

Supporting Information

for

The photocatalytic NO-removal activity of g-C₃N₄ significantly enhanced by the synergistic effect of Pd⁰ nanoparticles and N vacancies

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S1 Experimental descriptions

S1.1 Preparation of the N vacancy modified g-C₃N₄ sample

To prepare the N vacancy modified g-C₃N₄, g-C₃N₄ was chosen as the raw material. Typically, 1 g of g-C₃N₄ samples were placed in the centre of a quartz tube in the tube furnace. Then, argon gas was flowed into quartz tube from one side (flow rate = 40 mL/min) and was discharged from another side (flow rate = 40 mL/min). This process was used to remove pre-existent oxygen and maintained for 30 min. Subsequently, the quartz tube was sealed with pistons and heated to 520 °C (heating rate = 10 °C/min) for 2 h. After heating, the temperature of the tube furnace was cooled to room temperature, and the obtained sample was denoted as the CN-C.

S1.2 Preparation of Pd⁰ modified g-C₃N₄ sample

The Pd⁰ modified g-C₃N₄ was prepared through chemical reduction method. Firstly, 2.4 g of prepared Pd-CN-0.5 sample were dispersed in 100 mL deionized water. Then, 10 mL of 0.1 mol/L NaBH₄ solution was slowly dripped into this suspension under constant stirring. After 30 min of reaction, the suspension was centrifuged, washed alternately with deionized water and ethanol. Finally, the obtained sample was dried at 60 °C for 12 h in a vacuum drying oven. The obtained samples are Pd⁰ modified g-C₃N₄ and denoted as Pd-CN-R.

S 1.3 Fluorescence determination of hydroxyl radical and hydrogen peroxide

The experimental method of generating H₂O₂ and ·OH is consistent with the literature we reported previously.^{1,2} The test method for H₂O₂ is as follows: 50 mg of the sample powder was placed in a beaker with 50 ml deionized water, and this beaker was placed in an ice water bath. Then, the suspension was irradiated with visible light. During irradiation, 3 ml of the suspension was taken out from the beaker every 10 minutes and filtered through a 0.22 μm filter. Subsequently, 50 μl of a fluorescent reagent was added to react with the generated H₂O₂. After 10 minutes, 1 ml of NaOH solution was added to terminate the reaction. Finally, the generated H₂O₂ was measured by a fluorescence spectrophotometer (emission at 409 nm, excitation at 315 nm).

As for the test process of ·OH: 50 mg sample was dispersed in 50 ml of terephthalic acid solution (1.25 Mmol / L) and placed on a magnetic stirrer. After the visible light was turned on, 4 ml of the suspension was taken out from the reaction beaker every 10 minutes. After filtering the suspension with a 0.22 μm filter, the filtered liquid was

subjected to the fluorescence test (emission at 426 nm and excitation at 312 nm).

S 1.4 The trapping experiment

The active species such as photogenerated electrons (e^-), holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide free radicals ($\cdot\text{O}_2^-$), which usually play the crucial role in the photocatalytic reactions. To illustrate the photocatalytic mechanism of NO removal, different scavengers were added to study the effects of these active species. Potassium iodide (KI), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), tert-butanol (TBA) and p-benzoquinone (PBQ) were used to capture the active species such as h^+ , e^- , $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, respectively. Typically, 50 mg photocatalysts and 0.01 g scavenger were added into 10 mL distilled water. After the ultrasonic treatment for 10 min, the above suspension was coated in the sample tray, which was then dried at 60 °C until the water is completely removed. Subsequently, this sample tray was used in the NO removal experiment.

