

# Supplementary Materials: Enhancing light-driven production of hydrogen peroxide by anchoring Au onto C<sub>3</sub>N<sub>4</sub> catalyst

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## ***Characterization and Photocatalytic measurements***

### *Preparation of catalysts with different gold loadings*

Similar to the synthesis of Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-2%, the Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-1% and Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-3% catalysts was synthesized by adding 1g C<sub>3</sub>N<sub>4</sub> to the pH=10.0 solution of 0.01g and 0.03g HAuCl<sub>4</sub>·3H<sub>2</sub>O in 60 mL water, respectively.

### *Preparation of Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-without dopa catalyst*

Similar to the synthesis of Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>) catalyst, the only difference was that the Au/C<sub>3</sub>N<sub>4</sub>-250 powder was annealed directly in a gas flow of nitrogen at 500 °C for 2 hr and was further annealed in air at 500 °C for 2 hr. The sample was named Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-without dopa.

### *Characterization*

The high-resolution transmission electron microscopy (HR-TEM) images were collected with a JEOL JEM-3010 microscope. For TEM observations, the samples were ultrasonically dispersed in ethanol, and then a drop of the suspension was deposited onto a carbon-coated copper grid followed by evaporation of the solvent in air. The energy dispersive X-ray spectroscopy (EDS) mapping analysis was recorded with a JEOL JEM-2100F microscope. The XRD patterns were obtained on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA, graphite-filtered CuK<sub>α</sub> radiation,  $\lambda = 0.15418$  nm). The solid-state UV-vis diffuse reflectance spectra were performed at room temperature using a Shimadzu UV-3000 spectrometer equipped with an integrating sphere attachment using BaSO<sub>4</sub> as background. The photoluminescence (PL) emission spectra were conducted on Hitachi F-7000 spectrofluorometer using a laser with an excitation of 400 nm at room temperature. The XPS spectra were carried out on a ThermoVG ESCALAB MK II X-ray photoelectron spectrometer at a pressure of about  $2 \times 10^{-9}$  Pa using AlK<sub>α</sub> X-ray as the excitation source (1486.6 eV). The thermogravimetric analysis (TGA) was measured on a TG209.

### *Photocatalytic production and decomposition of H<sub>2</sub>O<sub>2</sub>*

The catalyst (1 g L<sup>-1</sup>) was dispersed into a 5 vol% iso-propanol (total volume 30 mL) aqueous solution in a borosilicate glass bottle ( $\psi = 35$  mm, capacity of 50 mL) and then ultrasonicated for 10 min. The pH value of the suspension was modulated to 3 by adding 1 mol L<sup>-1</sup> HClO<sub>4</sub> solution. The bottle was sealed with a rubber septum cap with a gas inlet and outlet. The solution was purged firstly by oxygen bubbling while stirring for 30 min in dark. The solution was irradiated with a 300 W Xe lamp at an intensity of 100 mW cm<sup>-2</sup> under stirring. The oxygen purging was maintained all through the reaction. The solution was sampled at fixed time to monitor H<sub>2</sub>O<sub>2</sub> concentration. After the first run formation of H<sub>2</sub>O<sub>2</sub> for 240 min, the photocatalyst was removed by centrifugation and washed thoroughly with deionized water and dried in air. Subsequently, the obtained photocatalyst was reused in a fresh solution under the above conditions. The photocatalytic production of H<sub>2</sub>O<sub>2</sub> was also conducted by using a 420 nm cut-off filter and a 510 nm cut-off filter, respectively.

To investigate the H<sub>2</sub>O<sub>2</sub> decomposition on the catalysts, a catalyst (1 g L<sup>-1</sup>) was dispersed in an acidified H<sub>2</sub>O<sub>2</sub> solution with a 5 mM (pH 3) initial concentration and irradiated for 90 min under stirring. The concentration of H<sub>2</sub>O<sub>2</sub> was measured according to the method from the literature [1]. The stock solutions of N,N-diethyl-1,4-phenylene-diamine sulfite (DPD),

peroxidase (POD) horseradish, and potassium phosphate buffer were prepared as follows. 0.1 g DPD was dissolved in 10 mL 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, and 5 mg POD was dispersed in 5 mL H<sub>2</sub>O. The POD solution was kept in a refrigerator (4 °C) and was prepared once every 5 days. K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O of 1.4 g and KH<sub>2</sub>PO<sub>4</sub> of 6 g were dissolved in 100 mL H<sub>2</sub>O to make a potassium phosphate buffer solution. Aliquots of 2 mL were extracted by a syringe during the reaction at a fixed time and filtered by a 0.45 mm polytetrafluoroethylene (PTFE) filter. Phosphate buffer of 0.8 mL, sample aliquots of 2 mL, DPD of 0.1 mL, POD of 0.1 mL, and water of 2.24 mL were mixed and stirred vigorously for 90 s. Depending on H<sub>2</sub>O<sub>2</sub> concentration generated, the ratio of the sample liquor to water was adjusted to avoid exceeding the detection limit. The calibration curves were plotted according to the range of H<sub>2</sub>O<sub>2</sub> concentrations. The absorbance at 551 nm was monitored using a UV-vis spectrophotometer for quantitative analyses of the concentration.

