

*Electronic Supplementary Information (ESI)*

Rapid Joule heating synthesis of Pt/C<sub>3</sub>N<sub>4</sub>-NVs for  
photoelectrocatalytic water splitting to produce H<sub>2</sub>

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## 1. Experimental section

### 1.1. Chemicals

Melamine ( $C_3H_6N_6$ ,  $\geq 99\%$ ) was ordered from Sinopharm chemical Reagent co., Ltd.. Chloroplatinic acid hydrate ( $H_2PtCl_6 \cdot 6H_2O$ , AR), Palladium chloride ( $PdCl_2$ ,  $\geq 98\%$ ), Gold(III) chloride ( $AuCl_3$ ,  $\geq 99\%$ ), Silver nitrate ( $AgNO_3$ ,  $\geq 99\%$ ), Ruthenium chloride hydrate ( $RuCl_3 \cdot xH_2O$ ,  $\geq 99.95\%$ ) was bought from Shanghai Aladdin Biochemical Technology Co., Ltd.. Nafion (5%) was purchased from DuPont. Ultrapure water used throughout all experiments was purified through an ACMATE system.

### 1.2. Materials synthesis

Synthesis of  $C_3N_4$ : Typically, 10 g of melamine was put into a ceramic crucible covered with a layer of tin foil, and then heated to  $550^\circ C$  at a heating rate of  $10^\circ C/min$  in a muffle furnace for 4 h under an air atmosphere. Then, the yellow  $C_3N_4$  was collected after cooling down to room temperature.

Synthesis of  $C_3N_4$ -NVs: Firstly,  $C_3N_4$  was placed in a molybdenum boat and put into the Joule Heating equipment (In-situ High-tech, CIS-JH3.2), then evacuated and passed into Ar gas. Next,  $C_3N_4$ -NVs was synthesized by the fast Joule Heating treatment under an argon atmosphere. A high pulse voltage of 30 V was applied instantaneously to the  $C_3N_4$ , and a strong pulse current of 300 A caused the  $C_3N_4$  to rapidly reach the specified temperature within 3-4 seconds to obtain  $C_3N_4$ -NVs.

Synthesis of Pt/ $C_3N_4$ -NVs: Generally, 0.50 g of  $C_3N_4$  and the specified amount of  $H_2PtCl_6 \cdot 6H_2O$  were dispersed in 10 mL of deionized water and impregnated under a constant temperature water bath at  $60^\circ C$  for 4 h to obtain a suspension. The suspension was then separated by centrifugation and dried overnight in a vacuum drying oven at

80°C. The resulting product was named Pt<sub>x</sub>/C<sub>3</sub>N<sub>4</sub> (x = 0.1, 0.25, 0.5, 0.75), where x represented the percentage of the mass of platinum in the composite. For comparison, we also prepared Pd<sub>0.5</sub>/C<sub>3</sub>N<sub>4</sub>, Ru<sub>0.5</sub>/C<sub>3</sub>N<sub>4</sub>, Au<sub>0.5</sub>/C<sub>3</sub>N<sub>4</sub>, Ag<sub>0.5</sub>/C<sub>3</sub>N<sub>4</sub> with a mass fraction of 0.5 using PdCl<sub>2</sub> and RuCl<sub>3</sub>·xH<sub>2</sub>O, AuCl<sub>3</sub>, AgNO<sub>3</sub> as precursors. The above obtained samples were centrifuged and dried, and calcined by the fast Joule Heating method with the same parameters as for the preparation of C<sub>3</sub>N<sub>4</sub>-NVs, for different impregnation amounts, different loading metals, and different heating temperatures, where the best active sample was named Pt/C<sub>3</sub>N<sub>4</sub>-NVs.

