

Supplementary information for:

Self-regenerated Solar-driven Photocatalytic Water-Splitting by Urea
Derived Graphitic Carbon Nitride with Platinum Nanoparticles

Jinghai Liu^{1,2}, Yuewei Zhang¹, Luhua Lu¹, Guan Wu¹ and Wei Chen^{1*}

¹*i-Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese
Academy of Sciences, Suzhou 215123, P. R. China.*

*E-mail: wchen2006@sinano.ac.cn

² *College of Chemistry and Chemical Engineering, Inner Mongolia
University for the Nationalities, Tongliao, 028043, P. R. China.*

Materials and Methods:

1. Preparation of Pt loaded g-C₃N₄ (Pt-g-C₃N₄):

1.1 g-C₃N₄ preparation

The graphitic carbon nitride (g-C₃N₄) was prepared using the same method that we had previously reported. General speaking, urea (10g, AR, Sinopharm Chemical Reagent Co., Ltd) was put in a crucible with a cover under ambient pressure in air. After thermal treatment at 550 °C for 3 hours, the yellow colored g-C₃N₄ was obtained. Then, the sample was washed with nitric acid (0.1 mol L⁻¹) and distilled water (DI water). After filtering and drying at 80 °C, the obtained samples were waited to test.

1.2 Pt loaded g-C₃N₄

Pt loaded g-C₃N₄ (Pt-g-C₃N₄) was obtained by photodeposition. The 0.3 mL H₂PtCl₆ · 6H₂O (10 mg mL⁻¹, AR, Sinopharm Chemical Reagent Co.,Ltd) and 2 mL acetic acid (1 mol L⁻¹, Sinopharm Chemical Reagent Co., Ltd) were added into 100 mL g-C₃N₄ dispersion (1 mg mL⁻¹) to obtain 3 wt% Pt-g-C₃N₄. After N₂ bubbling for half an hour to remove the oxygen (O₂) in the system, the sample was irradiated by a 300 W Xe lamp (PLS-SXE 300) for three hours. Then, the Pt-g-C₃N₄ was obtained by filtering and drying at 80 °C.

2 Hydrogen (H₂) and peroxides (H₂O₂) production and test:

2.1 H₂ and H₂O₂ production

Photocatalytic water splitting reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system (Figure S15). 80 mg Pt-g-C₃N₄ was dispersed in 100 mL DI water by sonication. The obtained reactant dispersion was put into the reaction vessel and stirred. The reaction system was evacuated three times with half an hour each time to remove air completely prior to irradiation under a 300 W Xe lamp (PLS-SXE 300, trusttech) and a water filter. The wavelength of the incident light was controlled by using an appropriate cut-off filter, such as, visible light (> 400 nm, filter cut-off 400) and solar light (solar simulator filter). The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography (GC 7890II, Shanghai Techcomp Instrument Ltd.).

2.2 Total H₂O₂ (including bounded ones and H₂O₂ in solution) test with *o*-tolidine:

Hydrogen peroxide (H₂O₂) measurements were performed on 2.0 mL reaction suspension that was taken immediately after the irradiation. For each test, a 0.5 mL volume of 1% *o*-tolidine in 0.1 M HCl (Alfa Aesar, 98%, without further purification) ^[1] was added to the suspension. This mixture was allowed to react for 2 min. In the

presence of peroxides, a blue color is formed very quickly resulting from the oxidation of *o*-toluidine. Subsequently, the dispersion was acidified with 1 M HCl (2 mL), which caused the color of the dispersion to turn yellow. The yellow-coloured species is the protonated form of the 2-electron oxidation product of *o*-toluidine formed (See Figure S16). The dispersion was quickly filtered through a 0.22 μm membrane filter and the absorption spectrum of the filtrate was immediately recorded with a UV-Vis spectrophotometer (Shimadzu, UV-2550). The absorption spectrum of the 2-electron oxidized toluidine has a characteristic maximum at 438 nm.

