

Electronic Supplementary Information

**Synthesis of condensed C-PDA/g-C<sub>3</sub>N<sub>4</sub> composites with superior photocatalytic performance**

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## **Experimental Section**

### **1. Materials**

Melamine ( $C_3H_6N_6$ ) and chloroplatinic acid hexahydrate ( $H_2PtCl_6 \cdot 6H_2O$ ) were purchased from Sigma-Aldrich. Dopamine hydrochloride and tris(hydroxymethyl) aminomethane were purchased from Sigma-Aldrich (USA) and Aladdin (China), respectively. Triethanolamine (TEOA) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All chemicals were used as received without further treatment.

### **2. Preparation of photocatalysts.**

The pure g- $C_3N_4$  or C-PDA was prepared by directly heating melamine or PDA at 650 °C for 2 h in a gentle Argon flow. The C-PDA/g- $C_3N_4$  photocatalyst was prepared as follows: Firstly, 2 g melamine was dispersed in 50 mL Tris-HCl buffer (pH: ~8.5) by ultrasonication for 20 min to form a suspension. Subsequently, a certain mass of dopamine (20, 30, 60 mg) was respectively added to the suspension under continuous magnetic stirring at room temperature for 2 h. Afterwards, the polydopamine/melamine composite was collected by centrifugation, and washed three times with deionized water, and then dried at 60 °C in an oven for 12 h. Lastly, the mixture was transferred into an alumina boat and sintered in a gentle Argon flow at 650 °C for 2 h. The obtained composite was denoted as 1wt% C-PDA/g- $C_3N_4$ , 1.5wt% C-PDA/g- $C_3N_4$ , and 3wt% C-PDA/g- $C_3N_4$ , respectively.

### **3. Characterization.**

X-ray diffraction (XRD) were measured using a Rigaku D/max-2000 diffractometer with Cu K $\alpha$  radiation ( $\lambda=0.15406$  nm). Fourier transform infrared (FTIR) spectra were

measured utilizing IR Affinity-1 spectrometer. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Renishaw InVia) using an excitation source of 532 nm Ar<sup>+</sup> laser. Elemental analysis (EA) was performed on Vario EL cube elemental. The morphologies of the photocatalysts were carried out on a FEI, Tecnai G2 S-Twin transmission electron microscopy (TEM). The BET specific surface area was calculated from Nitrogen adsorption–desorption isotherms determined on an AUTOSORB-1-MP surface analyzer at 77 K. The UV–vis diffuse reflectance spectra (DRS) were recorded on a TU-1900 spectrophotometer and were converted from reflection to absorbance through the standard Kubelka–Munk method using BaSO<sub>4</sub> as the reflectance standard. The photoluminescence (PL) spectra and time-resolved fluorescence decay spectra were obtained on Edinburgh FLS 920 Fluorescence spectrometer at room temperature using 375 nm as the excitation wavelength.

#### **4. Photoelectrochemical Measurements.**

Electrochemical measurements were carried out in a standard three-electrode system on a CHI 660 C electrochemical instrument. Using Pt flake, Ag/AgCl (in saturated KCl), and prepared electrodes respectively act as counter electrode, reference electrode, and working electrodes. Using a 300 W Xe arc lamp with a UV-cut off filter ( $\lambda > 400$  nm) as light source and 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the electrolyte. EIS Nyquist plots were obtained with amplitude of 5 mV over the frequency range of 10<sup>5</sup> to 10<sup>-1</sup> Hz. Working electrodes were prepared as follows: First, FTO glass was cleaned by sonication with distilled water, acetone and ethanol respectively for 30 min. Then, 0.05 g of g-C<sub>3</sub>N<sub>4</sub> or C-PDA/g-C<sub>3</sub>N<sub>4</sub>

photocatalyst was ground with 1 mL terpineol to make slurry and the slurry was coated onto 1 cm × 2 cm FTO glass electrode by the spin coater. Last, the electrode was dried in an oven at 200 °C overnight.

