

## Supporting Information

### Unveiling localized Pt-P-N bonding states constructed on covalent triazine-based frameworks for boosting photocatalytic hydrogen evolution

*Ling-Ling Zheng,<sup>a,b</sup>¶ Dengke Wang,<sup>a,b</sup>¶ Shao-Lin Wu,<sup>a,b</sup> Xun-Heng Jiang,<sup>a,b</sup> Jun Zhang,<sup>a,b</sup> Qiu-Ju Xing,<sup>a,b</sup> Jian-Ping Zou<sup>a,b\*</sup> and Sheng-Lian Luo<sup>a,b</sup>*

<sup>a</sup> Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, PR China.

<sup>b</sup> National-Local Joint Engineering Research Center of Heavy Metals Pollutants Control and Resource Utilization, Nanchang Hangkong University, Nanchang 330063, PR China.

¶ These authors contributed equally to this manuscript.

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\* Author to whom all correspondences should be addressed.

E-mail: zjp\_112@126.com, Tel (Fax): 86-791-83953378

## Experimental Section

### 1. Materials

Bulk black phosphorus (BP) crystals were purchased from Nanjing XFNANO Materials Tech Co., Ltd. (XF161, >99.998%). N-methyl-2-pyrrolidone (NMP), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), anhydrous LiOH and terephthalonitrile ( $\text{C}_8\text{H}_4\text{N}_2$ , 98%) were obtained from Aldrich. Triflic acid (98%) and anhydrous  $\text{ZnCl}_2$  (98%) were acquired from Macklin. Trichloromethane ( $\text{CHCl}_3$ , 99.5%) was provided from Nanchang XinGuang Co.. Methanol (AR) was purchased from Xilong Chemical Co.. All of the chemicals were commercially available and used without further purification.

### 2. Syntheses

#### 2.1 Synthesis of covalent triazine frameworks (CTF-1)

CTF-1 was synthesized following a previously reported method with slight modifications. Typically, triflic acid (19.96 g, 133.0 mmol) was added into a pre-dried three-neck round bottom flask containing  $\text{CHCl}_3$  (30 mL) at 0 °C under Ar atmosphere. Then, terephthalonitrile (4.26 g, 33.25 mmol) dissolved in  $\text{CHCl}_3$  (200 mL) was slowly dropwised into the above resulted mixture with vigorous stirring. The resulted mixture was continuously stirred for 2 h at 0 °C and then heated to 40 °C for 48 h. After cooled down to room temperature, the solid precipitate was rapidly added to 660 mL of deionized water containing 34 mL of ammonia solution (25 %) and stirred for 2 h. The precipitate was obtained by filtration and washed successively with deionized water, ethanol, acetone and chloroform. The yellow product was dried overnight at 60 °C in an oven. The obtained yellow solid was thoroughly mixed with  $\text{ZnCl}_2$  in a mole ratio of 1 : 0.8, and treated at 400 °C under argon for 10 min. After cooling to room temperature, the solid was ground and washed with deionized water and dilute HCl solution (0.1 M) several times, and dried overnight at 60 °C in an oven.

#### 2.2 Synthesis of ultrathin BP nanosheets

Ultrathin BP nanosheets was synthesized by a mechanochemical ball-milling method. Typically, a mixture of 300 mg bulk BP powders and 700 mg anhydrous LiOH powder was put into a ball-milling jar containing steel balls with *ca.* 1 mm diameter. The jar was sealed under Ar atmosphere and finally equipped with planetary

ball-milling machine. The ball-milling process was performed at ambient temperature for 12 h with rotation speed of 250 rpm. After ball-milling, the N<sub>2</sub>-treated deionized water was added quickly to the jar to remove the excess LiOH. Then, the resulted suspension was collected by centrifugation, and dried under vacuum at 60 °C.