#### *Quantum yield measurements*

The apparent quantum yield is defined as  $\Phi(\%) = 2[\text{H}_2\text{O}_2 \text{ formed}]/(\text{photon number entered into the reaction vessel}) \times 100$ . The reaction vessel was irradiated by a monochromic light of 400 nm and the power density is 5.4 mW/cm<sup>2</sup>. The H<sub>2</sub>O<sub>2</sub> yield is 12.5 μmol within one and a half hour on the Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>).

#### *Electrochemical tests*

The electrochemical oxygen evolving reaction of the catalysts was studied with a three-electrode configuration connected to a potentiostat (CHI660E, CH instrument Co.). The Ag/AgCl electrode and Pt wire were used as reference and counter electrode, respectively. The working electrode was prepared by immobilizing samples on the FTO conductive glass by a drop-casting way. In brief, the 10 mg catalysts were dispersed in a mixed solution (ethanol: 800 mL; Nafion: 200 mL), and sonicated for 3 h. The suspension was cast drop wise on the surface of FTO electrode. The electrodes were connected to a copper tape and used as the working electrode. Mott–Schottky plots were measured in an acidic solution (pH 3) at frequencies of 1.0, 1.5 and 2.0 kHz in dark. The potentials measured were converted to a reversible hydrogen electrode (RHE) based on Eq. (1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl vs. NHE}} + 0.0592\text{pH} \quad (1)$$

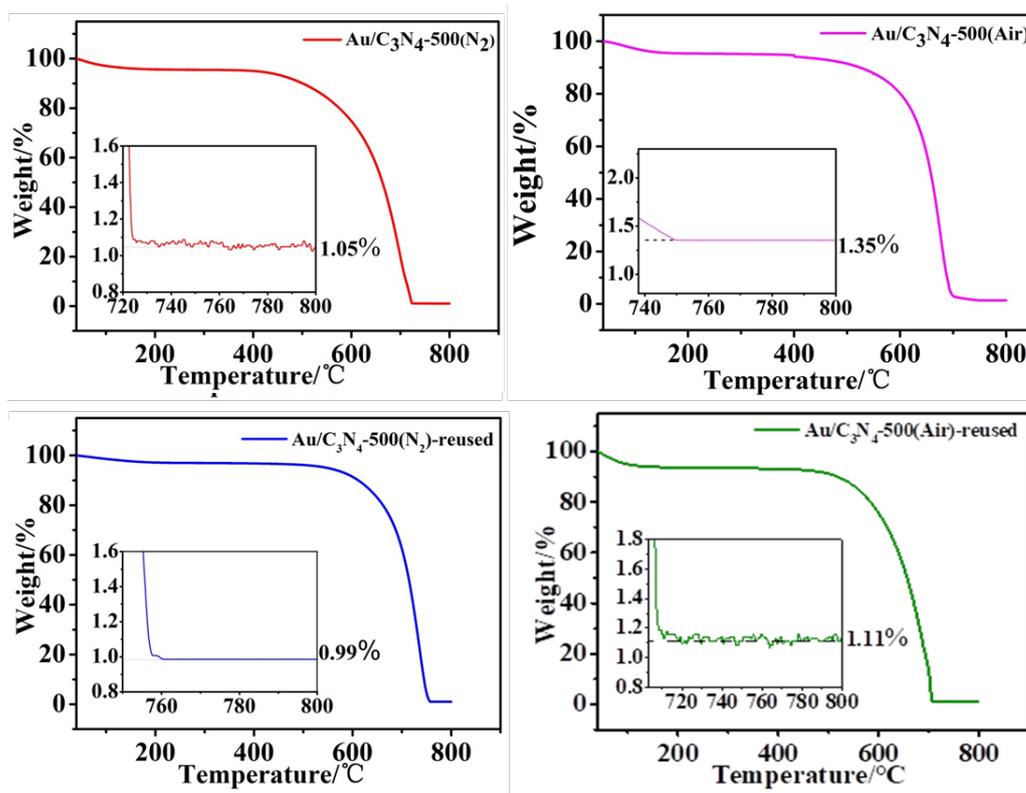
in which  $E_{\text{Ag/AgCl vs. NHE}}$  is the correction factor for Ag/AgCl referenced to the normal hydrogen electrode (NHE), and equals 0.197 V at 20 °C.