## **5. Photocatalytic Reactions**

### **5.1 Photocatalytic H<sub>2</sub> evolution Reactions.**

The photocatalytic H<sub>2</sub> evolution reactions were performed in a gas-tight circulation system with a side window. 0.1 g photocatalyst powder was suspended in 300 mL aqueous solution containing 10 vol % triethanolamine as a sacrificial agent, loading 1.5 wt % Pt as cocatalyst by photodeposition of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O. The suspensions were stirred and irradiated under a 300 W Xe lamp with a cutoff filter ( $\lambda > 400$  nm). Prior to irradiation, suspensions were dispersed by sonication for 5 min and N<sub>2</sub> was purged through the system for 25 min to remove oxygen. The amount of evolved H<sub>2</sub> was detected by an online gas chromatography (Agilent 7890, TCD) with Argon as the carrier gas.

### **5.2 Photocatalytic O<sub>2</sub> evolution Reactions**

Photocatalytic O<sub>2</sub> evolution reaction was measured in a vacuum system. 0.1 g catalyst powder was dispersed in 100 mL aqueous solution containing 0.01 mol L<sup>-1</sup> AgNO<sub>3</sub> as an electron acceptor and 0.2 g La<sub>2</sub>O<sub>3</sub> as a pH buffer agent. The reactant solution was deaerated in a vacuum system for 30 min to remove air completely prior to irradiation with a 300 W Xe lamp. The photocatalytic reaction was carried out at 278 K. The amount of evolved O<sub>2</sub> was detected by an online gas chromatography (Agilent 7890, TCD) with Argon as the carrier gas.

### 5.3 Photocatalytic degradation of RhB

The photo-oxidation activity of the photocatalysts was evaluated via the photocatalytic degradation of RhB under visible light irradiation ( $\lambda > 400$  nm). In a typical experiment, 0.05 g photocatalyst was suspended in 100 mL  $10 \text{ mg L}^{-1}$  RhB solution. The suspension was first dispersed by sonication for 5 min and stirred for 1 h in the dark to obtain adsorption–desorption equilibrium between the RhB and the photocatalyst. The suspension was then stirred and irradiated under a 300 W Xe lamp with a cutoff filter ( $\lambda > 400$  nm). During the irradiation process, about 4 mL of suspension was taken from the reaction cell every 10 min and centrifuged to remove the photocatalyst. The absorbance of the RhB solution in degradation was detected on TU–1900 UV–vis spectrophotometer.

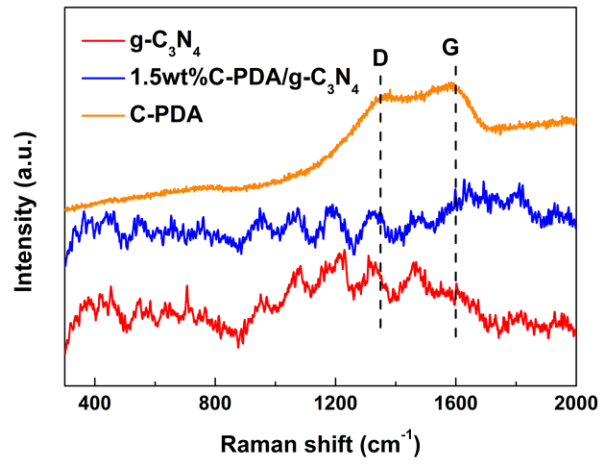
Calculation details of the apparent quantum efficiency (AQE)

The apparent quantum efficiency (AQE), which is widely used to evaluate the performance of photocatalysts for water splitting, could be calculated according to the following equations:

