

Electronic Supplementary Information

## Synthesis and Highly Efficient Photocatalyzed Applications of CdS QDs and Au NPs Co-modified KTaO<sub>3</sub> Perovskite Cube

Niuniu Zhang, Xia Wu, Kangjia Lv, Yujie Chu, Guan Wang\*, Dongdi Zhang\*

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and

Chemical Engineering, Henan University, Kaifeng, Henan 475000, China

### Experimental section

#### Materials and Chemicals

All chemicals are acquired from commercial suppliers and used without further treating unless specified otherwise: cadmium chloride hemi(pentahydrate) (98 % Adamas), cysteamine hydrochloride (98 % Aladdin), sodium sulfide nonahydrate (98 % Aladdin), isopropyl alcohol (99.7 % Alfa Aesar), potassium hydroxide (>85.0 % Deen reagent), potassium carbonate (99.0 % Kermel), tantalum oxide (98 % Aladdin), chloroauric acid hydrate (99 % Au: 50 % Adamas).

**Synthesis of CdS QDs.**<sup>1</sup> CdS QDs are synthesized as follows: cadmium chloride hemi(pentahydrate) (CdCl<sub>2</sub>·2.5 H<sub>2</sub>O 0.114 g, 0.5 mmol), cysteamine hydrochloride (0.142 g, 1.25 mmol) and sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O 0.150 g, 0.625 mmol) are dissolved in 25 mL deionized water. The reaction proceeded at 40 °C for 5 h and then at 60 °C for 5 h under vigorous stirring. The resulting solution is a homogeneous yellow colloid suspension. After slow cooling to room temperature naturally, then isopropyl alcohol is added and the solution become turbid, and the yellow precipitate is separated by centrifugation. After isolation, the precipitate is dissolved again in water and reprecipitated with isopropyl alcohol. This operation is repeated a further two times. Finally, the precipitate of CdS QDs is dried in vacuum at 40 °C for 24 h.

**Synthesis of KTaO<sub>3</sub> Cubes.** The KTaO<sub>3</sub> cubes are synthesized by traditional hydrothermal method. In a typical experiment, 11.3 g (0.201 mol) potassium hydroxide (KOH) and 2.5 g (0.018 mol) potassium carbonate are added to 7 ml of deionized water and stirred until dissolved. Following, 1.25 g (0.003 mol) of tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) is added to the former mixed solution. Keep stirring at room temperature for 30 minutes, the mixture is then transferred to a 25 mL of Teflon autoclave, which is

aged at 180 °C for 12 h. After the reaction, cool to room temperature, collect the white precipitate, and wash with water and ethanol three times to remove the unreacted impurities. and then dry in vacuum at 60 °C for 12 h.

**Synthesis of Au/KTaO<sub>3</sub> and Au/CdS.** KTaO<sub>3</sub> cubes are decorated with Au NPs through a photodeposition method.<sup>2</sup> Typically, 0.4 g of KTaO<sub>3</sub> powder is suspended in 200 mL of water by ultrasonic treatment, and then 0.102 g of chloroauric acid hydrate (HAuCl<sub>4</sub>·xH<sub>2</sub>O 0.3 mmol) is added and followed by irradiation with a xenon lamp (300 W) for 30 min under drastic agitation. The resultant gray product is collected by centrifugation and washed with deionized water three times. Afterward, the product is dried at 60 °C in vacuum to obtain Au decorated KTaO<sub>3</sub> cubes, denoted as Au/ KTaO<sub>3</sub>. The CdS/Au is synthesized according to the method of Au/KTaO<sub>3</sub>, but CdS QDs (0.09 g 0.60 mmol) is added instead of KTaO<sub>3</sub>.