2.3 Concentration of peroxides determined by the calibrated curve and fitting equation

The calibrated curve and fitting equation was made using H_2O_2 with different concentration as external standard materials. The *o*-toluidine as an indicator for H_2O_2 was the quick oxidation reaction of *o*-toluidine and H_2O_2 catalyzed by Pt^[2,3]. Without the catalyst, the colorization reaction was slow. Therefore, we used Pt-g- C_3N_4 without irradiation as the catalyst for the indicator reaction. The testing process was similar to the mentioned in 2.2, but the reaction suspension was 1 mL H_2O_2 solution and 1 mL Pt-g- C_3N_4 (0.8 mg mL^{-1}).

3 Regenerative process and loss of the H_2O_2 tested with *o*-toluidine:

3.1 Activity comparison and Regenerative process

The cyclic stability and deactivation of Pt-g- C_3N_4 for splitting water from pure water was tested by recycling the irradiation of the photocatalytic system to compare the H_2 yield. For continuous cycles without regenerative process, the reactant suspension was kept in the closed gas circulation system under N_2 atmosphere overnight in the dark at ambient temperature and pressure. But, for the regenerative process, the reactant suspension was open in air with other conditions unchanged.

3.2 H_2O_2 test for regenerative process

The total amounts of H_2O_2 (including peroxides attached on the Pt-g- C_3N_4 and H_2O_2 in solution) after regenerative process were tested according to the procedures mentioned in 2.2. And, for H_2O_2 in solution, 2 mL Pt-g- C_3N_4 suspension was centrifugated to obtain supernatant. The supernatant with volume of 1 mL was measured according to 2.3 with 1 mL Pt-g- C_3N_4 (0.8 mg mL^{-1}) without irradiation as catalyst.

4 Characterization:

TEM and HRTEM as well as STEM images were obtained on Tecnai G2 F20 S-Twin (FEI, 200 kV). XRD patterns were identified by powder XRD (Bruker AXS, D8 Advance, $\text{Cu } \text{k}\alpha$). UV-Vis diffuse-reflectance spectra (UV-Vis DRS) were recorded on Cary 5000 with Integrating Sphere Attachment (incidence angle to

reflecting sample: 12.5°). The photoluminescence (PL) spectra were carried on PL spectra were performed on f-4600 fluorescent spectrometer (Hitachi) with 370 nm excitation light. Both absorption and PL measurement used infinitely thick sample.

The light intensity was tested by noncontact light intensity measurement system with Standard Si Solar cell, AC/DC current probe (TCPA 300, tektronix) and Two channel color digital phosphor oscilloscope (TDS 3032B).

