

## Supporting Information

### **Facile synthesis of porous hybrid materials based on Calix-3 dye and TiO<sub>2</sub> for high photocatalytic water splitting performance with excellent stability**

Jian-Feng Huang<sup>a</sup>, Jun-Min Liu<sup>a,\*</sup>, Li-Min Xiao<sup>b</sup>, Yu-Hui Zhong<sup>a</sup>, Liang Liu<sup>a</sup>, Su Qin<sup>a</sup>,  
Jing Guo<sup>a</sup>, Cheng-Yong Su<sup>a</sup>

<sup>a</sup>School of Materials Science and Engineering and School of Chemistry, Sun Yat-sen University, Guangzhou, 510275, China. <sup>b</sup>School of Computer Science and Engineering, Beihang University, Beijing, 100191, China. Correspondence and requests for materials should be addressed to J.M.L. (\*e-mail: liujunm@mail.sysu.edu.cn)

## Table of Contents

<b>1. Materials and Methods</b> .....	<b>3</b>
<b>2. Fig. S1.</b> N <sub>2</sub> adsorption-desorption isotherms of Calix-3-TiO <sub>2</sub> (5 wt%), Gel-TiO <sub>2</sub> and P25-TiO <sub>2</sub> measured under 77 K.....	<b>7</b>
<b>3. Fig. S2.</b> The pore size distribution of A) Calix-3-TiO <sub>2</sub> (5 wt%) and B) Gel-TiO <sub>2</sub> .....	<b>7</b>
<b>4. Table S1.</b> BET surface area, pore volume and pore width of Calix-3-TiO <sub>2</sub> (5 wt%), Gel-TiO <sub>2</sub> and P25-TiO <sub>2</sub> derived from 77 K N <sub>2</sub> sorption isotherms.....	<b>8</b>
<b>5. Fig. S3.</b> EDX of Pt/Calix-3-TiO <sub>2</sub> (5 wt%).....	<b>8</b>
<b>6. Fig. S4.</b> ATR-IR spectra of <b>Calix-3</b> and Calix-3-TiO <sub>2</sub> (7.5 wt%).....	<b>9</b>
<b>7. Table S2.</b> H <sub>2</sub> production data of Pt/Calix-3-TiO <sub>2</sub> with different dye content, Pt/Gel-TiO <sub>2</sub> /Calix-3 (2.87 wt%), and Pt/P25-TiO <sub>2</sub> /Calix-3 (2.35 wt%) materials.....	<b>9</b>
<b>8. Table S3.</b> Performances of organic photosensitizers in photocatalytic H <sub>2</sub> production studies in recent years.....	<b>10</b>
<b>9. Table S4.</b> H <sub>2</sub> production and AQY results of Calix-3-TiO <sub>2</sub> after 1 h irradiation under 450 nm LED light source.....	<b>10</b>
<b>10. Table S5.</b> Cyclic H <sub>2</sub> production data of Calix-3-TiO <sub>2</sub> (7.5wt%) hybrid material.....	<b>11</b>
<b>11. Fig. S5.</b> Photocatalytic H <sub>2</sub> production over the recyclability of Gel-TiO <sub>2</sub> /Calix-3 (2.87 wt%) with 0.5 wt% Pt loading under visible light irradiation ( $\lambda > 420$ nm) in 100 mL H <sub>2</sub> O/TEOA (9:1, v/v).....	<b>12</b>
<b>12. Fig. S6.</b> Photocatalytic H <sub>2</sub> production over the recyclability of P25-TiO <sub>2</sub> /Calix-3 (2.35 wt%) with 0.5 wt% Pt loading under visible light irradiation ( $\lambda > 420$ nm) in 100 mL H <sub>2</sub> O/TEOA (9:1, v/v).....	<b>12</b>
<b>13. Fig. S7.</b> A) Emission spectra and B) photoluminescence decays of <b>Calix-3</b> , physical-mixing P25-TiO <sub>2</sub> /Calix-3 (5 wt%), and Calix-3-TiO <sub>2</sub> (5 wt%).....	<b>13</b>