**Synthesis of CdS/Au/KTaO<sub>3</sub>.** CdS/Au/KTaO<sub>3</sub> is obtained using a facile one-step precipitation method. Normally, 0.1163 g of Au/KTaO<sub>3</sub> powder, 0.625 mmol (0.071 g) of cysteamine hydrochloride and 0.25 mmol (0.06 g) of sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O) are dissolved in 50 mL deionized water under magnetic stirring 15 minutes. Subsequently, 0.25 mmol (0.057 g) of cadmium chloride hemi(pentahydrate) (CdCl<sub>2</sub>·2.5 H<sub>2</sub>O) is added to the mixed solution. And kept the reaction at 40 °C for 5 h and then at 60 °C for 5 h under vigorous stirring. The homogeneous yellowish of colloid suspension is acquired. After slow cooling to room temperature naturally, the resulting precipitate is separated from the solution by centrifugation and washed with deionized water and isopropyl alcohol several times to remove the impurities. Finally, the precipitate is dried at 60 °C in vacuum for 24 h. The as-synthesized yellowish powder is labeled as 13%CdS/1.3%Au/KTaO<sub>3</sub>. The similar procedure is followed to prepare 6%CdS/1.3%Au/KTaO<sub>3</sub>, 27%CdS/1.3%Au/KTaO<sub>3</sub> and 40%CdS/1.3%Au/KTaO<sub>3</sub> by adding 0.8 g, 0.2 and 0.08 g of KTaO<sub>3</sub> powder in Au/KTaO<sub>3</sub> synthesis, respectively. For comparison, CdS decorated KTaO<sub>3</sub> cubes is also synthesized by the same synthesis method, but 0.034 g of KTaO<sub>3</sub> cubes are added into the preceding solution, and the obtained sample is labeled as CdS/KTaO<sub>3</sub>.

### **Characterization**

The scanning electron microscopy (SEM) images and EDS spectra are obtained on a JSM-7610F scanning electron microscopy with an acceleration voltage of 5 kV. The XRD is performed on a Bruker D8 Advance instrument with Cu K $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). Raman spectra is performed on a confocal laser Raman spectroscopy instrument (RM5, Edinburgh) by using the 532 nm laser beam to excite

samples. IR spectra are recorded on an Avatar 360 Fourier transform infrared (FTIR) spectrophotometer using KBr pellets in the range of 4000-500  $\text{cm}^{-1}$ . The XPS is collected using a PHI 5000 Versa Probe (U1VAC-PHI). Ultraviolet absorption is used to test by Hitachi UH4150 UV-vis spectrophotometer. The PL spectra are collected by a Hitachi F-7000 fluorescence spectrophotometer. The electrochemical analyses are tested by a standard three-electrode configuration in an electrochemical workstation (CHI 760 E, Shanghai, China). For photocurrent-time curves and electrochemical impedance spectroscopy (EIS) tests, Ag/AgCl, Pt wire, and a catalyst-coated ITO (8  $\Omega$  per square) glass substrate are used as reference, counter, and working electrode, respectively. Electrochemical impedance spectroscopy (EIS) is obtained under a frequency range from 0.1 Hz to  $10^5$  Hz. Mott-Schottky (M-S) plots are recorded by conducting impedance-potential spectroscopy at 1 kHz over a range of potentials between -0.22 and 1.77 V by changing the Ag/AgCl electrode to saturated calomel electrode (SCE). The  $\text{Na}_2\text{SO}_4$  solution (0.1 M) is utilized as the electrolyte.

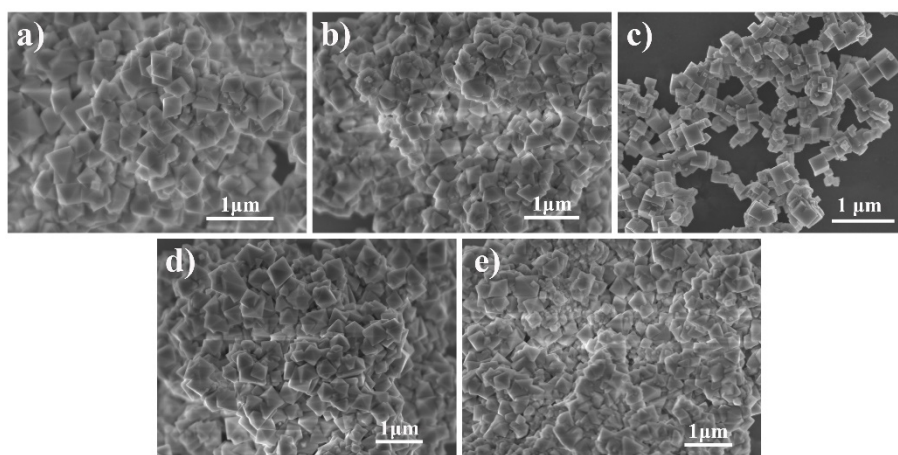
**Photocatalytic  $\text{H}_2$  production.** The photocatalytic  $\text{H}_2$  production experiment is performed in a closed glass gas circulation system (CEL-PAEM-D8, Beijing China Education Au-Light Technology Co., Ltd.), and a top-irradiated Xe lamp (300 W, wavelength range: 175-1052 nm) is equipped as light source. In a typical experiment, 2.1 g of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (8.74 mmol) and 1.58 g of  $\text{Na}_2\text{SO}_3$  (12.54 mmol) are dissolved into 50 mL of aqueous solution as sacrificial agent. After that, 50 mg of photocatalyst sample is dispersed into the solution by agitation and ultrasound technique. The generated  $\text{H}_2$  is tested by a gas chromatograph (TCD detector, GC-7900).

