° per minute. The solid state photoluminescence spectra were measured on the Cary Eclipse fluorescence spectrophotometer. UV-vis diffuse reflectance spectra were obtained on the Varian Cary 500 UV-vis spectrophotometer and the barium sulfate was used as the reference. The BET surface area tests and nitrogen adsorption experiments at 77K were performed on the ASAP 2020M apparatus (Micromeritics Instrument Corp., USA). All the samples were degassed in the vacuum at 200℃ for 12h. The X-ray photoelectron spectroscopy (XPS) measurements were carri -ed out on a Thermo Scientific ESCALAB 250 instrument with a monochromatic Al $K\alpha$ source. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained on a Tecnai G2 F20 field emission transmission electron microscope at an accelerating voltage of 200 kV. SEM experiments were carried out on the JEOL JSM-6700 field emission scanning electron microscope. Raman spectrum was recorded on the Renishaw inVia Raman system 1000 with a 532 nm Nd: YAG excitation source at room temperature. Thermogravimetric analysis was carried out on a NETZSCH STA 449F3 unit at a heating rate of 5℃/min under nitrogen atmosphere. ICP measurements were examined on the Ultima2 Inductively Coupled Plasma OES Spectrometer. Elemental analysis was measured on a Vario MICRO Elemental Analyzer instrument.

The electrochemical analysis: Fluorine-doped tin oxide (FTO) glasses were cleaned by sonication in the ethanol for half an hour and then dried at 80℃ for 12h in an oven. The clean and dry FTO glasses were further used as the working electrodes. 10mg sample was dispersed in the 0.5ml ethanol and sonication for several hours to get slurry. The conductive tape was used to adhere to part of FTO glasses to leave an area of 0.5×0.5 cm^2 for depositing the slurry and then dried at room temperature naturally. The electrochemical measurements were performed in the cell equipped with three electrodes, namely working electrode, counter electrode (Pt plate) and reference electrode (Ag/AgCl). These three electrodes were immersed in the 0.2M Na_2SO_4 aqueous solution (pH = 6.6). A 300W Xe lamp (Beijing perfectlight, PLS-SXE300c) with a 420 nm cut-off filter was prepared for the photocurrent tests. The photocurrent measurements were completed on the Epsilon electrochemical workstation and the analysis of Mott-Schottky and EIS were carried out on the Zahner electrochemical workstation.

Photocatalytic reaction experiment: Photocatalytic hydrogen production tests were carried out in a pyrex reaction cell connected to a closed gas circulation and evacuation system. 50mg photocatalysts were dispersed in the 50ml aqueous solution containing 0.1M Na_2S and 0.1M Na_2SO_3 and the loading of Pt was conducted by reducing H_2PtCl_6 through the photodeposition process. The suspension was degassed thoroughly and then irradiated by a 300W Xe lamp equipped with optical filter ($\lambda \geqslant 400$nm) to cut off the light in the UV region. The evolved hydrogen was detected by online gas chromatography (FULI; TDX-01 column, TCD, Ar Carrier).