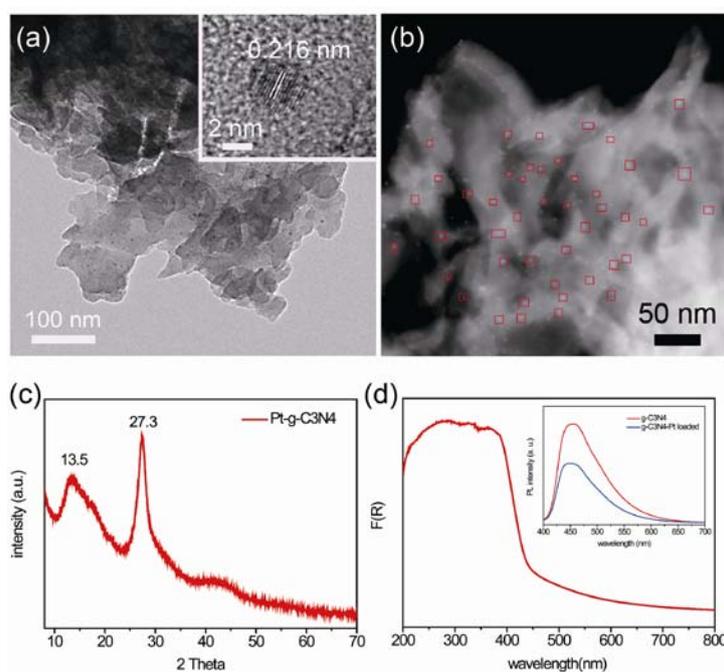


Figure S1. Morphology, structure and optical properties of g-C₃N₄ loaded with 1.13wt% Pt (Pt-g-C₃N₄). (a) TEM image of nanosized Pt loaded on the sheet of g-C₃N₄. Inset: HRTEM image of the Pt nanoparticles shows the lateral size was in the range of 2 to 3 nm. (b) STEM image of Pt nanoparticles uniformly dispersed on the g-C₃N₄. (c) XRD pattern of Pt-g-C₃N₄. (d) The absorption spectra of g-C₃N₄ measured by UV-Vis diffraction reflection spectrum (UV-Vis DRS). F(R) represents the absorption of g-C₃N₄, which is calculated by Kubelka-Munk (K-M) equation. The inset shows the comparison of the photoluminescence (PL) for g-C₃N₄ and Pt-g-C₃N₄.

The amount of deposited Pt with respect to the surface area of g-C₃N₄ is 0.016 mg/ (m² g⁻¹).

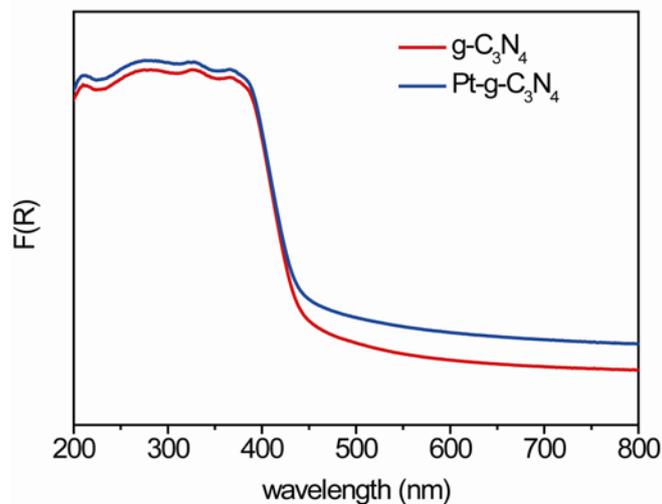


Figure S2 The UV-Vis DRS spectrum for Pt-g-C₃N₄ and g-C₃N₄.

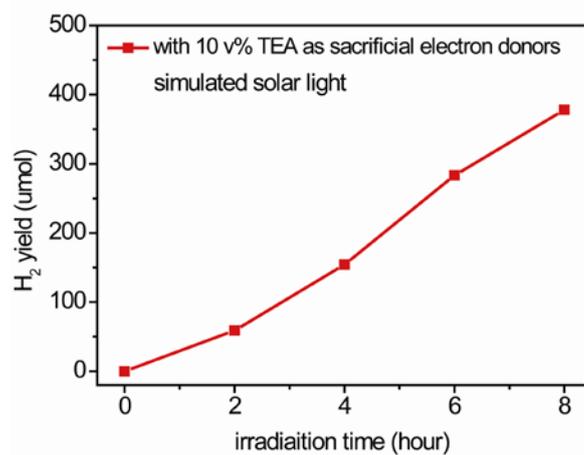


Figure S3 Solar-driven photocatalytic H₂ production by Pt-g-C₃N₄ with TEA as a sacrificial electron donor. Simulated solar light was obtained by AM1.5 filter with intensity of 56.07 mW cm⁻². The reaction system was 80 mg photocatalyst in 100 mL water. The volume of the TEA was 10 mL. H₂ evolution rate: 47.23 μmol h⁻¹.

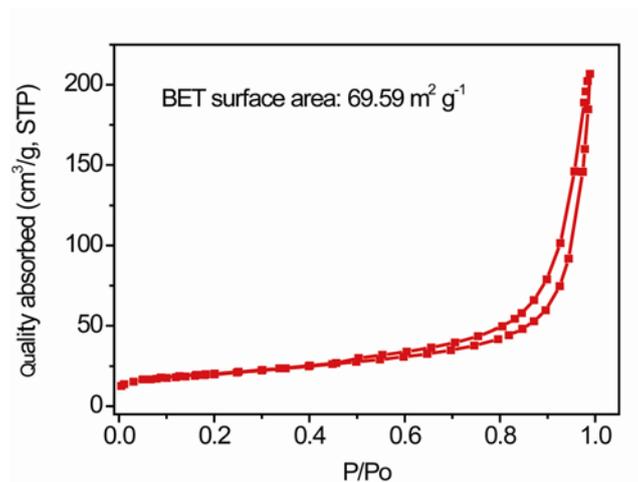


Figure S4 The adsorption-desorption curve and the BET surface area of g-C₃N₄ derived from urea, which is determined by the Brunauer-Emmett-Teller method at liquid-nitrogen temperature.