Preparation of photoanodes: C<sub>3</sub>N<sub>4</sub>-based photocatalysts (C<sub>3</sub>N<sub>4</sub>, C<sub>3</sub>N<sub>4</sub>-NVs and Pt/C<sub>3</sub>N<sub>4</sub>-NVs) were coated onto conductive glass (FTO) to prepare photoanodes in photoelectrocatalysis, and in order to ensure that the catalysts were not detached during the testing process, the following method was adopted: Firstly, 1 cm×2 cm size FTO conductive glass was selected and ultrasonically cleaned in acetone, anhydrous ethanol, and deionized water for 15 min to remove the surface stains, and then the cleaned FTO conductive glass was put into isopropanol for 2 h, then dried naturally in the air and set aside. Next, 10 mg of catalyst was dispersed into 200 μL of a 1:1 mixture of deionized water and isopropanol, and ultrasonicated for 30 min to make it uniformly dispersed. Finally, the FTO glass conductive surface was covered with transparent adhesive tape, leaving an exposed area of 1 cm × 1 cm for coating, and the mixed sample solution was dripped onto the exposed FTO conductive surface, which was left to dry naturally after the droplets were naturally spread out. Then Nafion was mixed with isopropanol (1:9 by volume), and 10 μL of the Nafion mixture was added dropwise to the air-dried electrode surface, and the corresponding photoanode was obtained after the droplets uniformly covered the whole electrode and dried.

### 1.3. Characterizations

A powder X-ray diffractometer Rigaku Miniflex 600 was used to determine X-ray diffraction (XRD) patterns. A Hitachi S-4800 equipped was used to obtain the scanning electron microscope (SEM). A JEOL JEM-2100Plus Electron Microscope with a spherical aberration corrector was used to obtain the transmission electron microscopy (TEM). The XPS tests were determined on the Thermo Scientific K-Alpha X-ray photoelectron spectrometer with Al K $\alpha$  source. A UV-vis spectrophotometer (PUXI TU-1901) was used to determine the UV-Vis diffuse reflectance spectroscopy (DRS), and UV-Vis absorption spectrum. The Brunauer-Emmett-Teller (BET) were recorded using Micromeritics ASAP 2460 gas sorption analyzer at 77 K. A contact angle meter (Dataphysics OCA20) was used to measure the static water contact angles.

#### **1.4. Photoelectrocatalytic H<sub>2</sub> generation tests**

The photoelectrocatalytic water splitting to generate H<sub>2</sub> was tested using a conventional three-electrode system, with the electrolyte solution being 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution, and the reactor being an H-type double-chambered quartz-based photoelectric reactor (P61-45, Beijing Perfectlight). A CHI 600E electrochemical workstation (Chenhua, Shanghai) was used to bias the electrodes, and a 300 W Xenon lamp was used as the light source, and the gaseous products generated in the reactor were connected to an automatic on-line trace gas analysis system (Labsolar-6A, Beijing Perfectlight). For the experiments, a Pt sheet was used as the photocathode, an Ag/AgCl electrode was used as the reference electrode, and the prepared photoanode was connected to the working electrode. Before the start of the reaction, vacuum was carried out to eliminate the interference of the original gas in the reactor and to ensure that all the gases detected by gas chromatography were generated by the decomposition of the catalyst. Then the light source was turned on and the applied bias pressure was set. Using the gas chromatography automatic sampling device, the amount of hydrogen generated at 30

min intervals was sent to the gas chromatography automatic detection, the peak area was analyzed, and the amount of hydrogen generated was calculated by the standard curve. In addition, after each test, the FTO glass coated with Pt/C<sub>3</sub>N<sub>4</sub>-NVs was removed and dried for 3 cycles of cyclic testing.