## **Materials and Methods**

### **Materials.**

Solvents were purified using an MBRAUN MB SPS-800 system. Anhydrous solvents used in the Suzuki coupling reaction were degassed by bubbling with N<sub>2</sub> for 20 min. All other chemicals and reagents were used as received from commercial sources without further purification. Specifically, butyl titanate (Ti(OBu)<sub>4</sub>) 99.0%, tetrahydrofuran (THF) 99.0%, acetic acid 99.5%, ethanol 99.5%, methanol 99.5%, TEOA 98.0%, H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O 99.95%. The P25-TiO<sub>2</sub> particle is a commercial product of Degussa AG without further treatment. **Calix-3** was prepared according to the method reported in our previous literature.<sup>1</sup>

### **Synthesis of Calix-3-TiO<sub>2</sub> materials.**

Calix-3-TiO<sub>2</sub> hybrid materials were prepared by sol-gel method. Specifically, for 1 wt% Calix-3-TiO<sub>2</sub>, butyl titanate (1 mL), THF (1 mL), acetic acid (168 μL) and distilled water (106 μL) were mixed together in a 20 mL glass sample bottle, then a solution of **Calix-3** (2.5 mg) in THF (1 mL) was added under stirring. The mixture was gently heated on a 50 °C hot plate and turned to be transparent gelatum in a few minutes. The gel was ground out, washed with distilled water in Soxhlet apparatus for 48 h and dried in vacuum to obtain bright orange powder. The other hybrid materials with different **Calix-3** contents and Gel-TiO<sub>2</sub> material were prepared by the same method.

### **Synthesis of Pt/Calix-3-TiO<sub>2</sub> materials.**

Hybrid material (50 mg), distilled water (80 mL), methanol (10 mL) and 10 mM H<sub>2</sub>PtCl<sub>6</sub> aqueous solution (167 μL) were added into a quartz reactor. The mixture was degassed by vacuuming and irradiated with 300 W xeon lamp (without filter) for 30 min, and then the Pt/Calix-3-TiO<sub>2</sub> materials were obtained. Pt loading (0.5 wt%) was testified by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

### **Synthesis of surface dye-sensitized Pt/TiO<sub>2</sub>/Calix-3 materials.**

Pt nanoparticles were loaded on Gel-TiO<sub>2</sub> (or P25-TiO<sub>2</sub>) by a typical photo deposition method. In total, Gel-TiO<sub>2</sub> or P25-TiO<sub>2</sub> (150 mg), methanol (20 mL), 10

mM  $\text{H}_2\text{PtCl}_6$  aqueous solution (0.5 mL), and distilled water (80 mL) were added to a pyrex bottle, and then oxygen was removed from the bottle by vacuuming. The mixture was stirred and irradiated by a 300 W xenon lamp for 1 h. After centrifugation and washing with distilled water, the grey powder (denoted as Pt/Gel-TiO<sub>2</sub> or P25-TiO<sub>2</sub>, Pt deposited amount: 0.5 wt%) was dried at room temperature in a vacuum drying chamber. Then **Calix-3** was adsorbed onto Pt/gel-TiO<sub>2</sub> or Pt/P25-TiO<sub>2</sub> by stirring 50 mg TiO<sub>2</sub> powder in **Calix-3** solution (2  $\mu\text{mol}$  of dye dissolved in 10 ml tetrahydrofuran) at room temperature for 12 h in the dark. After centrifugation and washing with fresh tetrahydrofuran, the powder (denoted as Pt/Gel-TiO<sub>2</sub> or P25-TiO<sub>2</sub>/Calix-3) was dried at room temperature in a vacuum drying chamber. The concentrations of dye solutions before and after use were determined to be 2.87 wt% for Pt/Gel-TiO<sub>2</sub>/Calix-3 or 2.35 wt% for Pt/P25-TiO<sub>2</sub>/Calix-3 by UV-vis spectra at 408 nm wavelength to calculate the adsorbing capacities of the catalysts.