S2 Results and Discussion

S 2.1 The analysis of N vacancies

In order to prove the presence of N vacancies, elemental analysis (EA) was used to determine the molar ratio of nitrogen to carbon (N/C) in Pd-CN and Pd-CN-C samples. The N/C molar ratio of Pd-CN is 1.35, which is higher than that of Pd-CN-C (1.14). This result indicates the presence of N vacancies. To further confirm the presence of N vacancies, the high-resolution XPS peaks of N1s of two samples were analyzed. The N 1s XPS spectra of two samples could be fitted with two peaks. The peaks at 400.95 and

398.90 eV can be attributed to the N–C₃ and C–N=C groups, respectively (Figure 2b). These two peaks with the area ratio (C–N=C/N–C₃) of 3.8 and 5.2 for Pd-CN and Pd-CN-C, indicating the amount of bridging N in Pd-CN-C is less than that in Pd-CN. Electron paramagnetic resonance (EPR) analysis was used to further prove the existence of N vacancies. As shown in Figure S3, Pd-CN displays a single Lorentzian line at $g = 2.002$, which is associated with the unpaired electrons of aromatic rings. As compared to the signal of Pd-CN, the intensity of EPR signal of Pd-CN-C gradually enhanced. According to the previous literatures,^{3, 4} this phenomenon can explain the generation of N vacancies in Pd-CN-C. These results not only prove the presence of N vacancies in Pd-CN-C sample, but also demonstrate the position of N vacancies is the site of bridging N.

S 2.2 The results of trapping experiment

In order to investigate the possible mechanism of photocatalytic NO removal over different samples, active species scavenging experiments were carried out, as shown in Figure S4. The results showed that adding KI completely inhibited the NO removal activity of all prepared samples, and suggesting that photogenerated holes are main active species. Moreover, adding K₂Cr₂O₇ and PBQ could distinctly depress the NO removal of all the prepared samples, indicating that photogenerated electrons and ·O₂⁻ greatly promoted the NO removal. However, adding the TBA scavenger into the photocatalysts, the activity of the NO removal was inhibited a little, indicating that the ·OH is not the main active species. In the active species scavenging experiments, we concluded that NO was removed by holes and reactive oxygen species (ROSs such as

$\cdot\text{O}_2^-$ and $\cdot\text{OH}$).

Reference:

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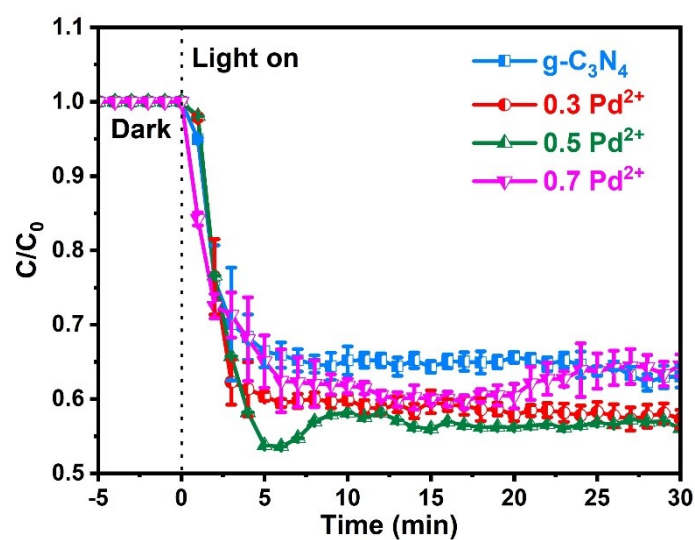


Figure S1. Photocatalytic NO removal activities of different samples.

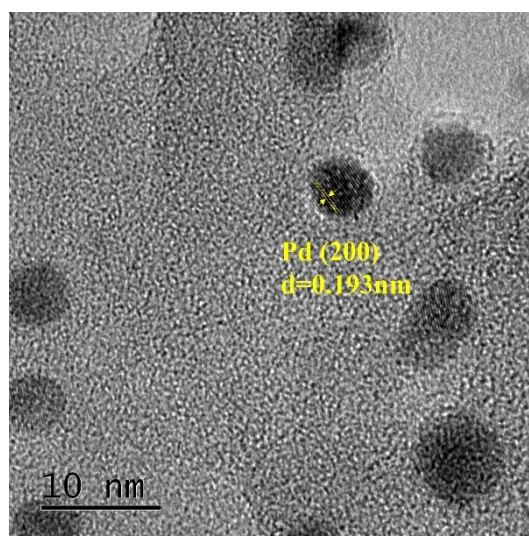


Figure S2. The HRTEM image of Pd-CN-C.