**Photodegradation of aqueous organic dyes.** The photocatalytic activity of the synthesized materials is evaluated by the photodegradation of aqueous MB, RhB and MO at room temperature under visible light irradiation. The photocatalytic experiments are performed on WATTCAS Parallel Light Reactor (WP-TEC-1020SL) with a 10W COB LED white light (wavelength range: 230-850 nm). The reactor is integrated with the water circulation system to keep the temperature constant. Typically, 5 mg of the photocatalysts are uniformly dispersed in 10 mL of 10 mg/L organic dye solutions, respectively. Before the photocatalytic reaction, the solutions are sonicated in the dark condition for 60 min to attain adsorption-desorption equilibrium between the photocatalyst and dye solution. Subsequently, the solution is then taken into the photochemical reactor consisting of white-light for a visible light source. At each 1 h interval, 4 mL aliquots of suspensions are withdrawn from the reactor and centrifuged immediately to separate the catalyst. After 6 h of total irradiation time, the

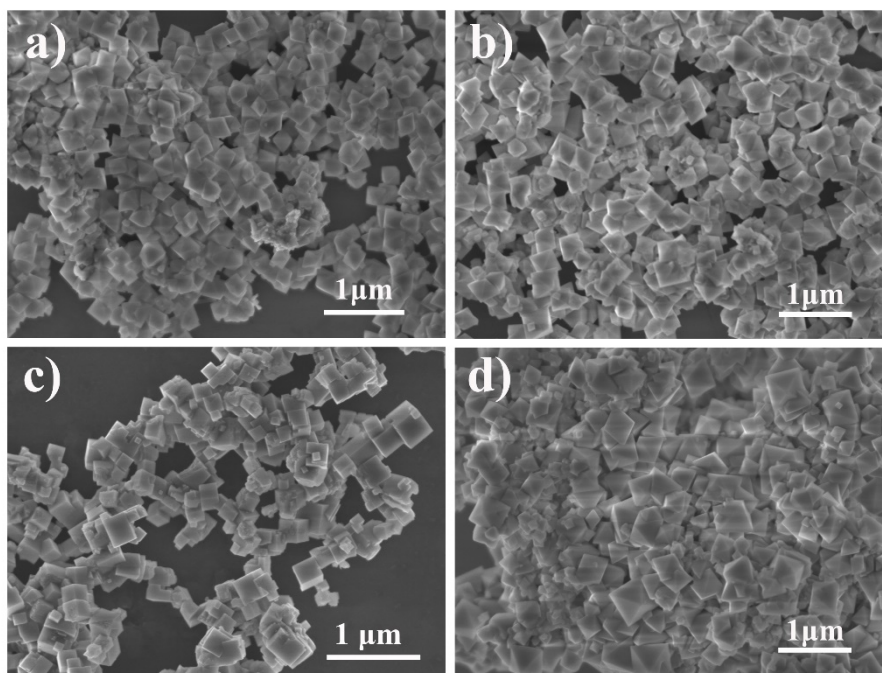
concentration of the residual is measured by using a UV-vis spectrophotometer (UH4150 UV-vis Hitachi) in the wavelength range of 200-800 nm. Finally, the photocatalytic degradation efficiency of the as-synthesized photocatalysts are evaluated by the following equation<sup>3</sup>:

