

## Supporting Information

For

# Selective Photocatalytic N<sub>2</sub> Fixation Dependent on the g-C<sub>3</sub>N<sub>4</sub> Induced by Nitrogen Vacancies

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### Simulations methods

The simulations were performed using the program package CASTEP, working in a plane wave basis set. The substrate is modeled by one layer of V-g-C<sub>3</sub>N<sub>4</sub> separated by a vacuum layer of 10 Å. The two uppermost substrate layers and the N<sub>2</sub> molecule are allowed to relax. The Brillouin zones of the supercells were sampled by a grid of 3 × 3 × 1 (V-g-C<sub>3</sub>N<sub>4</sub>) K-points. Based on the structure of bulk V-g-C<sub>3</sub>N<sub>4</sub>, the V-g-C<sub>3</sub>N<sub>4</sub> (001) surface was modeled to study the N<sub>2</sub> adsorption properties.

### Isotopic labeling experiments

Labeled <sup>15</sup>N<sub>2</sub> gas was purchased from Sigma-Aldrich Chemical Company. It was used to confirm that the detected ammonia originates from N<sub>2</sub>. In the experimental process, reaction mixture was firstly flushed with Ar for 30 min

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to eliminate air and some possible adsorbed ammonia. Then,  $^{15}\text{N}_2$  was passed through the reaction mixture for 30 min. The reactor was then sealed and exposed to visible light. Other experiment conditions of the photocatalytic  $\text{N}_2$  fixation under  $^{15}\text{N}_2$  isotope-labeled  $\text{N}_2$  atmosphere were the same as those for  $^{14}\text{N}_2$ . Estimation of obtained  $^{15}\text{NH}_4^+$  was done indirectly using the indophenol method, owing to the low mass of  $^{15}\text{NH}_4^+$  for LC-MS studies. The samples for LC-MS analysis were prepared as follows. 0.5 ml of the reaction reacted with 0.1 ml of 1% phenolic solution in 95% ethanol. Then, 0.375 ml of 1% NaClO solution and 0.5 mL of 0.5% sodium nitroprusside (SNP) solution were added in above reaction solution. MS studies were carried on an Ultimate 3000-TSQ (LCMS-ESI).

### **Photocurrent experiments**

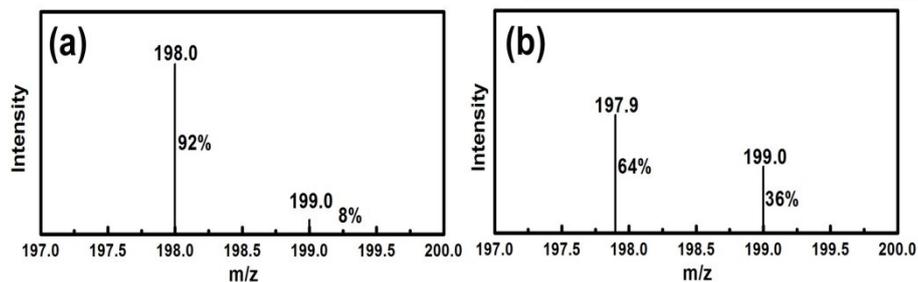
Photocurrent experiments were performed in a conventional three-electrode cell with g- $\text{C}_3\text{N}_4$  or V-g- $\text{C}_3\text{N}_4$  as the working electrode, a platinum plate ( $1 \times 1 \text{ cm}^2$ ) as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode and  $\text{Na}_2\text{SO}_4$  (0.1 M) aqueous solution as the electrolyte. Before the photocurrent measurement, Ar or  $\text{N}_2$  was purged into the electrolyte to remove the dissolved air for 30 min and kept purging during the photocurrent measurement. During the photocurrent measurement, the working electrode was positioned in the middle of electrolyte with the glass side facing the incident light. A 300 W Xe lamp with a 420 nm cutoff filter was chosen as a visible light source.

The working electrodes were prepared by a spin coating method. Typically, the aqueous slurries of g- $\text{C}_3\text{N}_4$  and V-g- $\text{C}_3\text{N}_4$  were spin-coated on ITO glass substrate at a spin rate of 3000 rpm for 30 s under low vacuum. The films on ITO glass substrate were dried in air and annealed at 200 °C for 1 h as the final photoelectrodes.