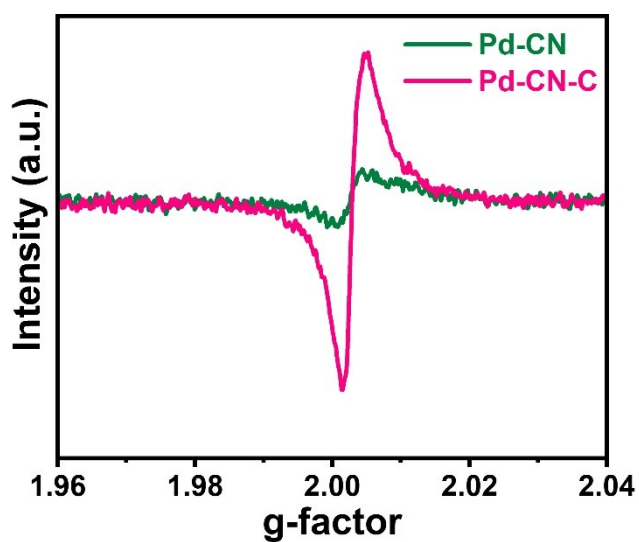


Figure S3. EPR spectra of Pd-CN and Pd-CN-C.

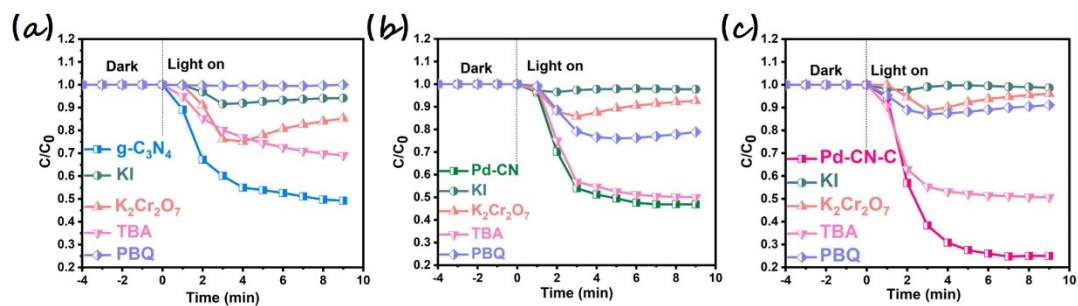


Figure S4. Active-species scavenging experiments in $g-C_3N_4$ system (a); active-species

scavenging experiments in Pd-CN system (b); active-species scavenging experiments in Pd-CN-C system (c).

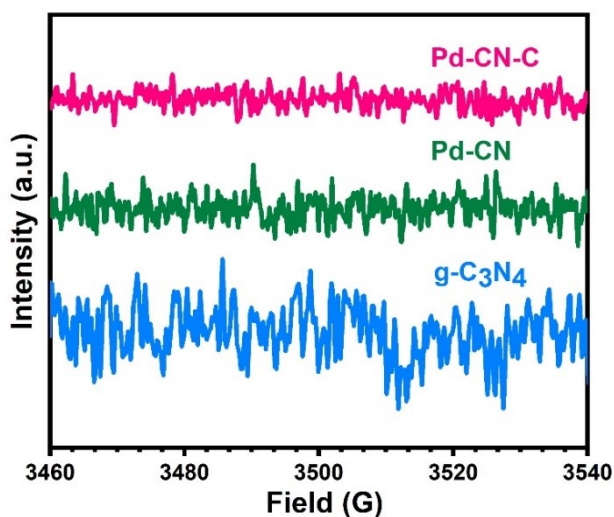


Figure S5. The EPR signal of $\cdot\text{O}_2^-$ in different sample systems under the dark condition.