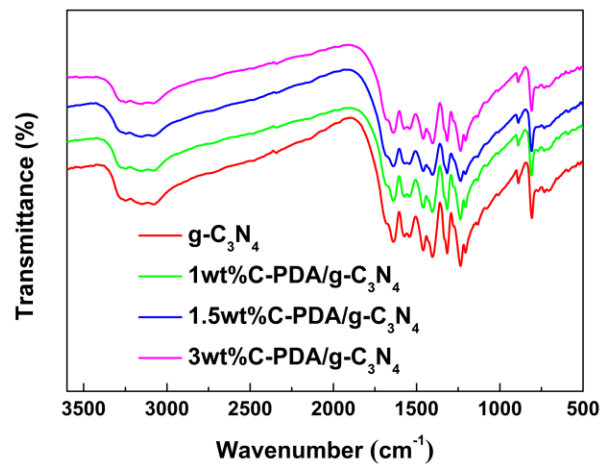
$$\begin{aligned} \text{QE}[\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ \text{AQE}[\%] &= \frac{2 \times \text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100 \\ &= \frac{2n_{\text{H}_2,t} N_A hc}{PSt\lambda_{\text{inc}}} \times 100 \end{aligned}$$

where  $n$  (mol) is the amount of evolved  $\text{H}_2$  over the irradiation time ( $t$ ) of the incident light,  $N_A$  ( $\text{mol}^{-1}$ ) is Avogadro's constant,  $h$  ( $\text{J}\cdot\text{s}$ ) is Planck's constant,  $c$  ( $\text{m s}^{-1}$ ) is the speed of light and  $\lambda_{\text{inc}}$  (m) is the wavelength of the incident monochromatic light,  $P$  ( $\text{W m}^{-2}$ ) is the power density of the incident monochromatic light,  $S$  ( $\text{m}^2$ ) is the irradiated area and  $t$  (s) is the irradiation time of incident light.

The Apparent quantum yields (AQE) of 1.5wt%C-PDA/g- $\text{C}_3\text{N}_4$  composite was measured under the irradiation of 420 nm monochromatic light for one hour. The intensity of incident light was measured to be  $6.7 \text{ mW cm}^{-2}$  by a FZ-A radiometer. The irradiation area was measured to be  $19.6 \text{ cm}^2$ . The photocatalytic  $\text{H}_2$  evolution rate of 1.5wt%C-PDA/g- $\text{C}_3\text{N}_4$  composite irradiated at 420 nm monochromatic light is  $20.6 \mu\text{mol h}^{-1}$ , with an apparent quantum efficiency of 2.3%.

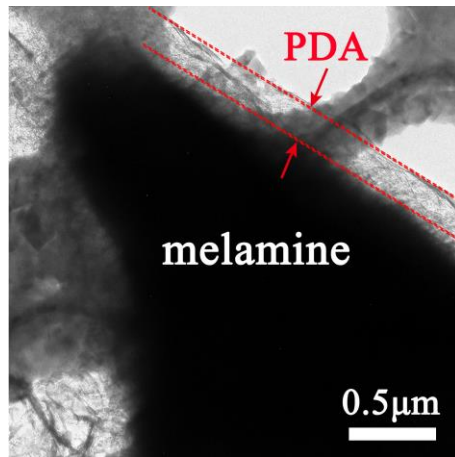


**Fig. S1** Raman spectra of pure g-C<sub>3</sub>N<sub>4</sub>, 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite and C-PDA, suggesting the existence of C-PDA in the C-PDA/g-C<sub>3</sub>N<sub>4</sub> composites.

