Dopamine modified g-C_3N_4 and its enhanced visible-light photocatalytic H_2-production activity

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■ EXPERIMENTAL SECTION

Synthesis of g-C₃N₄. The g-C_3N_4 sample was fabricated by previous reports.[1] In detail, 15 g urea was put into a crucible with the cover and it was heated to 550 °C for 4 h at the rate of 5 °C/min in a muffle furnace. When it was finally cooled down to room temperature, the pale yellow samples were carefully collected and labeled as UP0.

Synthesis of g-C₃N₄/PDA composite. PDA was synthesized according to well-estabilished protocols.[2,3] The synthetic procedures of the composites were described as follows: 0.5 g of g-C_3N_4 obtained from the previous procedure was dispersed in 95 mL of tris(hydroxymethyl)-aminomethane (Tris, pH = 8.5) buffer by sonication for 30 min. After that, 5 mL of 0.05 M dopamine aqueous solution was quickly added into the above mixture with rapid agitation at 10 °C. Subsequently, the suspension was sampled and then quickly filtered by pumping after 2, 5, 10, 20, 30, 40 min, and for simplicity, the samples, after thoroughly dried, are labeled as UP2, UP5, UP10, UP20, UP30 and UP40, respectively,.

Photocatalytic experiment and apparent quantum yield (AQY) measurement. In a typical experiment, 50 mg of as-prepared photocatalysts were dispersed in 72 mL of deionized water with ultrasonic treatment. Next, 8 mL of triethanolamine as the scavengers was added into above suspension under rapid agitations. Then 3% Pt was deposited on the photocatalyst surface by photochemical reduction method. After that, the mixed solution was first purged with N_2 for 30 min to remove the air and then

irradiated by a 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm). The hydrogen yield was finally analyzed using a gas chromatography (SHIMADZU, Japan). In addition, a LED lamp with monochromatic light ($\lambda = 420$ nm) was used as the light source to carry out the experiments related to apparent quantum yield. Apparent quantum yield (AQY) can be calculated by the following equation:

$$AQE = \frac{2 \times \text{amount of } H_2 \text{ produced in unit time}}{\text{number of incident photons in unit time}} \times 100\% \qquad (1)$$

Cycling test of photocatalytic H$_2$ production. 50 mg of as-prepared photocatalysts were dispersed in the mixed solution with 72 mL deionized water and 8 mL triethanolamine under rapid stirring. Then 3% Pt was deposited on the photocatalyst surface by photochemical reduction. After that, the mixed solution was first purged with N$_2$ for 30 min to remove the air and then irradiated by a 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm). At the interval of every 1 hour, the hydrogen yield was analyzed using a gas chromatography (SHIMADZU, Japan). After 4-hour irradiation of the visible light, the reactor with the photocatalysts was purged with N$_2$ for 30 min again to remove the air. This photocurrent response to the chopped light illumination was recorded. And the whole process was repeated for four times.

Photoelectrochemical measurement. The working electrode was prepared by coating the photocatalysts on a piece of FTO glass. Specifically, the as-prepared samples were dispersed in the alcohol to form the emulsion of 5 mg/mL under ultrasonic conditions. After that, the emulsion was spin-coated on a cleansed FTO

glass. Finally, this FTO glass with photocatalyst was thoroughly dried in a vacuum drying oven to obtain the working electrode. A platinum plate and 0.5 M Na_2SO_4 solution were selected as the reference electrode and electrolyte, respectively. All the photoelectrochemical measurements were performed on a CHI 760 electrochemical workstation (CHENHUA, China). The transient state photocurrent was measured using a LED lamp (UVEC-4II, LAMPLIC, China) as the light source ($\lambda = 365nm$).