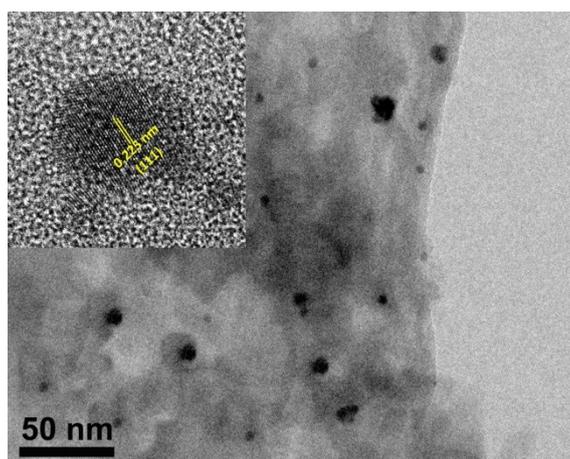
### **The deposition of Pd on the surface of V-g- $\text{C}_3\text{N}_4$**

Normally, 0.30 g V-g- $\text{C}_3\text{N}_4$  and 0.015 g  $\text{PdCl}_2$  were mixed in 100 ml deionized water. The suspension was then irradiated by a 300 W Xe lamp (Through an UV cutoff filter,  $\lambda > 420 \text{ nm}$ ) under continuous stirring. After 5 h

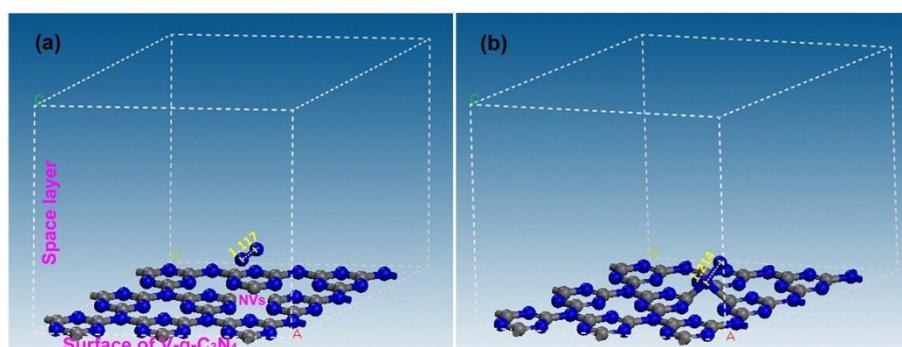
photo-deposition, the suspension was filtered, washed with deionised water for more than three times, and finally dried at 60 °C for overnight.



**Fig. S1** The mass spectra of the indophenol prepared from different atmosphere. (a) The mass spectra of the indophenol prepared from  $^{14}\text{N}_2$  atmosphere; (b) The mass spectra of the indophenol prepared from  $^{15}\text{N}_2$  atmosphere.

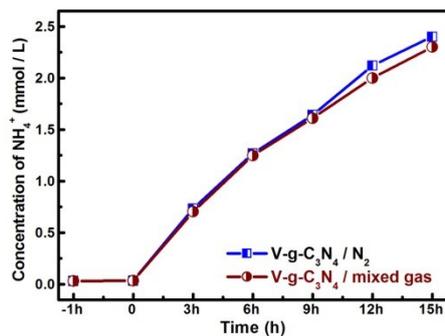


**Fig. S2** TEM image of Pd deposited V-g-C<sub>3</sub>N<sub>4</sub>; insert is the HRTEM of Pd deposited V-g-C<sub>3</sub>N<sub>4</sub>.

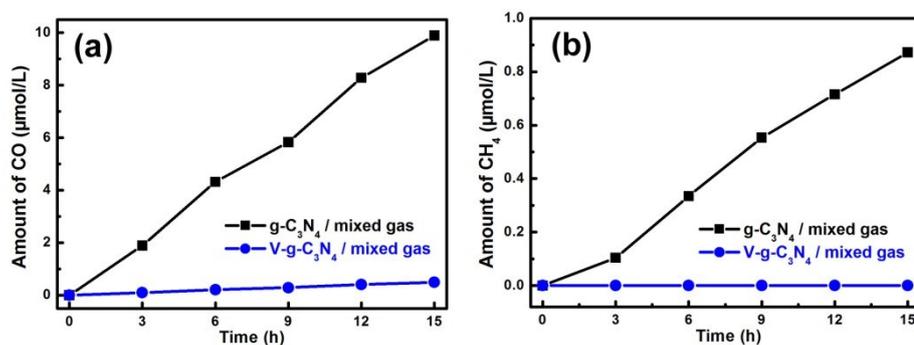


**Fig. S3** View for original adsorption models (a) and optimal adsorption models (b) of N<sub>2</sub> adsorbed on V-g-

C<sub>3</sub>N<sub>4</sub>.



**Fig. S4** N<sub>2</sub> was instead by mixed gas (N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> with the volume ratio of 1:1:1) in the photocatalytic N<sub>2</sub> fixation experiment.



**Fig. S5** (a) CO generation over g-C<sub>3</sub>N<sub>4</sub> and V-g-C<sub>3</sub>N<sub>4</sub> samples in mixed gas condition; (b) CH<sub>4</sub> generation over g-C<sub>3</sub>N<sub>4</sub> and V-g-C<sub>3</sub>N<sub>4</sub> samples in mixed gas condition.