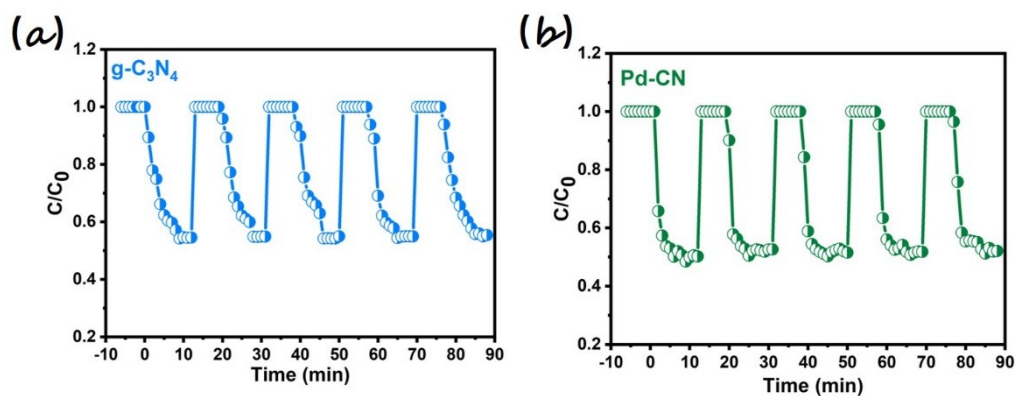


Figure S6. The activity stability of g-C₃N₄ (a); the activity stability of Pd-CN (b).

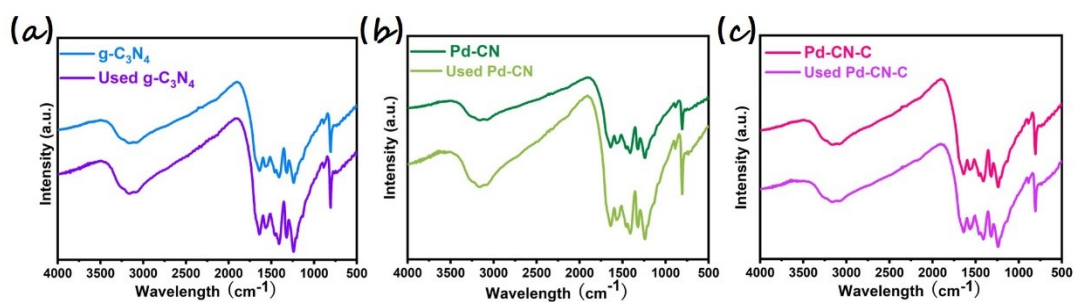


Figure S7. The FTIR spectra of g-C₃N₄ (a), Pd-CN (b), and Pd-CN-C (c).

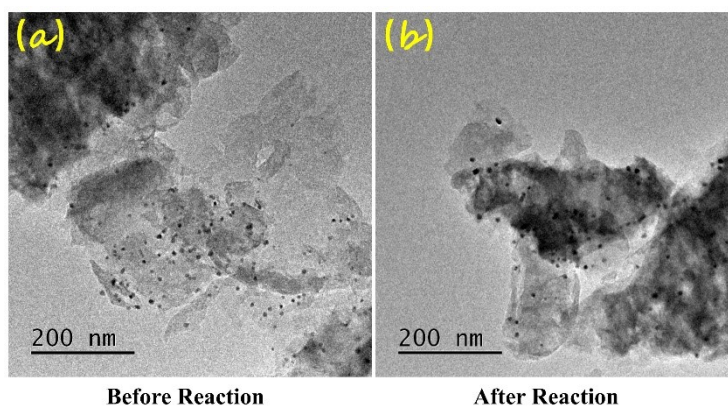


Figure S8. TEM image of Pd-CN-C before (a) and after (b) the light illumination.