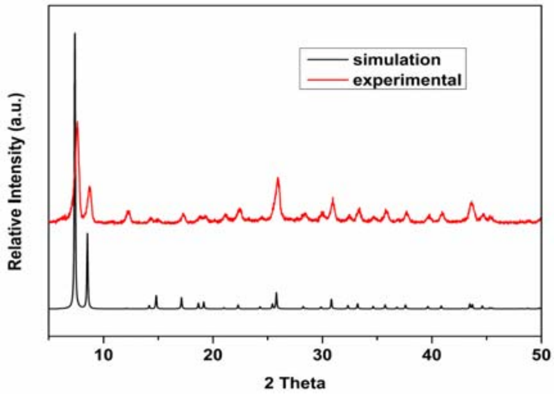

Fig. S1 The XRD pattern of UiO-66

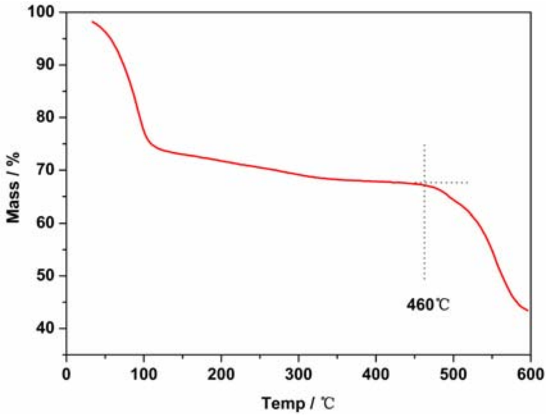

Fig. S2 The thermogravimetric graph of UiO-66 under nitrogen atmosphere.