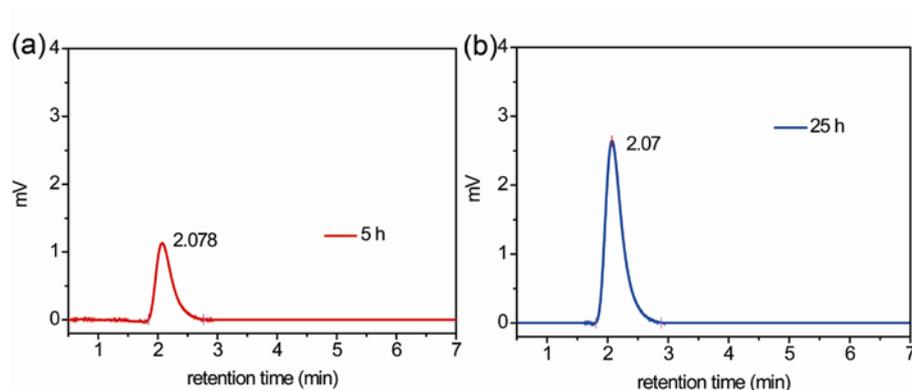


Figure S5 The detected evolving gas by Gas Chromatogram (TCD as detector, packed column, molecular sieve 5A 60-80 mesh, column serial number 100526-01) with N₂ as carrier gas during water-splitting under simulated solar light and visible light irradiation. The single peak represents one component in the evolving gas, and this peak is identified to be H₂ by retention time.

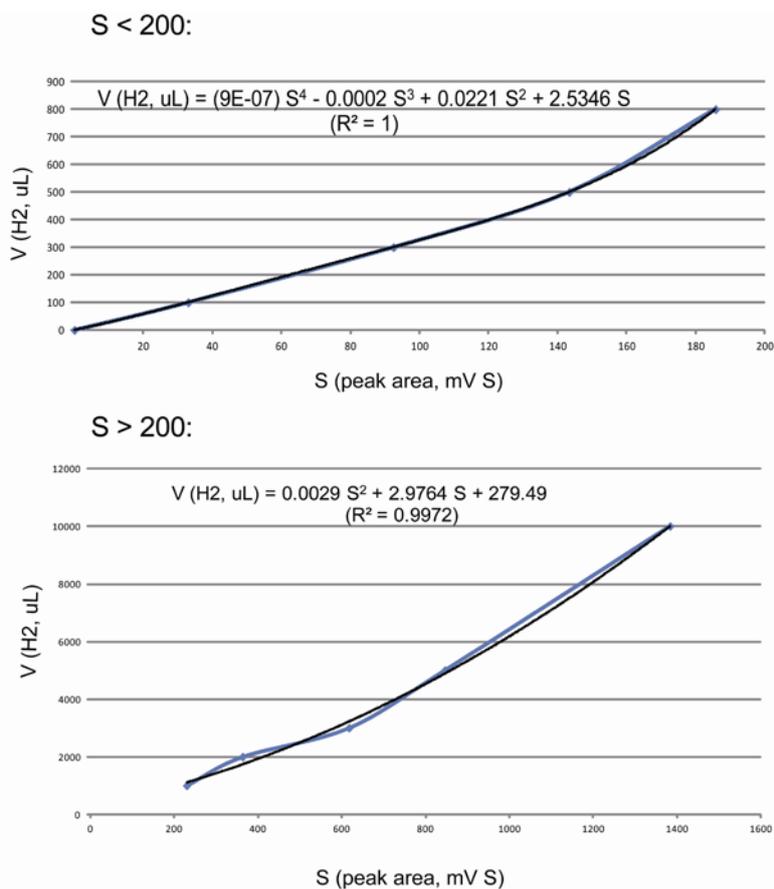


Figure S6 The calibration curve and fitting equation of produced H₂ and the peak area obtained from GC test, which are determined by external standard method using H₂ (99.999%) as standard materials with different volume under the same experimental and GC conditions as the water-splitting experiment.