### **2.3 Synthesis of CTF-BP composite**

The as-prepared CTF-1 (93 mg) was added into NMP solvent (10 mL) under sonication condition to form homogeneous suspension. Then, BP nanosheets were added into above suspension and continued ultrasound for 4 h. The resulted mixture was kept stirring overnight. Afterward, the sample was collected by centrifugation and washed with ethanol thoroughly, and dried overnight in an oven at 60 °C.

### **2.4 Synthesis of the CTF-BP-Pt**

CTF-BP-Pt was prepared via a self-assembly method followed by a photo-deposition approach. CTF-BP (200 mg) was placed into a Schlenk tube containing methanol (20 mL) under stirring conditions. Then, X wt% Pt loading amount (X represents the weight ratio of Pt in final sample, X = 0.05, 1, 2, 5) was performed by adding certain amount of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O into the above mixture. The resulting mixture was stirred under a N<sub>2</sub> atmosphere for 30 min and irradiated with a 300 W Xe lamp equipped with a UV-cut filter to remove light with wavelengths < 420 nm and an IR-cut filter to remove light with wavelengths > 800 nm. After being illuminated for 4 h, the resultant sample was filtered, further washed with MeOH, and dried overnight at 60 °C in an oven. For comparison, Pt doped CTF-1 (denoted as CTF/Pt) was prepared with procedures similar to CTF-BP-Pt.

## **3. Characterizations**

X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded at a scanning rate of  $0.02^\circ/2\theta \text{ s}^{-1}$  with  $2\theta$  ranging from  $5^\circ$  to  $60^\circ$ . UV-visible diffuse reflectance spectra (UV-vis DRS) of the powders were obtained with BaSO<sub>4</sub> used as a reflectance standard. The scanning electron microscopy (SEM) images were collected with a Nova Nano SEM 230 microscope (FEI, Hillsboro, OR,

USA). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL model JEM 2010 EX instrument. Fourier transformed infrared (FTIR) spectra of the samples were recorded by a VERTEX-70 spectrometer using KBr as reference. Raman spectra were obtained on an inVia-Reflex micro-Raman spectroscopy system (Renishaw Co.) with 633 nm line of an Ar ion laser at room temperature. The element composition and valence state of catalysts were identified by X-ray photoelectron spectroscopy (XPS) (VG 250 Escalab spectrometer and Al-K = 1486.7 eV). Solid-state NMR spectra (crosspolarization magic-angle spinning (CP/MAS)) were carried out on a Bruker Avance 400 MHz spectrometer operating at 100.6 MHz for  $^{31}\text{P}$ . Photoluminescence (PL) spectra were carried out on a fluorescence spectrometer (Hitachi F-4500). Time-resolved fluorescence decay spectroscopy was measured using a time correlated single-photon counting system (FS5 Spectrofluorometer, Edinburgh Instruments) which used a 380 nm picosecond pulsed diode laser (EPLD-380, Max Average Power 40  $\mu\text{W}$ ) as the excitation source. Zeta potential of the as-prepared samples was measured by a zeta potential analyzer (Malvern) in pH=7.5 NMP solutions (NMP: refractive index = 1.468, viscosity = 1.65).

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China), in the standard three-electrode cell system. There were platinum electrodes as counter electrode and standard calomel reference electrode in saturated KCl. The working electrodes were prepared by dip-coating method. Typically, the samples were dip-coated onto a 1 cm  $\times$  1 cm fluorine-tin oxide (FTO) glass electrode and dried at room temperature.  $\text{Na}_2\text{SO}_4$  (0.5 M) was used as electrolyte. As for photocurrent measurements, a 300 W Xe lamp (Perfect light PLS-SXE300C) was used as the source of simulated solar irradiation and the other conditions were the same as those of electrochemical measurements. Electrochemical impedance spectroscopy (EIS) and linear sweep voltammograms (LSV) were carried out in  $\text{Na}_2\text{SO}_4/\text{K}_3(\text{Fe}(\text{CN})_6)/\text{K}_4(\text{Fe}(\text{CN})_6)$  mixed solution with the frequency ranging from 0.01 Hz to 100 kHz at 0.24 V, and the amplitude of the applied sine wave potential in each case was 5 mV.