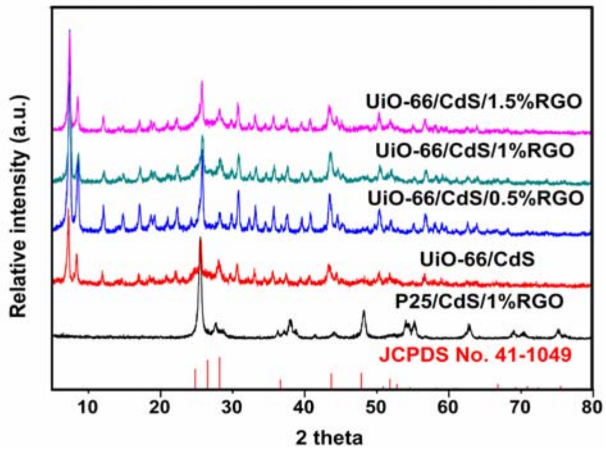

Fig. S3 The XRD of CdS contained composites

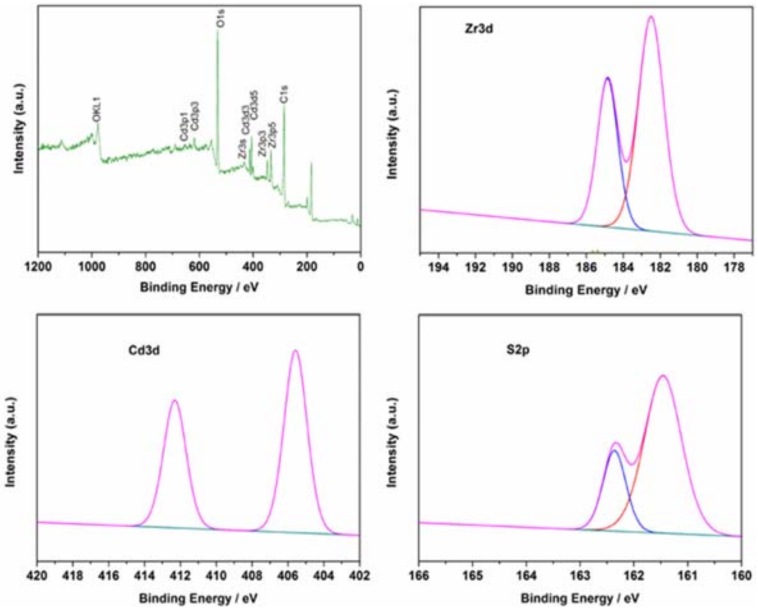

Fig. S4 The XPS pattern of UiO-66/CdS/1%RGO

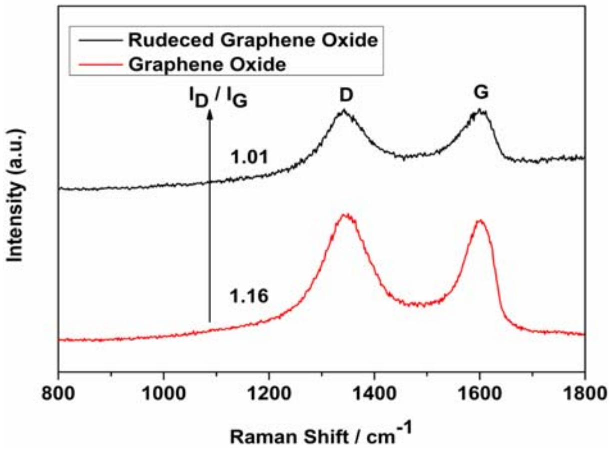

Fig. S5 The Raman spectra of GO and RGO

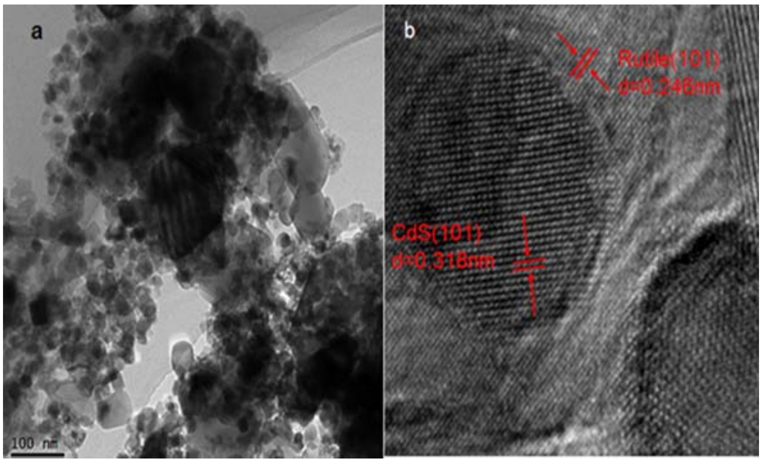

Fig. S6 (a) TEM image of CdS supported on P25 and (b) HRTEM image of P25/CdS/1%RGO

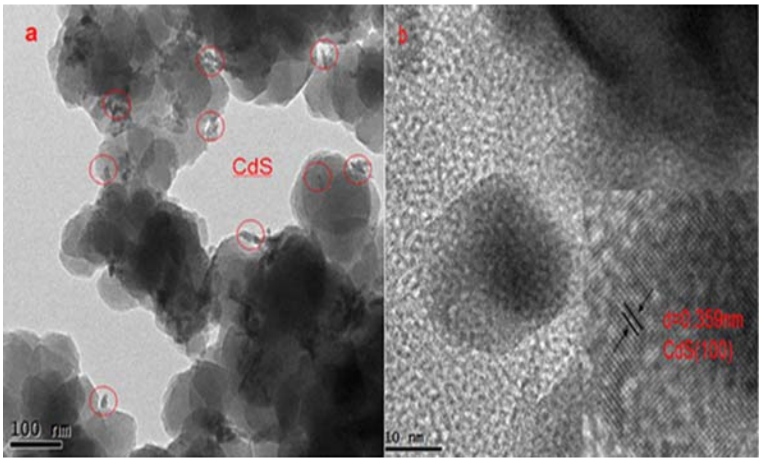

Fig. S7 (a)TEM image of CdS embeded on UiO-66 and (b) HRTEM image of UiO-66/CdS/1%RGO

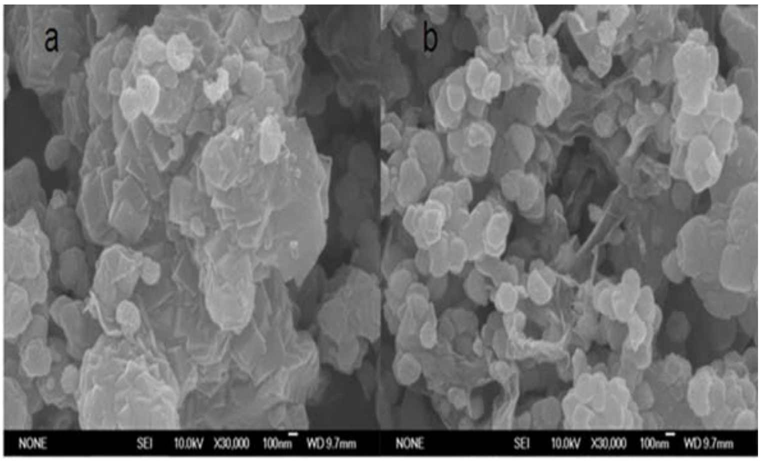

Fig. S8 (a) the SEM graph of UiO-66/CdS and (b)
The SEM graph of UiO-66/CdS/1%RGO