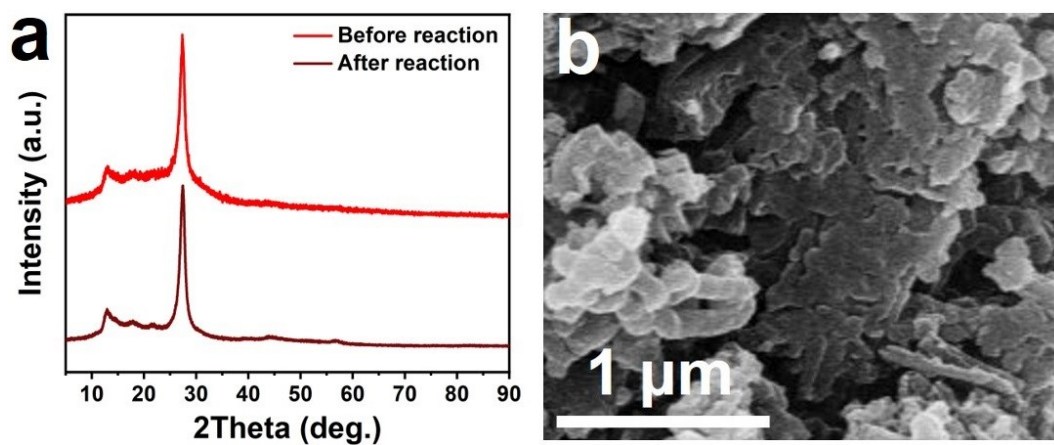
### **1.5. Electrochemical tests**

The photoelectrochemical testing process was performed using a three-electrode system, with a platinum sheet for the counter electrode, a saturated Ag/AgCl electrode for the reference electrode, and an FTO conductive glass coated with the sample to be tested for the working electrode, and a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 7.0) was used as the electrolyte solution to perform the photocurrent density curves (*i*-T), the electrochemical impedance spectroscopy (EIS) for the catalysts in the electrochemical workstation, LSV curve, and *i*-t curve measurements. In the experiments, the EIS test was performed at a bias potential of 0 V, and the *i*-t curve was measured at a potential of 0.62 V (vs. Ag/AgCl). The potential was calculated as follows.

$$E(\text{V vs. RHE}) = E(\text{V vs. Ag/AgCl}) + 0.197 + 0.0592 \text{ pH}$$

Preparation of working electrode: The working electrode was prepared by loading the catalyst to be tested onto FTO glass, which was firstly cleaned by ultrasonic cleaning in acetone and deionized water in a beaker for 15 min and then dried. Weighing 5 mg of the sample to be tested in a 1.5 ml centrifuge tube, 150  $\mu$ L of anhydrous ethanol and 10  $\mu$ L of Nafion solution were added and dispersed by ultrasonication for 30 min. Finally, the mixed solution was added dropwise to an area of 1 cm  $\times$  1 cm on the FTO glass and dried naturally.

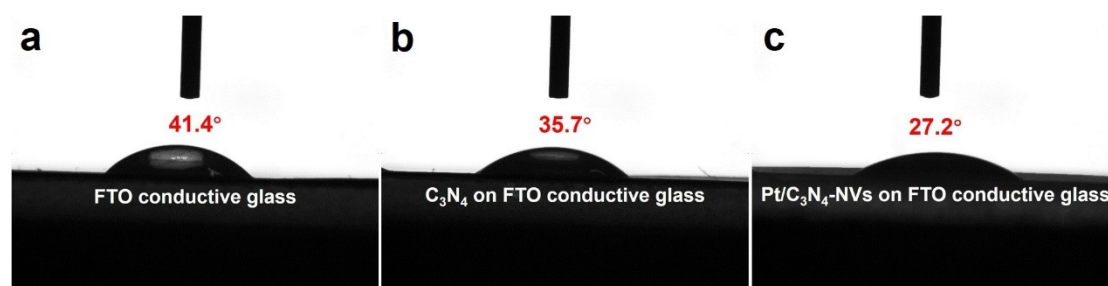
## 2. Supporting figures



**Fig. S1.** (a) XRD patterns and (b) SEM image of Pt/C<sub>3</sub>N<sub>4</sub>-NVs before and after recycling tests.

### 3. Hydrophobicity test results

The hydrophobicity of the photoanodes was explored using a water contact angle meter. Fig. S2a exhibited the water contact angle of pure FTO conductive glass, which was  $41.4^\circ$ , showing hydrophilicity. Fig. S2b illustrated the water contact angle of the  $C_3N_4$  photoanode, which was  $36.7^\circ$  on the  $C_3N_4$  growth side, indicating the transition to hydrophilicity, and owing to the excellent hydrophilicity of the  $C_3N_4$  catalysts, where water was absorbed and transported by capillary force.<sup>1</sup> Fig. S2c showed that the water contact angle of the photoanode prepared from Pt/ $C_3N_4$ -NVs sample after Joule heating was  $27.2^\circ$ , which became particularly hydrophilic, thus more favorable for accelerating the process of photoelectrocatalytic water splitting for hydrogen generation.<sup>2</sup>