### **Characterizations.**

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz spectrometer. The absorption spectra were observed with a Shimadzu UV-3600 spectrometer and fluorescence spectra were measured with an Edinburgh Instruments Ltd FLS980 spectrometer. Powder X-ray diffraction (XRD) was recorded on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-K $\alpha_1$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDX) elemental mapping were obtained by a JEM-2100F transmission electron microscope at 300 kV. Scanning electron microscope (SEM) micrographs were recorded on Hitachi Ultra-high Resolution FE-SEM SU8010 microscope. Gas adsorption measurements were performed using ultra-high purity N<sub>2</sub> and CO<sub>2</sub> gas on Quantachrome Auto-sorb-iQ2-MP analyzer. The Mott-Schottky curves were measured using a CHI760E electrochemical analyzer (China) in a three-electrode cell. Pt plate was used as counter electrode and Ag/AgCl electrode (3 M KCl) was used as reference electrode. The electrolyte was a 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution. The working electrode was prepared on fluorine-doped tin oxide

(FTO) glass by dipping the mixed slurry containing the sample and H<sub>2</sub>O, and the exposed area of the electrode was 0.25 cm<sup>2</sup>. Cyclic voltammograms (CV) were recorded using a CHI-760E electrochemical workstation with platinum plate as working electrode, Ag/AgCl (3 M KCl) as reference electrode, Pt wire as counter electrode. CVs were measured using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte in CHCl<sub>3</sub> with a scan rate of 100 mV s<sup>-1</sup>. The photocatalytic hydrogen production system was Perfect Light Lab Solar-IIIAG and H<sub>2</sub> measurement was performed on Agilent Technologies 78. The amounts of Pt NPs were detected by ICP-AES (spectra range: 120-800 nm, holographic grating, 2924 line/mm, SPECTRO CIROS VISION). Attenuated total reflection Fourier transformed infrared (ATR-IR) spectra were monitored by Frontier FT-IR spectrometer (spectra range 4000-450 cm<sup>-1</sup>, an average of 64 scans). Electrochemical impedance spectra (EIS) and photocurrent-time (i-t) curves were obtained using a CHI-760E electrochemical workstation and a 300 W Xe lamp equipped with an electric shutter and an optical filter ( $\lambda > 420$  nm) to cut off the light in the ultraviolet region. The electrochemical cell used was equipped with three electrodes including a carbon bar counter-electrode, an Ag/AgCl reference electrode (3 M KCl) and a fluorin-doped tin oxide (FTO) glass functionalized with photocatalysts as working electrode. Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) was used as the supporting electrolyte. Specifically, EIS measurements were implemented with 10 mV amplitude sinusoidal perturbation in a scanning frequency range of 10<sup>-2</sup> - 10<sup>6</sup> Hz and an applied bias potential of 0.5 V (vs. Ag/AgCl) under illumination, while i-t curves were obtained with an applied bias potential of 0.5 V (vs. Ag/AgCl) under on-off switching illumination.

### **Photocatalytic hydrogen production.**

The photocatalytic hydrogen evolution by water splitting was performed in a glass reaction cell with quartz cover connected to a closed gas circulation, which was swept by high purity Ar before illumination. 50 mg photocatalysts were dispersed in 100 mL of 10 vol% TEOA aqueous solution (pH  $\approx$  12). Then the suspension was exposed to a 300 W Xe lamp equipped with an optical filter ( $\lambda > 420$  nm). The reaction solution

was stirred continuously and cooled to room temperature by a circulation of cooling water. The amount of hydrogen evolved was determined at an interval of 1 h with online gas chromatography.

#### **Determination of apparent quantum yield (AQY).**

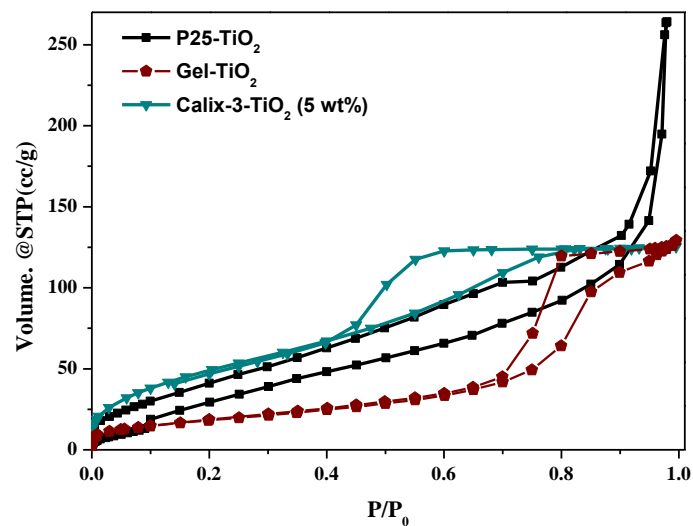
The photocatalytic mixture was irradiated by an incident LED light source (Zolix, MLED4-1, M450L,  $\lambda = 450$  nm, light intensity  $100 \text{ mW cm}^{-2}$ , irradiating area  $0.8 \text{ cm}^2$ ) at  $20^\circ\text{C}$ . The number of incident photons was measured by a standard method using a  $\text{K}_3[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]$  actinometer and the photon flux was determined to be  $1083 \mu\text{mol h}^{-1}$ . The generated  $\text{H}_2$  gas was analyzed by an Agilent 7820A gas chromatography with a thermal conductivity detector (TCD).