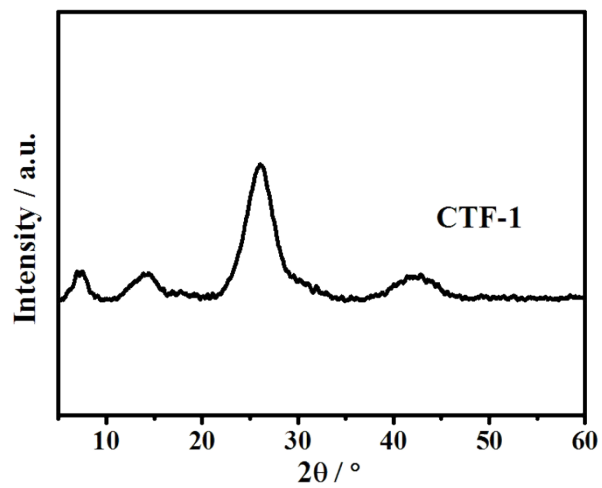
#### 4. Test of photocatalytic activity

The experiments of photocatalytic H<sub>2</sub> evolution were carried out using a Pyrex top-irradiation reaction vessel connected to a glass closed gas system (Prefect Light, Beijing, Labsolar-III(AG) in a Pyrex flask). A 300 W Xe lamp (Perfect light PLS-SXE300C; Wavelength range:  $\lambda > 420$  nm, light intensity: 160 mW/cm<sup>2</sup>) was used as the visible light source. The as-prepared catalyst (20 mg) was uniformly dispersed in 80 mL of aqueous solution containing triethanolamine (8 mL). The system was vacuum-treated several times to remove the dissolved air. The amount of H<sub>2</sub> evolved was determined using an on-line gas chromatograph equipped with a TCD detector. In order to ensure the reliability of the experimental results, the experiments of photocatalytic H<sub>2</sub> evolution were repeated three times and the final values shown in the text are the mean values of triplicate results.

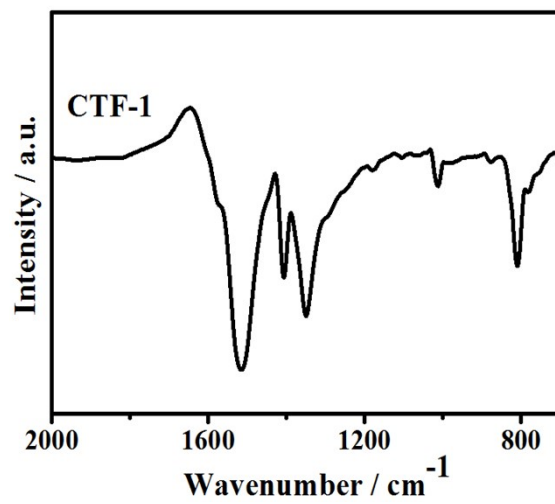
#### 5. Turnover Frequency (TOF)

The turnover Frequency (TOF) is defined the number of molecules of reactants converted per active center per unit time, TOF<sub>Pt</sub> is defined the number of molecules of reactants converted per Pt nanoparticles per unit time.

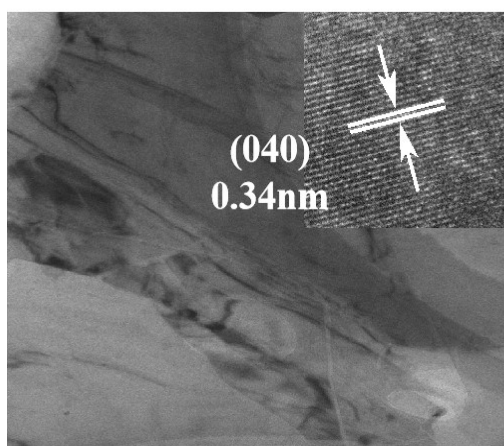
$$\text{TOF} = \frac{\text{mol}_{\text{H}_2}}{\text{mol}_{\text{cat.}} * \text{time}} \quad \text{TOF}_{\text{Pt}} = \frac{\text{mol}_{\text{H}_2}}{\text{mol}_{\text{Pt.}} * \text{time}}$$