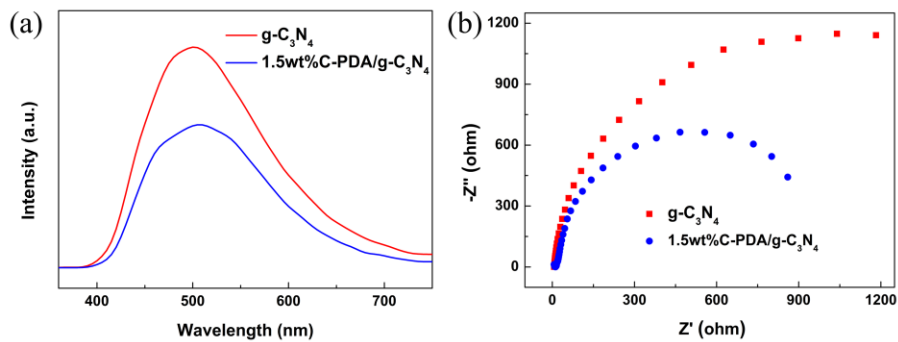


**Fig. S2** FT-IR spectra of pure g-C<sub>3</sub>N<sub>4</sub> and C-PDA/g-C<sub>3</sub>N<sub>4</sub> composites, which confirms the C-PDA/g-C<sub>3</sub>N<sub>4</sub> composites maintain the original structure of g-C<sub>3</sub>N<sub>4</sub>, and suggest the more complete condensation of melamine.

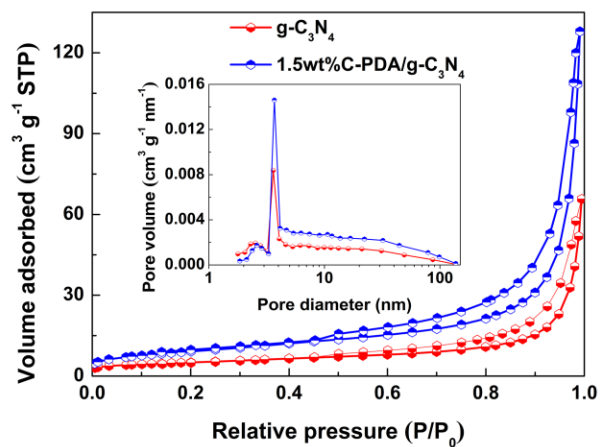




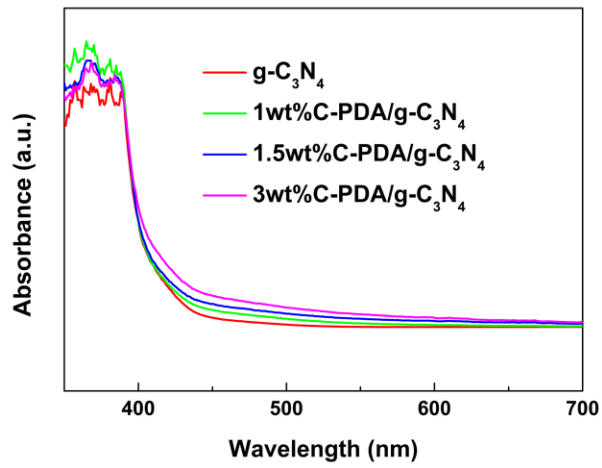
**Fig. S3** TEM image of 1.5wt% PDA/melamine composite, indicating the PDA coating formed on the surface of melamine.



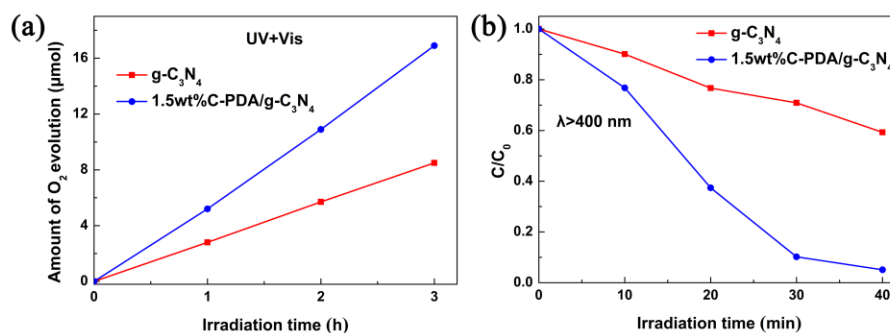
**Fig. S4** (a) Photoluminescence spectra under 375 nm excitation at room temperature and (b) EIS Nyquist plots obtained at an AC voltage over the frequency range of  $10^5$  to  $10^{-1}$  Hz with amplitude of 5 mV in  $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  aqueous solution under visible light irradiation ( $\lambda > 400$  nm) for g-C<sub>3</sub>N<sub>4</sub> and 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite.