AQY ( $\Phi$ ) was calculated according to the following equation:

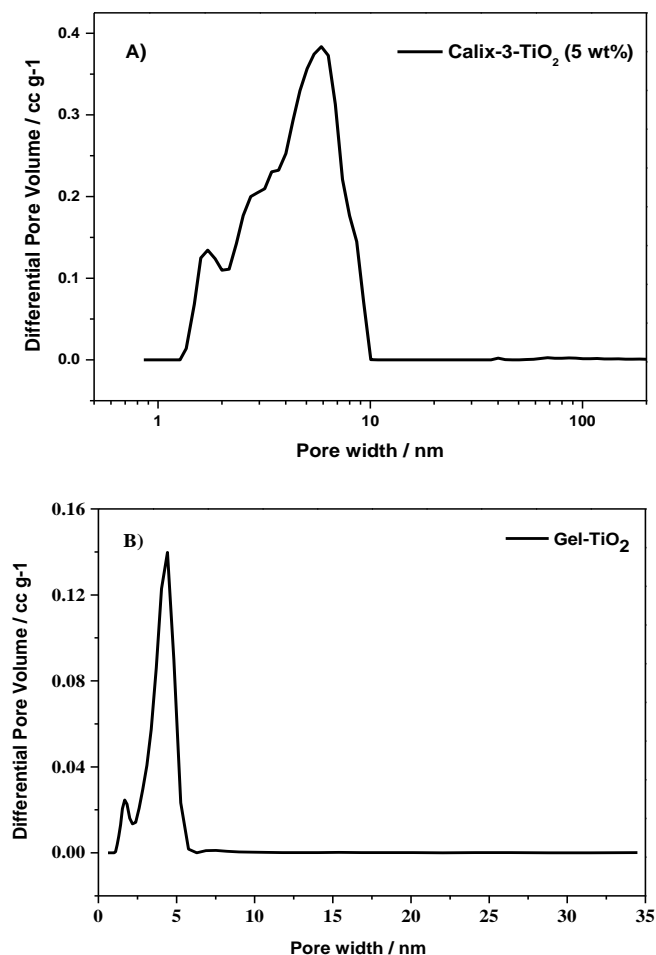
$$\phi = \frac{\text{number of transferred electrons}}{\text{number of incident photons}} \times 100\% = \frac{n(\text{H}_2) \times 2}{n(\text{photons})} \times 100\%$$

