# Platinum nanoparticles strongly associated with graphitic carbon nitride as efficient co-catalysts for photocatalytic hydrogen evolution under visible light

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# **Electronic Supplementary Information (ESI†)**

# **Catalyst preparation**

**g-C<sub>3</sub>N<sub>4</sub>:** this was synthesized according to literature procedure,<sup>[1]</sup> as follows: melamine (9.0 g) was added to a porcelain cup and calcined at 823 K for 4 h, with the heating rate being 2.3 K min<sup>-1</sup>. Grinding of the resultant affords yellow powders of g-C<sub>3</sub>N<sub>4</sub>.

**Pt**<sub>0.3</sub>/g-C<sub>3</sub>N<sub>4</sub> (photoreduction method): this was synthesized according to literature procedure,<sup>[2,3]</sup> as follows: g-C<sub>3</sub>N<sub>4</sub> (0.1 g) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.8 mg) were added to a 10 % TEOA solution (30 mL) in a borosilicate glass bottle ( $\varphi$  35 mm; capacity, 50 mL). The bottle was sealed with a rubber septum cap and purged with Ar by the gas bubbling. The bottle was photoirradiated at  $\lambda$  >420 nm using a 2 kW Xe lamp (USHIO Inc.)<sup>[4]</sup> with magnetic stirring at 298 K for 6 h. The resultant was recovered by centrifugation, washed with water, and dried in vacuo at room temperature for 12 h, affording dark yellow powders of Pt<sub>0.3</sub>/g-C<sub>3</sub>N<sub>4</sub>. Annealing of Pt<sub>0.3</sub>/g-C<sub>3</sub>N<sub>4</sub> was carried out under N<sub>2</sub> or H<sub>2</sub> flow. The heating rate was 10 K min<sup>-1</sup>, and the temperature was kept for 2 h at 673 K.

**Pt**<sub>x</sub>/**g-C**<sub>3</sub>**N**<sub>4</sub> (**H**<sub>2</sub> reduction method): the catalysts [x (wt%) = 0.05, 0.1 0.2, 0.3, 0.4, 0.5, 0.8, and 1.0] were prepared as follows:<sup>[5]</sup> g-C<sub>3</sub>N<sub>4</sub> (1.0 g) and different amount of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.3, 2.7, 5.3, 8.0, 10.7, 13.3, 21.4, or 26.8 mg) were added to water (30 mL) in a borosilicate glass bottle and evaporated with vigorous stirring at 373 K for 12 h. The obtained powders were reduced under H<sub>2</sub> flow (0.1 mL min<sup>-1</sup>). The heating rate was 10 K min<sup>-1</sup>, and the temperature was kept for 2 h at designated temperature (473, 573, 673, 773 and 873 K).

## Photoreaction

Each respective catalyst (20 mg) was added to a 10% TEOA solution (5 mL) within a Pyrex glass tube (capacity, 20 mL). The tube was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and Ar gas was bubbled through the solution for

15 min. The bottle was immersed in a temperature-controlled water bath and photoirradiated at  $\lambda >$ 420 nm using a 2 kW Xe lamp (USHIO Inc.) with magnetic stirring at 298 K.<sup>[6]</sup> After the reaction, the amount of H<sub>2</sub> formed was determined by GC-TCD (Shimadzu; GC-8A).

#### Determination of apparent quantum efficiency

Photoreaction was performed with a 10% MeOH solution (30 mL) containing each respective catalyst (100 mg) within a borosilicate glass bottle (capacity, 50 mL), sealed with a rubber septum cap. The catalyst was dispersed by ultrasonication for 5 min, and Ar was bubbled through the solution for 15 min. The solution was photoirradiated with 2 kW Xe lamp (USHIO Inc.), where the incident light was monochromated by a band-pass glass filter ( $\lambda$  = 440 nm, Asahi Techno Glass Co.). The full-width at half-maximum (FWHM) of the light was 11 nm. The temperature of solution during irradiation was kept at 298 K with a temperature-controlled water bath. The photon number entered into the reaction vessel was determined with a spectroradiometer USR-40 (USHIO Inc.). The apparent quantum efficiency ( $\Phi_{AQE}$ ) for H<sub>2</sub> evolution was calculated using the equation:<sup>[7]</sup>  $\Phi_{AQE}$  (%) = {[H<sub>2</sub> evolved (µmol)] × 2} / [photon number entered into the reaction vessel] × 100.

### Analysis

XPS anaysis was performed using a JEOL JPS-9000MX spectrometer using Mg Kα radiation as the energy source. TEM observations were performed using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.<sup>[8]</sup> XRD patterns were measured on a Philips X'Pert-MPD spectrometer. Total Pt amounts on the catalysts were determined by an X-ray fluorescence spectrometer (Seiko Instruments, Inc.; SEA2110). Diffuse-reflectance UV-vis spectra were measured on an UV-vis spectrophotometer (JASCO Corp.; V-550) equipped with Integrated Sphere Apparatus ISV-469, using BaSO4 as a reference.

### References

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**Fig. S1** (top) Diffuse reflectance UV-vis spectra of respective  $g-C_3N_4$  and  $Pt_{0.3}/g-C_3N_4$  catalysts. (bottom) Results of band gap determination.



Fig. S2 XRD patterns for respective  $g-C_3N_4$  and  $Pt_{0.3}/g-C_3N_4$  catalysts.



Fig. S3 XPS chart for (top) C1s and (bottom) N1s levels of  $g-C_3N_4$  and  $Pt_{0.3}/g-C_3N_4$ .

Pt<sub>0.3</sub>/g-C<sub>3</sub>N<sub>4</sub> (photoreduction@298 K + N<sub>2</sub> annealing@673 K)



Pt<sub>0.3</sub>/g-C<sub>3</sub>N<sub>4</sub> (photoreduction@298 K + H<sub>2</sub> annealing@673 K)





Pt<sub>0.3</sub>/g-C<sub>3</sub>N<sub>4</sub> (H<sub>2</sub> reduction@873 K)



Pt<sub>0.1</sub>/g-C<sub>3</sub>N<sub>4</sub> (H<sub>2</sub> reduction@673 K)



Pt<sub>1.0</sub>/g-C<sub>3</sub>N<sub>4</sub> (H<sub>2</sub> reduction@673 K)



**Fig. S4** Typical TEM images of  $Pt_x/g-C_3N_4$  catalysts and size distributions of Pt particles.