**Fig. S2.** Hydrophobicity test of of (a) FTO conductive glass, (b)  $C_3N_4$  and (c) Pt/ $C_3N_4$ -NVs on FTO conductive glass.

## 4. Supporting tables

**Table S1.** Photoelectrocatalytic H<sub>2</sub> generation performance comparison of C<sub>3</sub>N<sub>4</sub>-based catalyst.

Catalyst	Light source	Bias voltage	H <sub>2</sub> generation rate	Ref.
P/g-C <sub>3</sub> N <sub>4</sub>	PLS-SXE-300C lamp (800 nm cutoff filter)	0.6 V versus Ag/AgCl	1.27 μmol h <sup>-1</sup> g <sup>-1</sup>	3
Pt-NCN-CC	300 W Xe lamp	0.66 V (vs. Ag/AgCl)	13.49 mmol/h/m <sup>2</sup>	4
Pt <sub>0.3</sub> -C <sub>3</sub> N <sub>4</sub> -N	300-W Xe lamp	0.6 V (vs. Ag/AgCl)	23.1 mmol/h/m <sup>2</sup>	5
g-C <sub>3</sub> N <sub>4</sub> Nanosheets	UV-Vis lamp (50 W)	1.7 V	5 mA/cm <sup>2</sup>	6
WO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub> NSAs	Xe lamp (300 W)	1.23 V versus RHE	0.73 mA cm <sup>-2</sup>	7
g-C <sub>3</sub> N <sub>4</sub> /Sn <sub>3</sub> O <sub>4</sub>	300 W xenon arc lamp	0.8 V vs. Ag/AgCl	0.49 mmol/L	8
RGO@g-C <sub>3</sub> N <sub>4</sub> /BiVO <sub>4</sub>	visible-light (500 W halogen lamp)	-0.05 V vs. Ag/AgCl	63.5 mmol/h	9
BiVO <sub>4</sub> /GQD/g-C <sub>3</sub> N <sub>4</sub>	500 W halogen lamp (AM 1.5G)	1.0 V vs Ag/AgCl	84.9 mmol/h	10
pg-C <sub>3</sub> N <sub>4-x</sub> -FeNi	300 W xenon lamp	1.23 V vs. RHE	1859.4 μmol·cm <sup>-2</sup> ·h <sup>-1</sup>	11
Nd-g-C <sub>3</sub> N <sub>4</sub> /BiOI	visible light (AM 1.5 G)	0.05 V (with respect to Ag/AgCl)	288 μmol h <sup>-1</sup> cm <sup>-2</sup>	12
g-C <sub>3</sub> N <sub>4</sub> /α-Fe <sub>2</sub> O <sub>3</sub>	Xenon lamp (100 mW cm <sup>-2</sup> )	1.6 V vs NHE	317 μmol cm <sup>-2</sup> h <sup>-1</sup>	13
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> -NTAs	300 W Xe lamp (> 420 nm filter)	0.5 V vs. SCE	4.58 μmol h <sup>-1</sup> cm <sup>-2</sup>	14
g-C <sub>3</sub> N <sub>4</sub> /rGO	visible light (λ > 420 nm)	0.4 V (vs. SCE)	6.0 μmol·h <sup>-1</sup> ·cm <sup>-2</sup>	15
Pt/C <sub>3</sub> N <sub>4</sub> -NVs	300 W Xenon lamp	1.23 V (vs. RHE)	717.82 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	This work



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