#### **Reference**

1. L.-L. Tan, J.-M. Liu, S.-Y. Li, L.-M. Xiao, D.-B. Kuang, C.-Y. Su. *ChemSusChem*, 2015, **8**, 280.



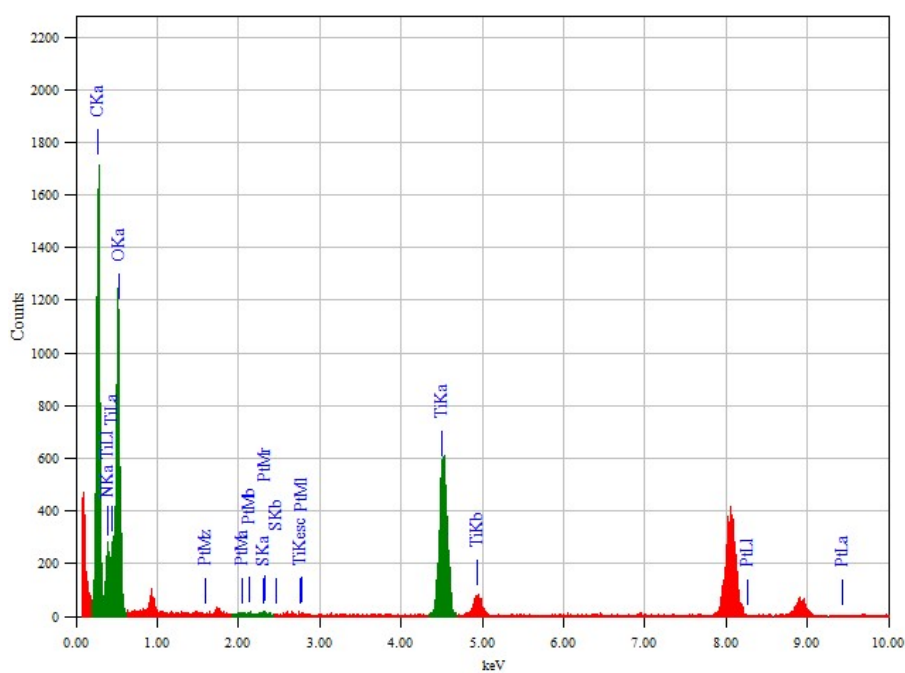
**Fig. S1.** N<sub>2</sub> adsorption-desorption isotherms of Calix-3-TiO<sub>2</sub> (5 wt%), Gel-TiO<sub>2</sub> and P25-TiO<sub>2</sub> measured under 77 K.



**Fig. S2.** The pore size distribution of A) Calix-3-TiO<sub>2</sub> (5 wt%) and B) Gel-TiO<sub>2</sub>.

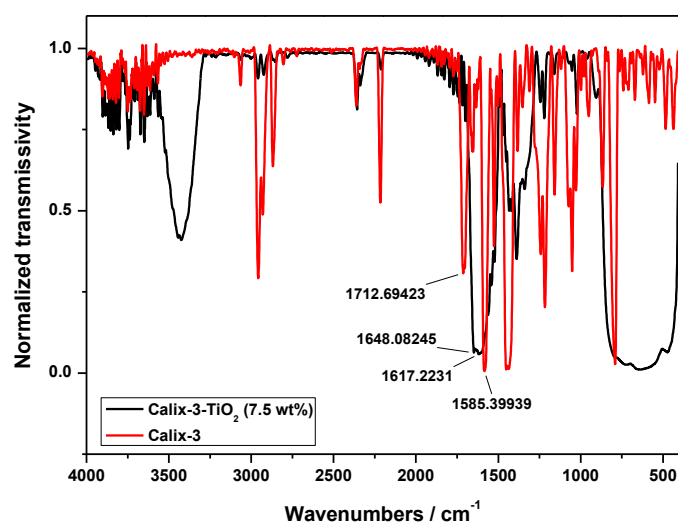
**Table S1.** BET surface area, pore volume and pore width of Calix-3-TiO<sub>2</sub> (5 wt%), Gel-TiO<sub>2</sub> and P25-TiO<sub>2</sub> derived from 77 K N<sub>2</sub> sorption isotherms.

Sample	Surface Area (m <sup>2</sup> /g)	Pore volume (ml/g)	Pore width (nm)	
			mesopore	micropore
P25-TiO <sub>2</sub>	55.4	0.162	29.40	
Calix-3-TiO <sub>2</sub> (5.0 wt%)	190.1	0.202	5.88	1.71
Gel-TiO <sub>2</sub>	162.9	0.233	4.41	1.68



**Fig. S3.** EDX of Pt/Calix-3-TiO<sub>2</sub> (5 wt%).





**Fig. S4.** ATR-IR spectra of **Calix-3** and Calix-3-TiO<sub>2</sub> (7.5 wt%).

**Table S2.** H<sub>2</sub> production data of Pt/Calix-3-TiO<sub>2</sub> with different dye content, Pt/Gel-TiO<sub>2</sub>/Calix-3 (2.87 wt%), and Pt/P25-TiO<sub>2</sub>/Calix-3 (2.35 wt%) materials.