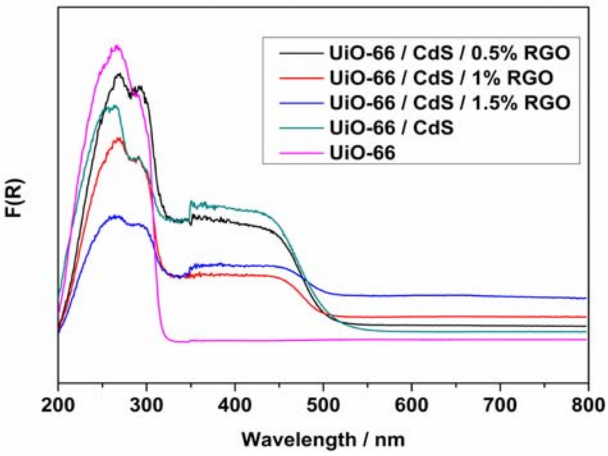

Fig. S9 The Diffraction Reflectance Spectra

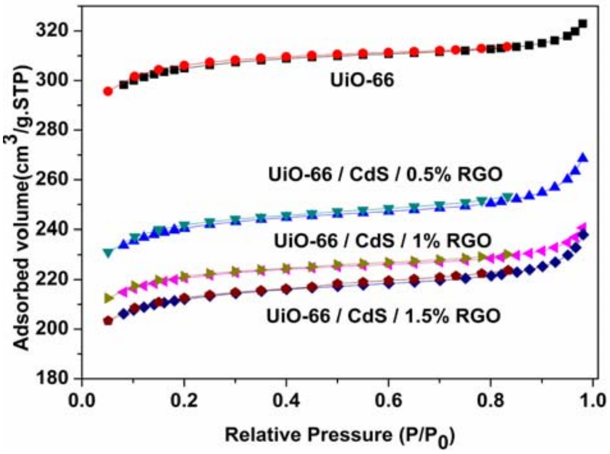

Fig. S10 The N_2 adsorption/desorption isotherms

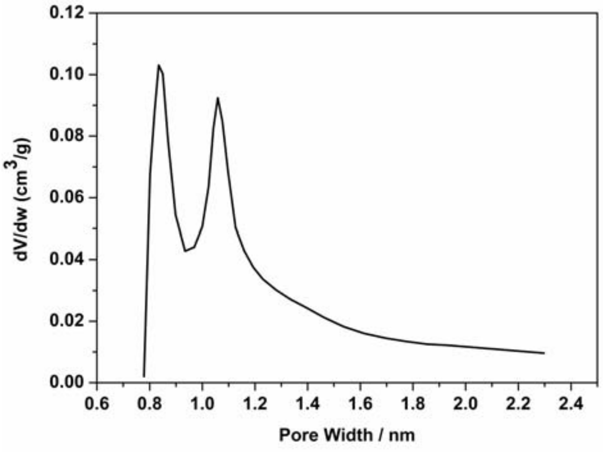

Fig. S11 Pore width of UiO-66

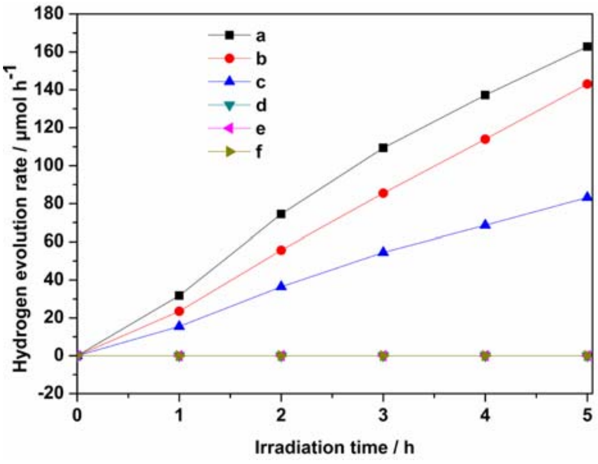

Fig. S12 the hydrogen production activity of (a) UiO-66/CdS/1%RGO; (b) UiO-66/CdS/1.5%RGO; (c) UiO-66/CdS/0.5%RGO; (d) UiO-66; (e) RGO; (f) UiO-66/CdS/1%RGO in the dark.