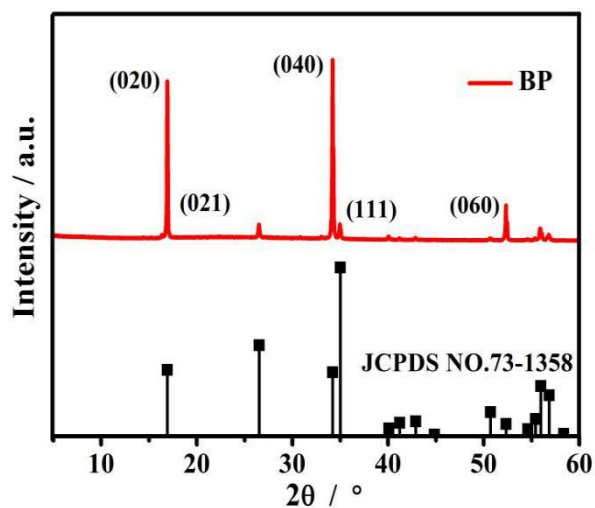
**Fig. S1** XRD patterns of the CTF-1.



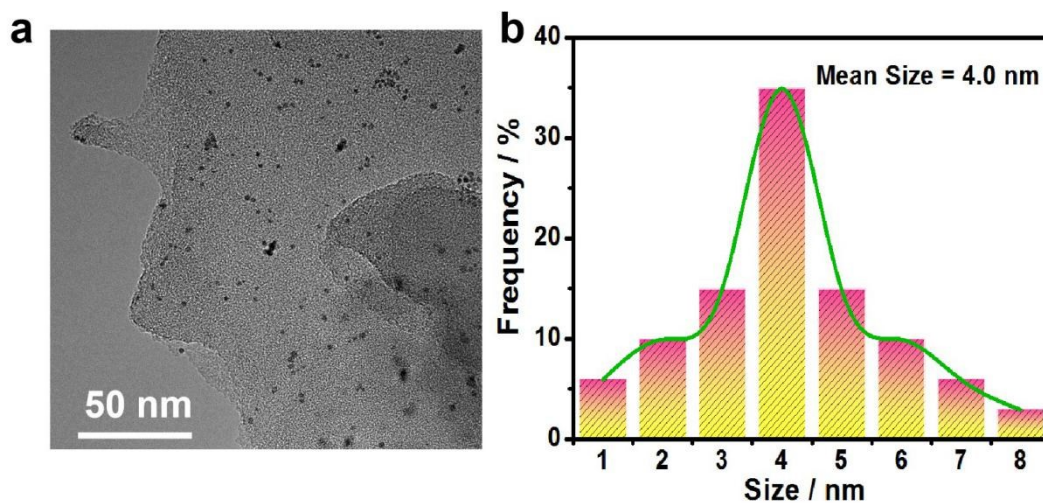
**Fig. S2** FTIR of the CTF-1.