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \%$$

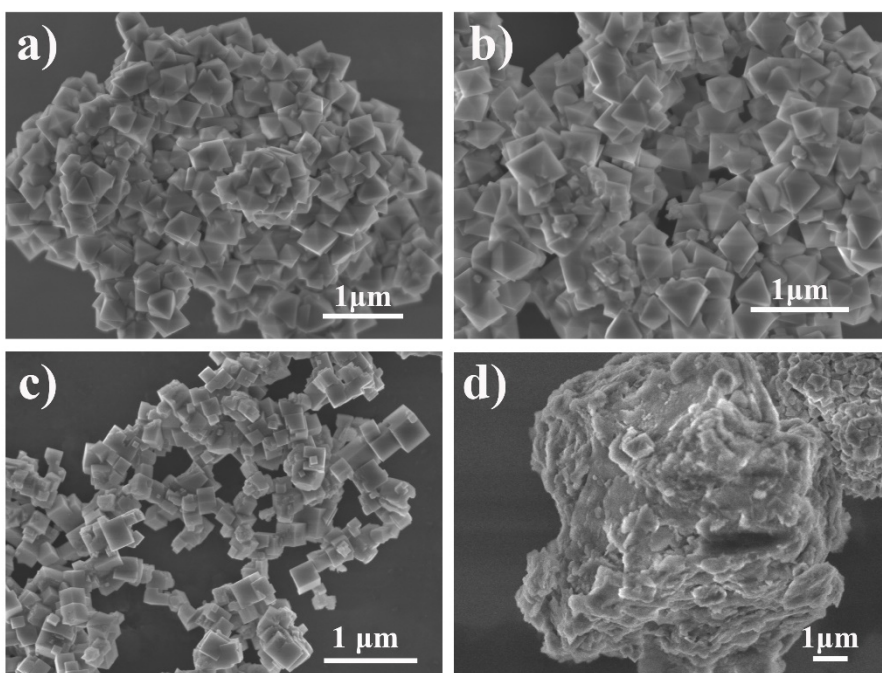
A series of control experiments are carried out to explore the morphology of KTaO<sub>3</sub>. Figure S1, Figure S2 and Figure S3 show the SEM images of KTaO<sub>3</sub> at different synthesis conditions, such as reaction times, temperatures and amounts of Ta<sub>2</sub>O<sub>5</sub>. Firstly, reaction time is an important factor in the synthetic process. As shown in Figure S1, five different reaction times are employed to study the influence on KTaO<sub>3</sub> cube. When the reaction time is less than 12 h, the cube morphology is not fully formed or integrated. Along with the time extension, uniform KTaO<sub>3</sub> cubes are observed clearly. However, when the reaction times more than 12 h, KTaO<sub>3</sub> cubes are agglomerated together. Considering the influence of reaction temperatures on the morphology of products, KTaO<sub>3</sub> cubes are prepared under different temperatures. When the temperature is raised from 140 °C to 200 °C, a large number of broken cubes are collected, indicating that elevated temperature would destroy the KTaO<sub>3</sub> cube. Beyond that, additional test is carried out to investigate the dosage of Ta<sub>2</sub>O<sub>5</sub> precursor. With the increasing of Ta<sub>2</sub>O<sub>5</sub>, the KTaO<sub>3</sub> cubes are aggregated to bulk. In conclusion, only with the suitable reaction conditions, KTaO<sub>3</sub> can develop the uniform cube morphology.



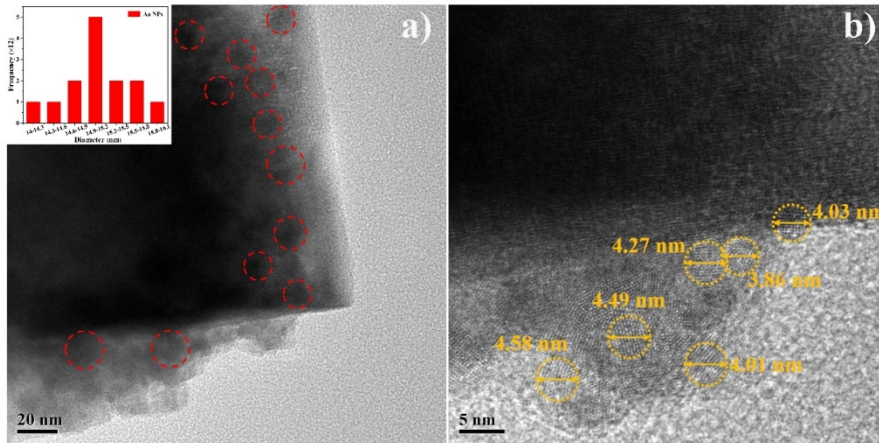
**Figure S1.** SEM images of KTaO<sub>3</sub> prepared under different reaction times: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h and (e) 20 h.