Materials	Activity/	Activity/	TON <sub>[Pt]</sub> (5 h) <sup>[c]</sup> TON <sub>[dye]</sub> (5 h) <sup>[d]</sup>	
	mmol g <sup>-1</sup> h <sup>-1</sup> <sup>[a]</sup>	mmol g <sup>-1</sup> <sub>[Pt]</sub> h <sup>-1</sup> <sup>[b]</sup>		
Pt/Calix-3-TiO <sub>2</sub> (1 wt%)	4.85	970	946	4881
Pt/Calix-3-TiO <sub>2</sub> (2 wt%)	7.18	1437	1401	3614
Pt/Calix-3-TiO <sub>2</sub> (5 wt%)	10.36	2072	2020	2084
Pt/Calix-3-TiO <sub>2</sub> (7.5 wt%)	12.22	2444	2384	1639
Pt/Calix-3-TiO <sub>2</sub> (10 wt%)	11.29	2258	2202	1136
Pt/Gel-TiO <sub>2</sub> /Calix-3 (2.87 wt%)	3.62	724	706	1269
Pt/P25-TiO <sub>2</sub> /Calix-3 (2.35 wt%)	2.09	418	407	895

[a] = (H<sub>2</sub> amount in 5 h/ total mass of catalysts) / 5 h

[b] = H<sub>2</sub> amount vs. Pt loading mass = [a] / Pt loading mass fraction = [a] / 0.005

[c] = H<sub>2</sub> amount vs. Pt loading amount = [b] × 5 × 195.05 / 1000

[d] = H<sub>2</sub> amount vs. dye loading amount = [a] × 5 × 0.001 × 2012<sup>[e]</sup> / corresponding dye loading mass fraction

[e] Molecular weight of Calix-3

**Table S3.** Performances of organic photosensitizers (PS) in photocatalytic H<sub>2</sub> production studies in recent years<sup>a</sup>

No.	reference	PS	activity	TON <sub>[dye]</sub>	time
1	<i>ChemSusChem</i> , 2018, <b>11</b> , 793.	AD418	4359 $\mu\text{mol/g}$	872 <sup>b</sup>	20 h
2	<i>Appl. Energy Mater.</i> , 2018, <b>1</b> , 2813.	ChI+Ind	4176 $\mu\text{mol/g}$	1044 <sup>b</sup>	6 h
3	<i>Org. Lett.</i> , 2017, <b>19</b> , 1048.	S1	63112 $\mu\text{mol/g}$	10200	48 h
4	<i>Susta. Energy Fuels</i> , 2017, <b>1</b> , 694.	CBZ-Th	10083 $\mu\text{mol/g}$	2017	20 h
5	<i>Int. J. Hydro. Energy</i> , 2017, <b>42</b> , 15731.	ChI-2	1,580 $\mu\text{mol/g}$	—	6 h
6	<i>Dyes Pigm.</i> , 2017, <b>139</b> , 7.	YFT-2	10438 $\mu\text{mol/g}$	712 <sup>b</sup>	10 h
7	<i>Dyes Pigm.</i> , 2016, <b>134</b> , 498.	D2	106,667 $\mu\text{mol/g}$	1640 <sup>b</sup>	16 h
8	<i>J. Mater. Chem. A</i> , 2015, <b>3</b> , 21713.	C16	42,576 $\mu\text{mol/g}$	2930 <sup>b</sup>	20 h
9	<i>Int. J. Hydro. Energy</i> , 2015, <b>40</b> , 9069.	DN5	93,200 $\mu\text{mol/g}$	1864 <sup>b</sup>	6 h
10	<i>New J. Chem.</i> , 2015, <b>39</b> , 713.	D2@NPT	566.9 $\mu\text{mol/g}$	10901	6 h
11	<i>Phys. Chem. Chem. Phys.</i> , 2015, <b>17</b> , 13710	DNPT	1208 $\mu\text{mol/g}$	9664	10 h

<sup>a</sup>Only the best performance in each study is listed.

<sup>b</sup>In the references, TON values were calculated by the equal:  $\text{TON} = (2 \times \text{amount of H}_2) / \text{amount of dye}$ .