**Fig. S5** Nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves (inset) of pure g-C<sub>3</sub>N<sub>4</sub> and 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite.

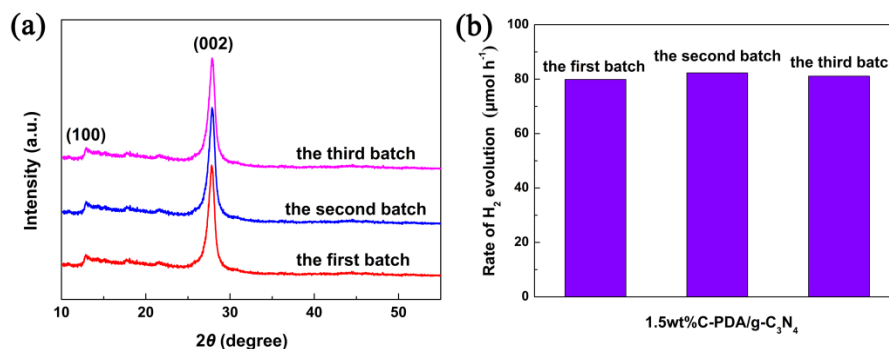


**Fig. S6** UV-vis absorption spectra converted from reflection to absorbance by the standard Kubelka-Munk method of pure g-C<sub>3</sub>N<sub>4</sub> and C-PDA/g-C<sub>3</sub>N<sub>4</sub> composites.



**Fig. S7** (a) Photocatalytic O<sub>2</sub> evolution from water using 0.01 mol L<sup>-1</sup> AgNO<sub>3</sub> as an electron acceptor and 0.2 g La<sub>2</sub>O<sub>3</sub> as a pH buffer agent under 300 W Xe lamp irradiation; (b) Photodegradation of RhB under visible light irradiation ( $\lambda > 400$  nm) for pure g-C<sub>3</sub>N<sub>4</sub> and 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite.

The photocatalytic performance for water oxidation and RhB degradation of pure g-C<sub>3</sub>N<sub>4</sub> and 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite has been investigated. The photocatalytic O<sub>2</sub> evolution reaction was first performed under UV+Vis light irradiation. Pure g-C<sub>3</sub>N<sub>4</sub> exhibits a moderate oxygen evolution rate (OER) of 2.8  $\mu\text{mol h}^{-1}$ , whereas 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite show enhanced OER of 5.6  $\mu\text{mol h}^{-1}$  at the same conditions (Fig. S7a). The photodegradation of RhB reaction was performed under visible light irradiation ( $\lambda > 400$  nm). 40 % of RhB is degraded on the pure g-C<sub>3</sub>N<sub>4</sub> after 40 min; while for the 1.5wt% C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite, RhB is almost completely degraded at the same conditions (Fig. S7b). This indicates that the C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite not only exhibits enhanced photocatalytic water oxidation activity, but also displays superior photocatalytic performance for RhB degradation.



**Fig. S8** (a) XRD patterns and (b) Photocatalytic H<sub>2</sub> evolution of 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite synthesis from three different batches.

In order to confirm the reproducibility of the synthesis of C-PDA/g-C<sub>3</sub>N<sub>4</sub> composites from batch to batch, the XRD patterns and the photocatalytic H<sub>2</sub> evolution performance of the 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite synthesis from three different batches have been investigated. The XRD patterns of 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite with three different batches exhibit two typical diffraction peaks at 13.0° and 27.7° (Fig. S8a). No position and intensity of the characteristic peaks change on the patterns of 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite from batch to batch, indicating that the as-prepared 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite maintains good reproducibility.

The photocatalytic H<sub>2</sub> evolution rate of 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite with three different batches is 79.9, 82.3, and 81.1 μmol h<sup>-1</sup> respectively, which further confirms the good reproducibility of 1.5wt%C-PDA/g-C<sub>3</sub>N<sub>4</sub> composite (Fig. S8b).