**Figure S2.** SEM images of  $\text{KTaO}_3$  prepared under different reaction temperatures: (a) 140 °C, (b) 160 °C, (c) 180 °C, and (d) 200 °C.

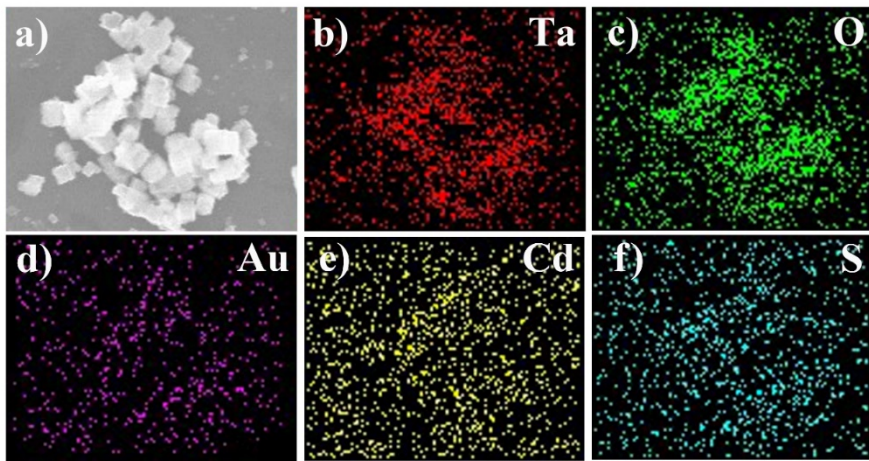


**Figure S3.** SEM images of  $\text{KTaO}_3$  at different of  $\text{Ta}_2\text{O}_5$  adding amounts: (a) 0.42 g, (b) 0.84 g, (c) 1.25 g, and (d) 1.68 g.



**Figure S4.** (a) and (b) TEM image of 13%CdS/1.3%Au/KTaO<sub>3</sub> (The inset in Figure S1a is the particle size distribution of Au NPs, which is approximately 15.07 nm in size. And the red circle indicates the size of an Au NP.

The yellow circle in Figure S1b indicates the size of CdS QDs, which is about 4.21 nm).



**Figure S5.** (a) SEM image. (b-f) EDS mappings of 13%CdS/1.3%Au/KTaO<sub>3</sub>.



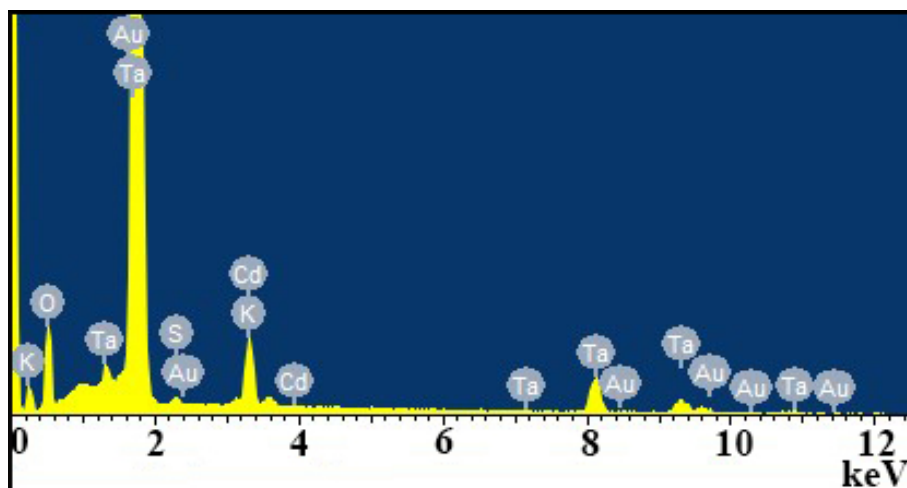


Figure S6. EDS spectra of 13%CdS/1.3%Au/KTaO<sub>3</sub>.