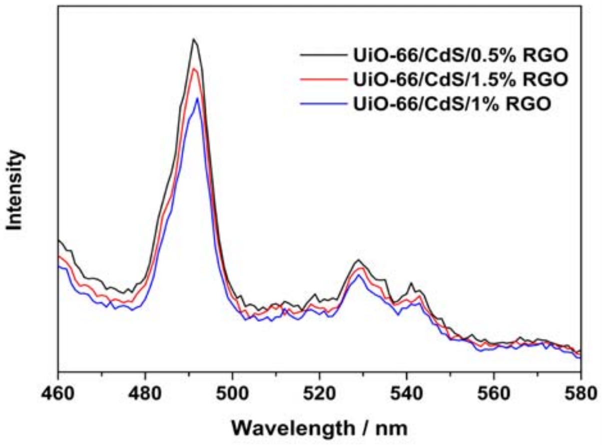

Fig. S13 The photoluminescence spectra

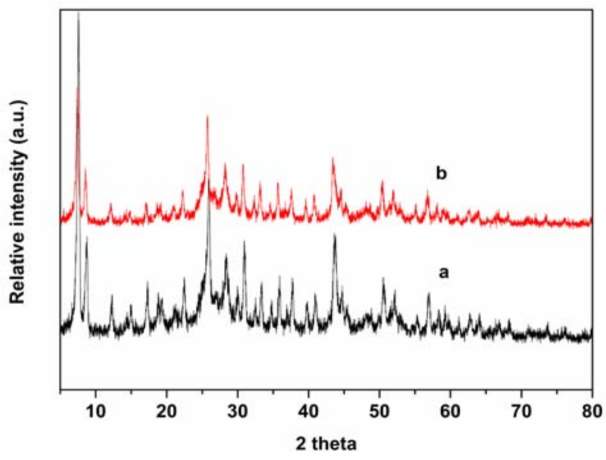

Fig. S14 (a) the XRD of fresh UiO-66/CdS/1%RGO and (b) the XRD of UiO-66/CdS/1%RGO after water splitting reaction without the addition of sacrificial agents.

Sample	Cd wt%(ICP)	S wt%(Elemental analysis)	CdS wt%
P25/CdS/1%GR	9.49	2.52	12.01
UiO-66/CdS	12.06	3.14	15.20
UiO-66/CdS/1%GR	11.92	3.22	15.14

Table. S1 The mass fraction of CdS in the composite

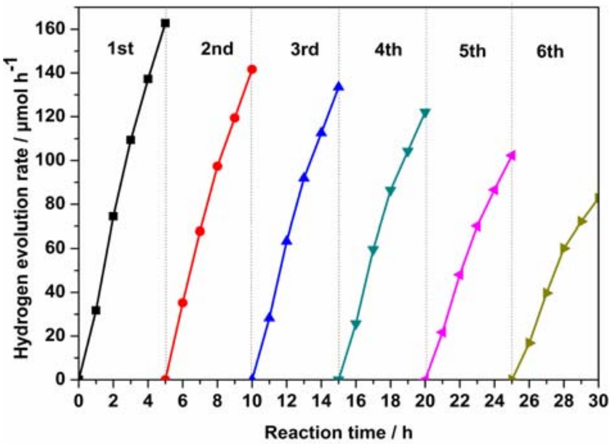

Fig. S15 H_2 production over UiO-66/CdS/1%RGO

Notes and References

S1. N. Zhang, Y. Zhang, M. Yang, Z. Tang and Y. Xu, *J. Catal*., 2013, **299**, 210