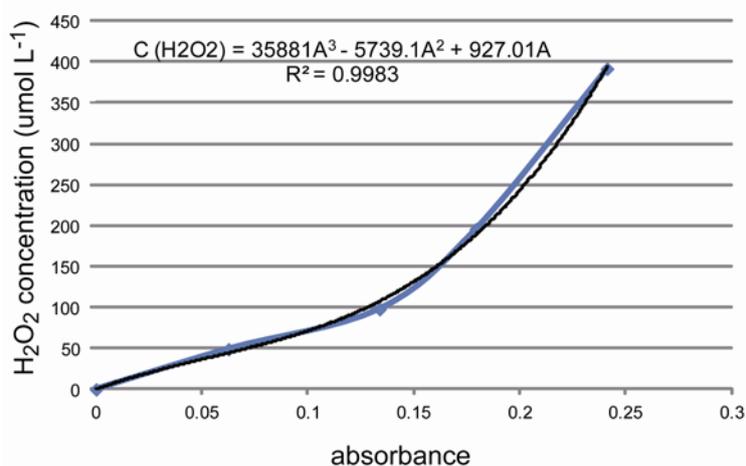


Figure S7 The calibration curve and the fitting equation of the H₂O₂ concentration and absorbance, which are determined by external standard method using H₂O₂ as

standard materials with different concentration under the same experimental conditions.

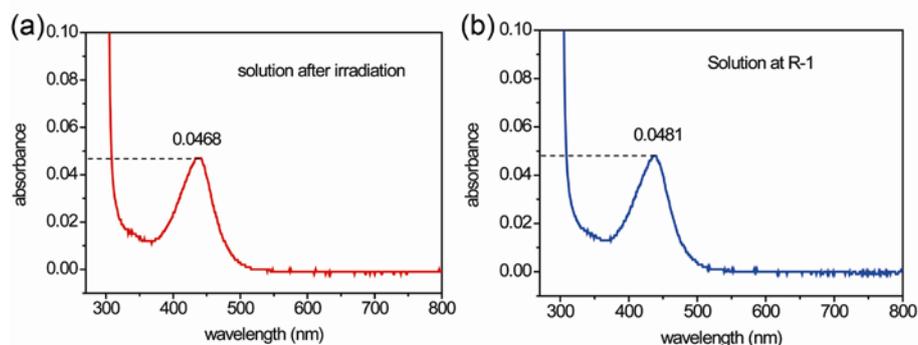


Figure S8 The H_2O_2 free in solution (no bound on $\text{g-C}_3\text{N}_4$) was unchanged after regenerative process. (a) The supernatant was obtained by centrifugating the suspension immediately after stopping the irradiation (named as solution after irradiation). (b) The supernatant was obtained by centrifugating the suspension after regenerative process (R-1) of keeping open in air overnight under ambient pressure and temperature in dark (named as solution after R-1).

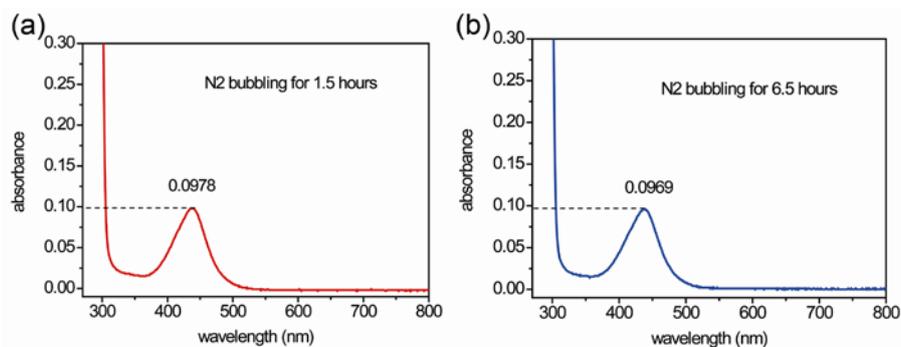


Figure S9 Extending the bubbling induced no loss of H_2O_2 . (a) Under N_2 bubbling for 1.5 hours. (b) Under N_2 bubbling for 6.5 hours.