**Table S4.** H<sub>2</sub> production and AQY results of Calix-3-TiO<sub>2</sub> after 1h irradiation under 450 nm LED light source.

photocatalyst	n(H <sub>2</sub> ) / $\mu\text{mol}$	AQY / %
Pt/Calix-3/P25-TiO <sub>2</sub>	2.02	0.37
Pt/Calix-3/Gel-TiO <sub>2</sub>	3.40	0.63
Pt/Calix-3-TiO <sub>2</sub> (1 wt%)	4.45	0.82
Pt/Calix-3-TiO <sub>2</sub> (2 wt%)	8.63	1.59
Pt/Calix-3-TiO <sub>2</sub> (5 wt%)	12.70	2.34
Pt/Calix-3-TiO <sub>2</sub> (7.5 wt%)	15.67	2.89
Pt/Calix-3-TiO <sub>2</sub> (10 wt%)	13.14	2.43

**Table S5.** Cyclic H<sub>2</sub> production data of Calix-3-TiO<sub>2</sub> (7.5 wt%) hybrid material.

Cycle	Activity /mmol g <sup>-1</sup> h <sup>-1</sup> [a]	Cumulative	Cumulative	TON <sub>[Pt]</sub> <sup>[d]</sup>	TON <sub>[dye]</sub> <sup>[e]</sup>
		hydrogen production/ mmol g <sup>-1</sup> [b]	hydrogen production/ mmol g <sup>-1</sup> [Pt] <sup>[c]</sup>		
1st	12.22	61.10	12221	2384	1639
2nd	12.30	122.60	24521	4783	3289
3rd	12.27	183.94	36788	7176	4935
4th	12.51	246.49	49297	9615	6612
5th	12.72	310.09	62018	12097	8319
6th	12.81	374.12	74825	14595	10036
7th	13.04	439.33	87867	17138	11786
8th	12.72	502.94	100588	19620	13492
9th	13.30	569.45	113891	22214	15277
10th	12.30	630.97	126193	24614	16927

[a] = (H<sub>2</sub> amount in 5 h/ total mass of catalysts) / 5 h

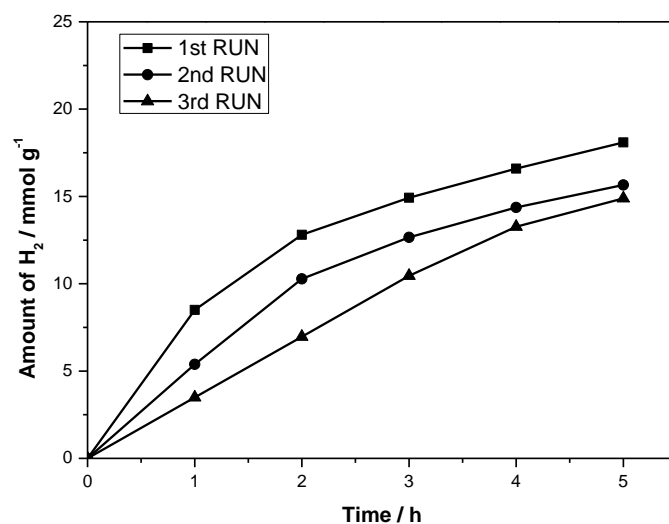
[b] Previous total hydrogen production

[c] H<sub>2</sub> amount vs. Pt loading mass = [b] / Pt loading mass fraction = [a] / 0.005

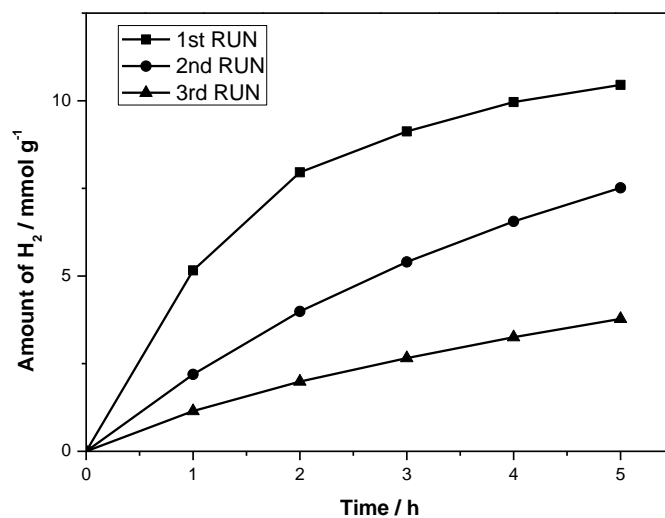
[d] H<sub>2</sub> amount vs. Pt loading amount = [c] \*195.05 / 1000