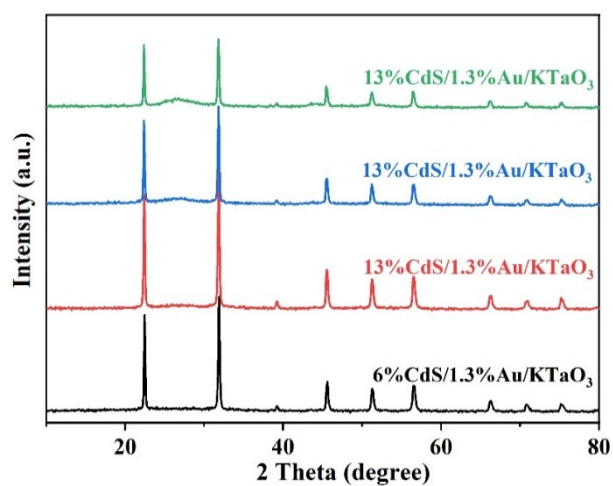


Figure S7. XRD patterns of CdS/Au/KTaO<sub>3</sub> with different deposition amount of CdS QDs.

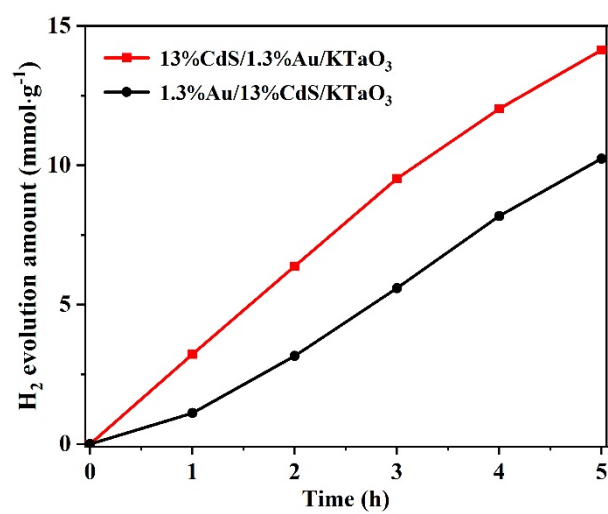
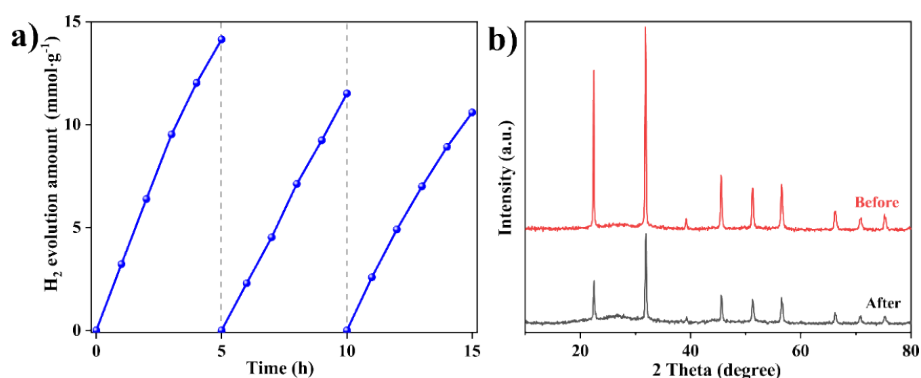
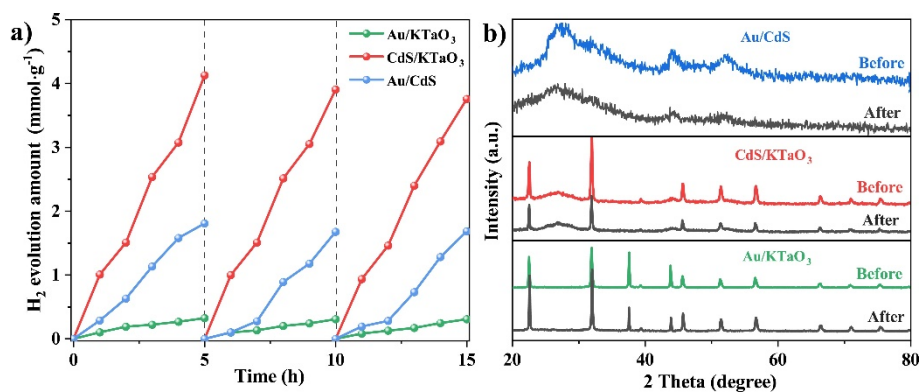