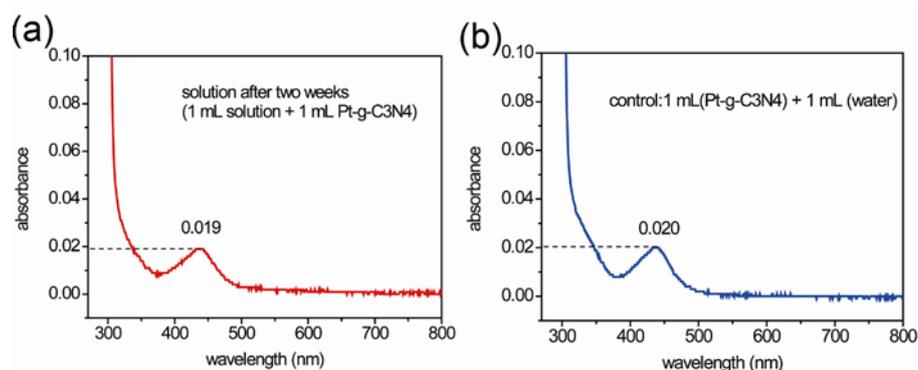


Figure S10 The H_2O_2 free in solution (no bound on $\text{g-C}_3\text{N}_4$) after the regenerative process of keeping open in air for two weeks. (a) The H_2O_2 in solution, where the $\text{Pt-g-C}_3\text{N}_4$ as catalyst for the colorization reaction of H_2O_2 and *o*-tolidine was not experienced irradiation. (b) The control experiment using water instead of solution, in which the $\text{Pt-g-C}_3\text{N}_4$ was not experienced irradiation. Compared the absorbance of the sample with the control, the H_2O_2 in solution is completely decomposed under the regeneration conditions.

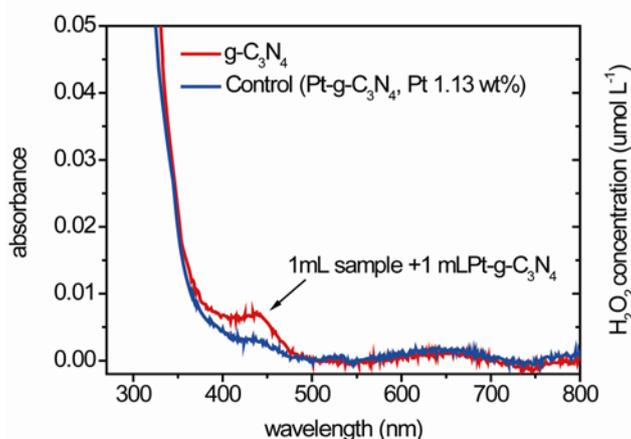


Figure S11 No H_2O_2 was detected for pure $\text{g-C}_3\text{N}_4$ irradiated under simulated solar light. The UV-Vis absorbance was obtained by using 1 mL $\text{g-C}_3\text{N}_4$ and 1 mL $\text{Pt-g-C}_3\text{N}_4$ (Pt 1.13%), where the $\text{Pt-g-C}_3\text{N}_4$ was not experiencing irradiation. Compared with control (1 mL water + 1 mL $\text{Pt-g-C}_3\text{N}_4$), absorbance of the sample is ignoring. Therefore, no H_2O_2 produces for pure $\text{g-C}_3\text{N}_4$ without Pt nanoparticles under simulated solar light. Besides, no H_2 is yet detected in this reaction system during the photocatalytic water-splitting process.