[e] = H<sub>2</sub> amount vs. dye loading amount = [c] ×0.001 × 2012<sup>[f]</sup> / 0.075

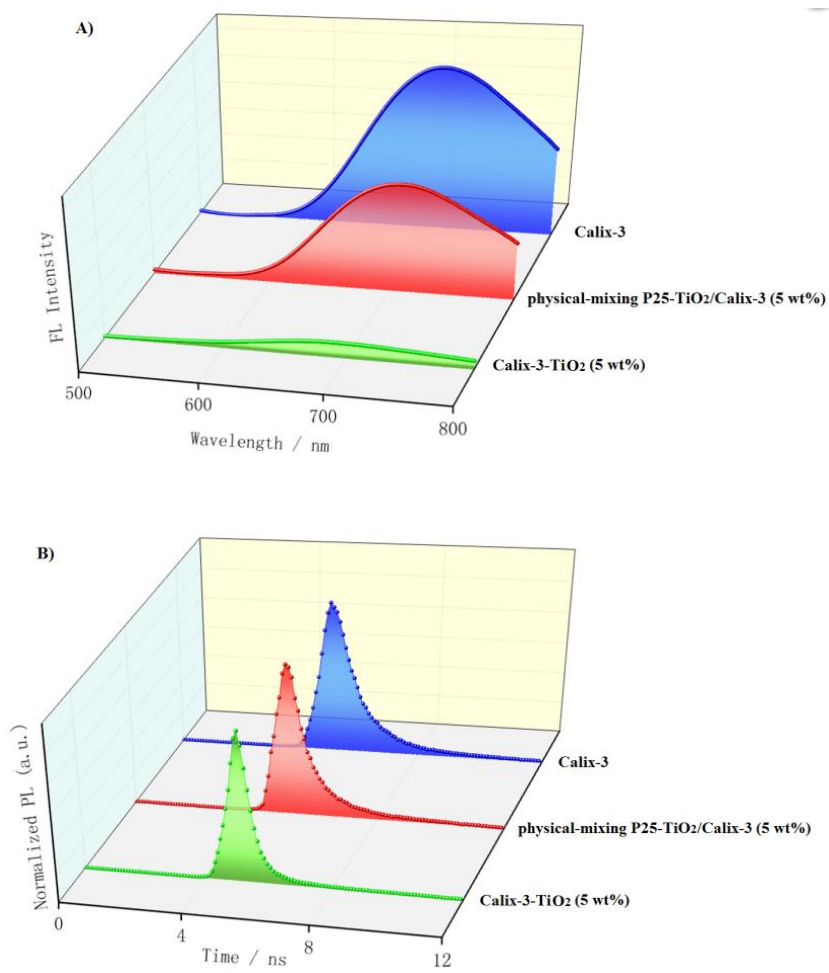
[f] Molecular weight of Calix-3



**Fig. S5.** Photocatalytic H<sub>2</sub> production over the recyclability of Gel-TiO<sub>2</sub>/Calix-3 (2.87 wt%) with 0.5 wt% Pt loading under visible light irradiation ( $\lambda > 420$  nm) in 100 mL H<sub>2</sub>O/TEOA (9:1, v/v).



**Fig. S6.** Photocatalytic H<sub>2</sub> production over the recyclability of P25-TiO<sub>2</sub>/Calix-3 (2.35 wt%) with 0.5 wt% Pt loading under visible light irradiation ( $\lambda > 420$  nm) in 100 mL H<sub>2</sub>O/TEOA (9:1, v/v).



**Fig. S7.** A) Emission spectra and B) photoluminescence decays of **Calix-3**, physical-mixing P25-TiO<sub>2</sub>/Calix-3 (5 wt%), and Calix-3-TiO<sub>2</sub> (5 wt%).