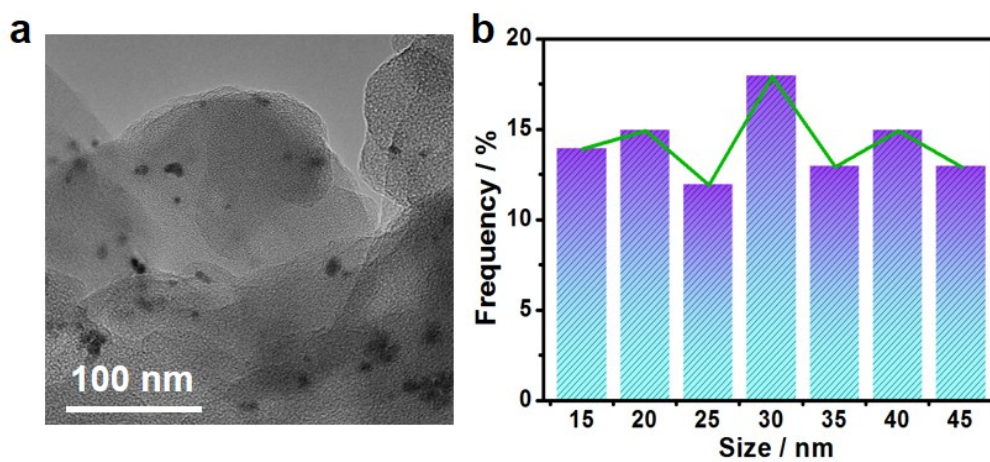
**Fig. S3** TEM of the BP nanosheets exfoliated by ball Milling



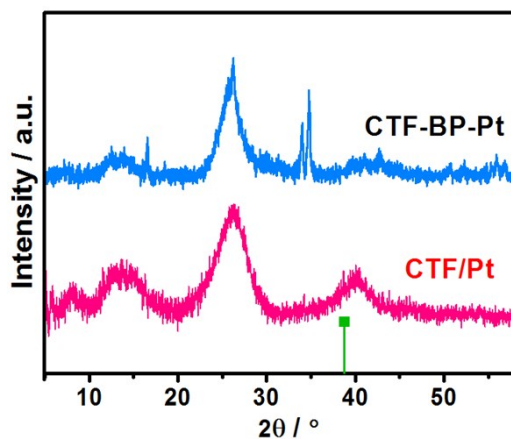
**Fig. S4** XRD patterns of the BP nanosheets.



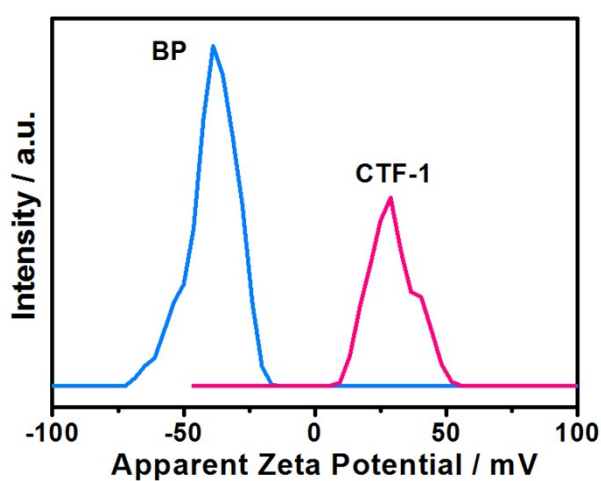
**Fig. S5** (a) TEM image and (b) Pt nanoparticles size distribution histogram of the used CTF-BP-Pt.



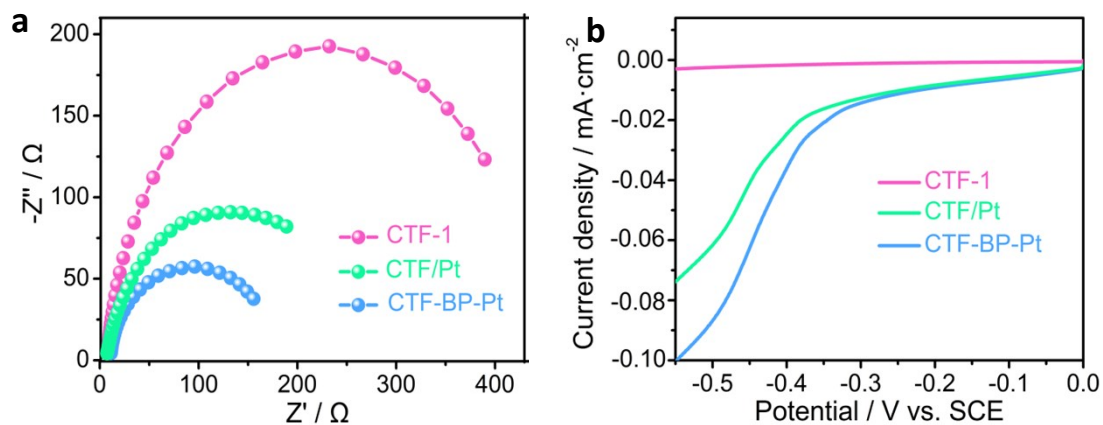
**Fig. S6** (a) TEM image and (b) Pt nanoparticles size distribution histogram of the used CTF/Pt.