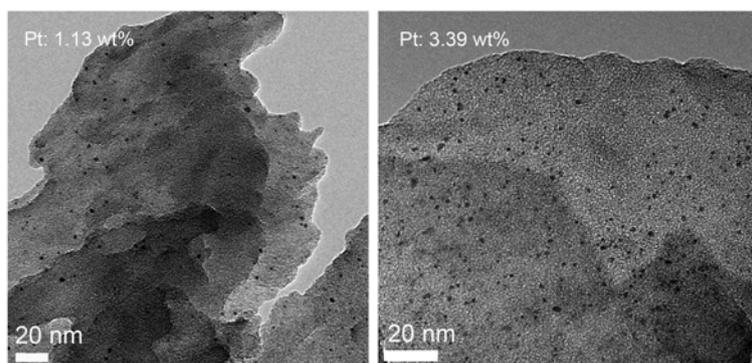


Figure S12 The distribution density and size of deposited Pt nanoparticles on g-C₃N₄ with 1.13 wt% and 3.39 wt%, characterized by TEM. The TEM images show the distribution density of Pt nanoparticles on the sheet of g-C₃N₄ clearly increases. But, the size change of Pt nanoparticles is not obviously observed.

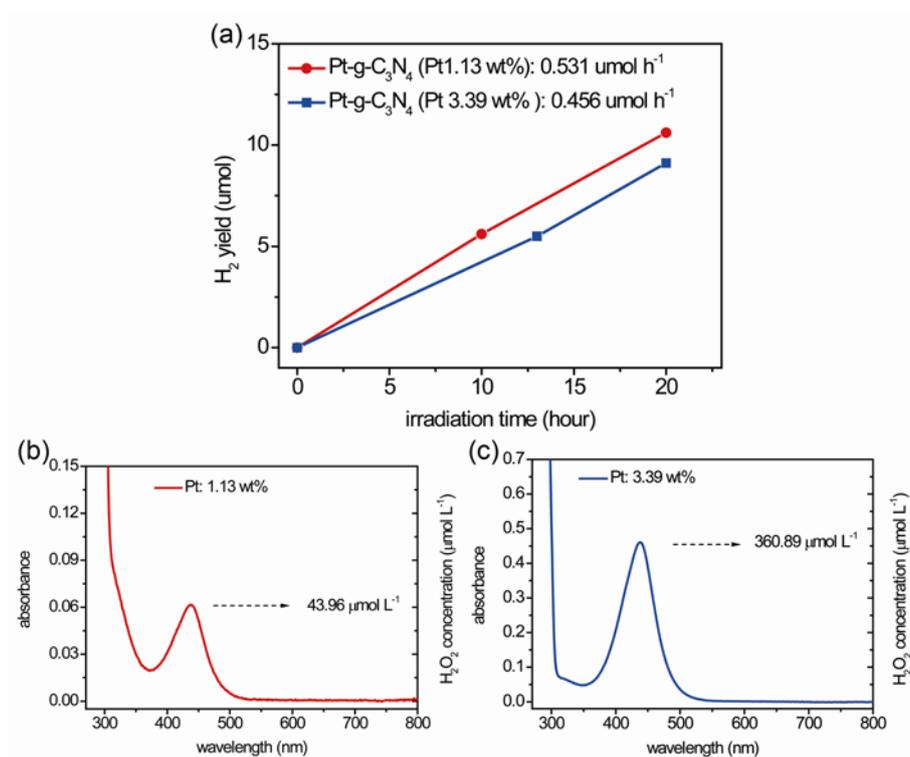


Figure S13 The amount and size of Pt show influence on the production of H₂ and H₂O₂. The H₂ evolution rate decreased from 0.531 $\mu\text{mol h}^{-1}$ for Pt-g-C₃N₄ with Pt amount of 1.13 wt% to 0.456 $\mu\text{mol h}^{-1}$ for the one with Pt amount of 3.39 wt%. The H₂O₂ concentration is changed to 8.2 times when the amount of Pt increases 3 times for Pt-g-C₃N₄. The fitting equation of the H₂O₂ concentration and absorbance for Pt-g-C₃N₄ (3.39 wt%) is $y=7517.5x^3-4750.4x^2+1680.2x-142.72$, where y: H₂O₂ concentration and x: absorbance.