Figure S8. The photocatalytic hydrogen evolution of 13%CdS/1.3%Au/KTaO<sub>3</sub> and 1.3%Au/13%CdS/KTaO<sub>3</sub> (Au NPs)

and CdS QDs loaded on KTaO<sub>3</sub> in different order); After 5 hours, the hydrogen production of 13%CdS/1.3%Au/KTaO<sub>3</sub> and 1.3%Au/13%CdS/KTaO<sub>3</sub> are 14.46 mmol·g<sup>-1</sup> and 10.24 mmol·g<sup>-1</sup>, respectively.

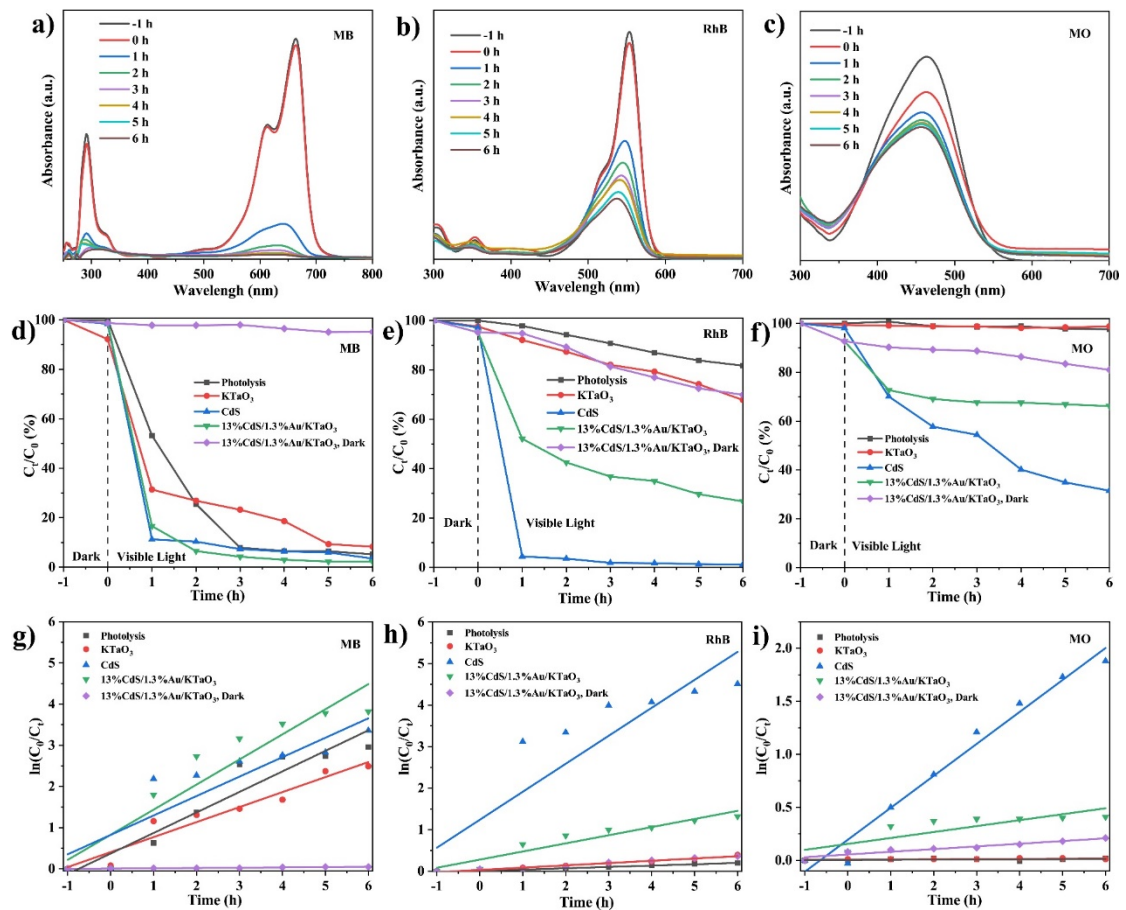


**Figure S9.** (a) Cyclic runs for the photocatalytic H<sub>2</sub> evolution over 13%CdS/1.3%Au/KTaO<sub>3</sub> within 15 h (evacuation every 5 h) and (b) XRD patterns of 13%CdS/1.3%Au/KTaO<sub>3</sub> before and after photocatalytic 15 hours' reaction; After three cycles, the H<sub>2</sub> generation amount of 13%CdS/1.3%Au/KTaO<sub>3</sub> has evident reduction, which may be caused by photocorrosion of CdS.<sup>4</sup>



**Figure S10.** (a) Cyclic runs for the photocatalytic H<sub>2</sub> evolution over Au/KTaO<sub>3</sub>, CdS/KTaO<sub>3</sub>, and Au/CdS within 15 h (evacuation every 5 h) and (b) XRD patterns of Au/KTaO<sub>3</sub>, CdS/KTaO<sub>3</sub>, and Au/CdS before and after photocatalytic 15 hours' reaction.





**Figure S11.** (a), (b) and (c) Absorption profile of MB, RhB and MO dye degradation in aqueous solution under visible light irradiation over 13%CdS/1.3%Au/ $\text{KTaO}_3$ , respectively. (d), (e) and (f) Percentage degradation of MB, RhB and MO dye using photolysis,  $\text{KTaO}_3$ , CdS, 13%CdS/1.3%Au/ $\text{KTaO}_3$  and 13%CdS/1.3%Au/ $\text{KTaO}_3$  Dark, respectively. (g), (h) and (i) Kinetic plots of  $\ln(C_0/C_t)$  vs time for the photocatalytic degradation of MB, RhB and MO dyes with different conditions, respectively.

**Table S1. The estimated  $E_g$  values for samples.**

samples	$E_g$ (eV)
KTaO <sub>3</sub>	3.8
CdS	2.44
Au/KTaO <sub>3</sub>	3.74
CdS/KTaO <sub>3</sub>	2.46
CdS/Au	2.15
6%CdS/1.3%Au/KTaO <sub>3</sub>	2.54
13%CdS/1.3%Au/KTaO <sub>3</sub>	2.5
27%CdS/1.3%Au/KTaO <sub>3</sub>	2.43
40%CdS/1.3%Au/KTaO <sub>3</sub>	2.5

**Table S2. Pseudo First Order Kinetic Rate Constant for MB, RhB and MO Degradation Using As-Synthesized Photocatalysts.**

Samples	$k$ (h <sup>-1</sup> )	Dyes		
		MB	RhB	MO
Photolysis		0.49	0.03	0.001
KTaO <sub>3</sub>		0.36	0.06	0.002
CdS		0.47	0.67	0.30
13%CdS/1.3%Au/KTaO <sub>3</sub>		0.61	0.20	0.06
13%CdS/1.3%Au/KTaO <sub>3</sub> , Dark		0.01	0.05	0.03

**References**

- 1 X. Xing, R. Liu, X. Yu, G. Zhang, H. Cao, J. Yao, B. Ren, Z. Jiang and H. Zhao, *J. Mater. Chem. A*, 2013, **1**, 1488-1494.
- 2 D. Ma, J.-W. Shi, D. Sun, Y. Zou, L. Cheng, C. He, Z. Wang and C. Niu, *ACS Sustainable Chemistry & Engineering*, 2018, **7**, 547-557.
- 3 M. Sabarinathan, S. Harish, J. Archana, M. Navaneethan, H. Ikeda and Y. Hayakawa, *RSC Advances*, 2017, **7**, 24754-24763.
- 4 L. J. Zhang, S. Li, B. K. Liu, D. J. Wang and T. F. Xie, *ACS Catalysis*, 2014, **4**, 3724-3729.