**Fig. S7** XRD patterns of the CTF-BP-Pt and CTF/Pt.

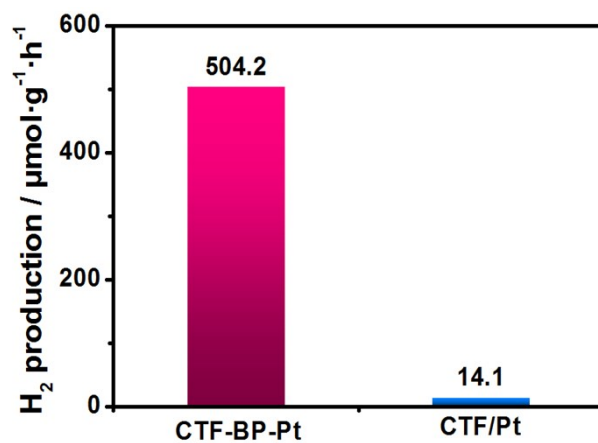


**Fig. S8** Zeta Potential of CTF-1 and BP nanosheets in pH=7.5 NMP solution.

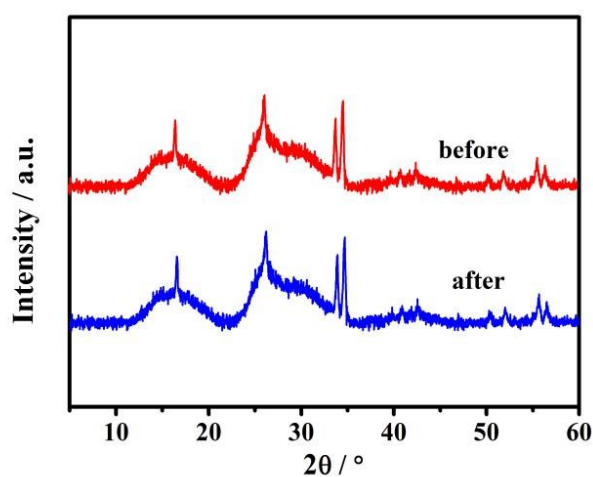


**Fig. S9** Electrochemical Impedance spectra nyquist plots and Linear sweep voltammograms of the CTF-1, CTF/Pt and CTF-BP-Pt.