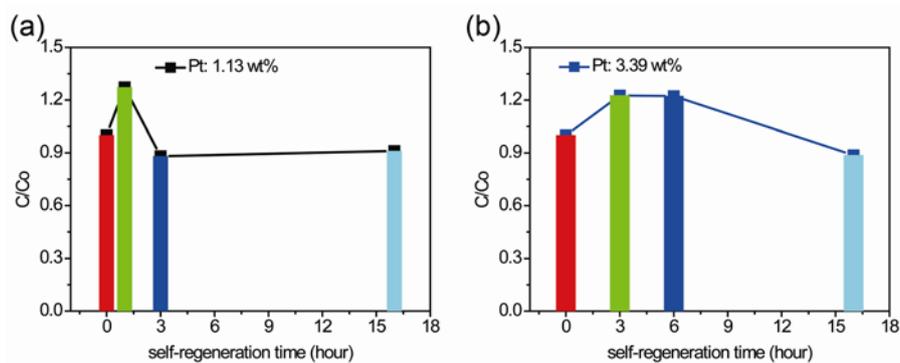


Figure S14 The effect of Pt nanoparticles on the surface reaction related to the activity regeneration. The kinetics of H₂O₂ decomposition by Pt-g-C₃N₄ with Pt amount of 1.13 wt% and 3.39 wt%. C: concentration of H₂O₂ at different regeneration time. Co: concentration of H₂O₂ just after finishing the irradiation.

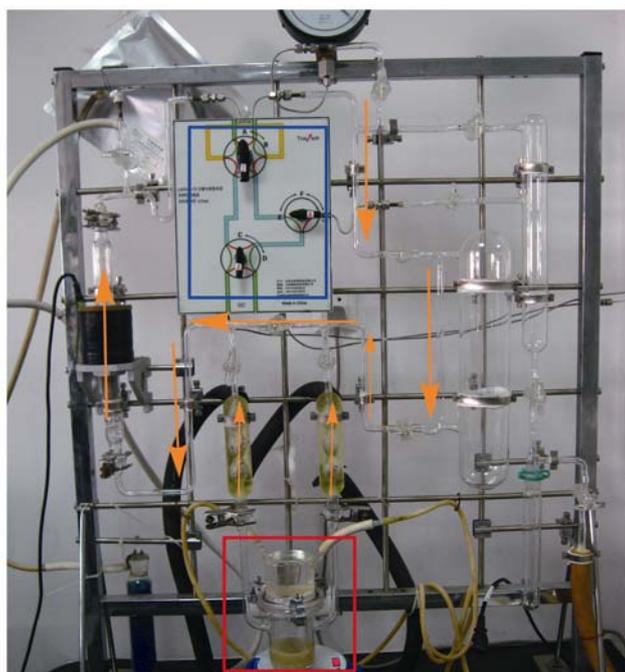


Figure S15 Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. The red square shows the reaction vessel, and the arrows guide the gas circulation in the closed system under vacuum. The blue square represents the operation panel for evolving gas testing on GC.

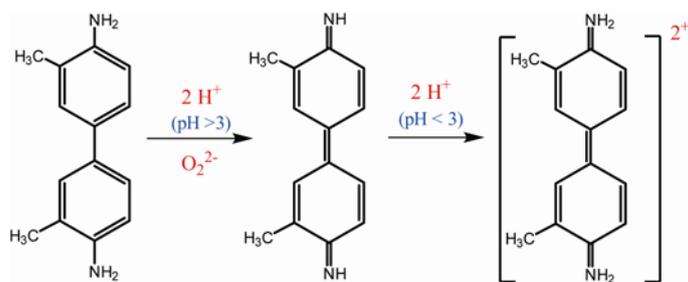


Figure S16 The forms of 2e-oxidation of o-tolidine (pH > 3) by peroxides and protonated monomer (pH < 3) with absorbance at 438 nm.

References:

- [1] O. C. Compton, F. E. Osterloh, J. Phys. Chem. C 2009, 113, 479-485.
- [2] D. Duonghong, M. Gratzel, J. Chem. Soc., Chem. Commun., 1984, 1073, 1597-1599.
- [3] J. Kiwi, M. Gratzel, J. Mol. Cat., 1987, 39, 63-70.