Characterization. Transmission electron microscope (JEM-2100F, JEOL, Japan) was used to obtain TEM images at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns of the as-prepared samples were obtained on a D/Max-RB X-ray diffractometer (Rigaku, Japan). Fluorescence spectrophotometer (F-7000, Hitachi, Japan) was used to record the photoluminescence (PL) emission spectra using a Xenon lamp as the light source. The thickness of the samples was evaluated by using an atomic force microscope (AFM) (Multimode 8, Bruker, Germany). An IR Affinity-1 FTIR spectrometer (Nicolet iS50, TMO, US) was used to measure the Fourier transform infrared spectra (FTIR). Field emission scanning electron microscope (JSM-7500, JEOL, Japan) with an accelerating voltage of 15 kV was employed to obtain the FESEM images of the samples. UV–visible diffuse reflectance spectra were recorded on a UV–visible spectrophotometer (UV-2600, Shimadzu, Japan), using $BaSO_4$ as the reference standard. Micromeritics ASAP 3020 equipment (USA) was used to obtain the N_2 adsorption-desorption isotherms of the samples. All of the as-prepared samples were degassed at 180 °C for 5 h prior to measurement. FLS920

fluorescence lifetime spectrophotometer (Edinburgh, Instruments,UK) was employed to record time-resolved photoluminescence (TRPL) spectra. Electron paramagnetic resonance (EPR) are performed on an ESR spectrometer (MEX-nano, Bruker) with a modulation frequency of 100 kHz and a microwave power of 15 mW. GC-MS spectra of as-prepared samples were obtained on a gas chromatography-mass spectrometer (TILON LC-D200M), using ultrapure nitrogen as the carrier gas.
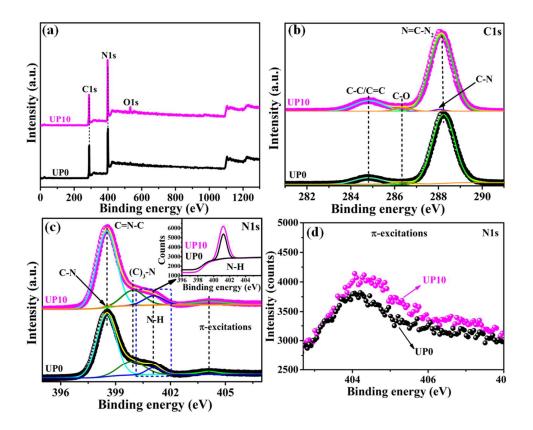
Figure S1. The survey XPS and corresponding high-resolution XPS spectra of UP10 and UP0.

Table S1: The summarized parameters obtained from N$_2$ adsorption-desorption isotherms.

Sample	V_{pore}	D_{pore}	S_{BET}
UP0	0.27	23.2	73
UP2	0.31	22.2	65
UP5	0.36	26.85 ·	59
UP10	0.48	19.9	51
UP20	0.33	21.5	37
UP30	0.22	24.8	36
UP40	0.14	27.6	34

V_{pore} represents total pore volume (cm^3/g), D_{pore} represents average pore width (nm), S_{BET} is the specific surface area (m^2/g)

Table S2: The fitted parameters obtained from decay curves of samples.

Sample	τ_1 (ns) (Rel. %)	τ_2 (ns) (Rel. %)	τ_3 (ns) (Rel. %)	τ_a
UP0	1.38 (67.41)	3.36 (28.39)	18.05 (4.2)	7.1
UP10	1.41 (51.54)	4.18 (39.55)	22.86 (8.91)	12.3

τ_a represents the average lifetime (ns) of photogenerated carriers; τ_1, τ_2 and τ_3 represent the lifetime (ns) in the radiative and non-radiative energy transfer process, respectively; A_1, A_2 and A_3 are the pre-exponential factors of decay curves.

Reference

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(3) Wei, L.; Ma, Z.; Bai, G.; Hu, J.; Guo, X.; Dai, B.; Xin, J. Dopamine-assisted one-step fabrication of Ag@AgCl nanophotocatalyst with tunable morphology, composition and improved photocatalytic performance. *Appl. Catal. B-Environ* **2015**, *s 174–175,* 43-48.