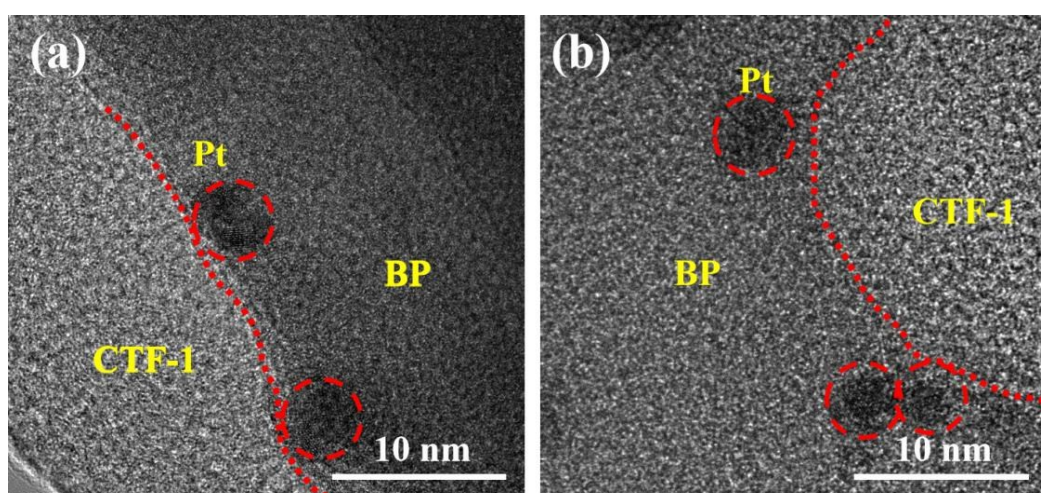




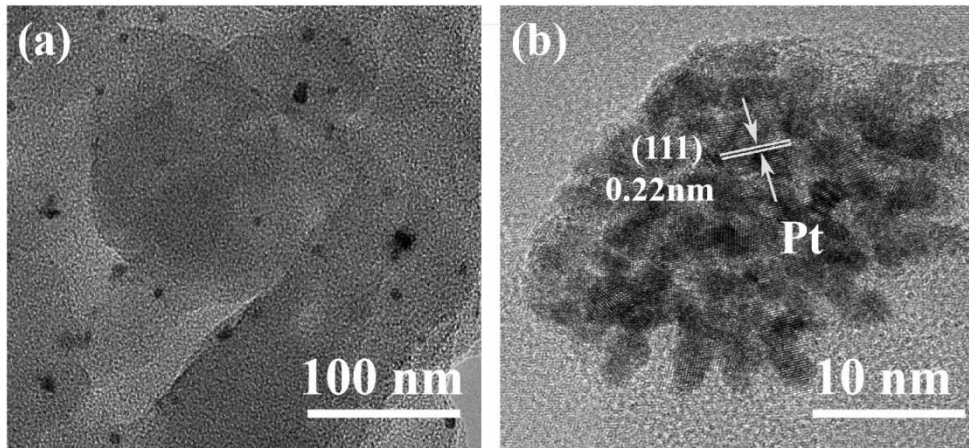
**Fig. S10** Photocatalytic H<sub>2</sub> evolution rate of CTF/Pt and CTF-BP-Pt (with 0.05 wt% Pt nanoparticles loading).



**Fig. S11** XRD patterns of CTF-BP-Pt before and after photocatalytic reaction.



**Fig. S12** TEM images of CTF-BP-Pt (a) before and (b) after photocatalytic reaction.



**Fig. S13** TEM of CTF/Pt after photocatalytic reaction.

**Table S1.** Exponential decay-fitted parameters of fluorescence lifetime for the CTF-1, CTF-BP-Pt and CTF/Pt samples.

Sample	$A_1$	$A_2$	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_{ave}$ (ns)
CTF-1	0.229	0.031	0.44	2.71	1.26
CTF/Pt	0.158	0.032	0.70	3.40	2.04
CTF-BP	0.134	0.033	0.78	3.92	2.15
CTF-BP-Pt	0.126	0.038	0.94	4.24	<b>2.84</b>

The tri-exponential function as follows:

$$R(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

Meanwhile, the average lifetime ( $\tau_{ave}$ ) was calculated using following equation

$$\tau_{ave} = \frac{\tau_1^2 A_1 + \tau_2^2 A_2}{\tau_1 A_1 + \tau_2 A_2} \quad (2)$$

where  $\tau_1$ , and  $\tau_2$  are the emission lifetimes, and  $A_1$ , and  $A_2$  are the corresponding amplitudes. In general, the longer decay lifetime component  $\tau_1$  is considered to free exciton recombination in the CTF-1 and its composites, and the shorter decay lifetime components  $\tau_2$  are ascribed to the surface-related nonradiative recombination of the charge carriers.