#### References

1. Moon, G.-H.; Kim, W.; Bokare, A.-D.; Sung, N.-h.; Choi, W. Solar production of H<sub>2</sub>O<sub>2</sub> on reduced graphene oxide–TiO<sub>2</sub> hybrid photocatalysts consisting of earth-abundant elements only. *Energy Environ. Sci.* 2014, 7, 4023–4028.

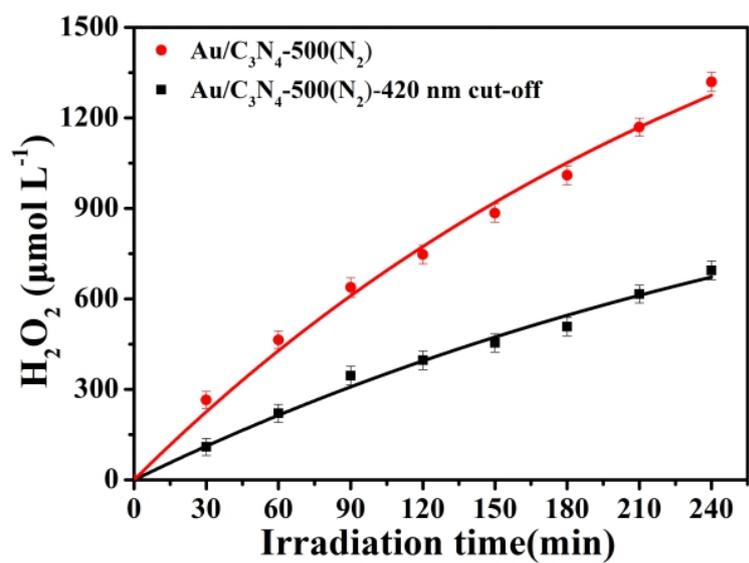
## Results

### 2.1. Catalyst characterization

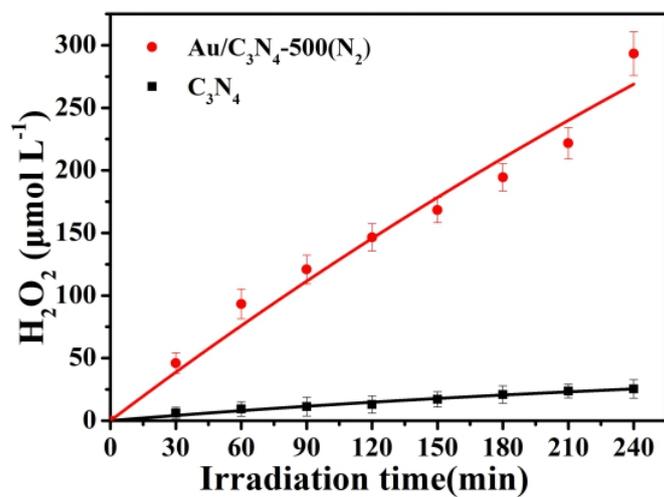


**Figure S1.** Thermogravimetric analysis curve of (a) Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>); (b) Au/C<sub>3</sub>N<sub>4</sub>-500(Air); (c) Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-reused; (d) Au/C<sub>3</sub>N<sub>4</sub>-500(Air)-reused .

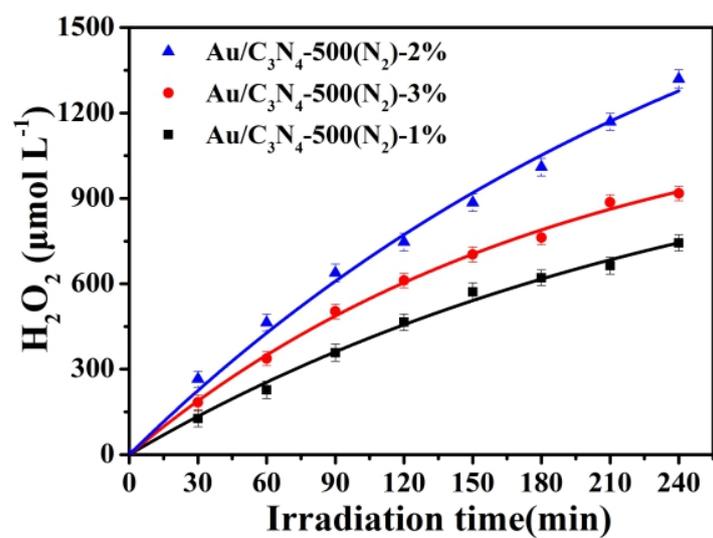
## 2.2. Photosynthesis of H<sub>2</sub>O<sub>2</sub>



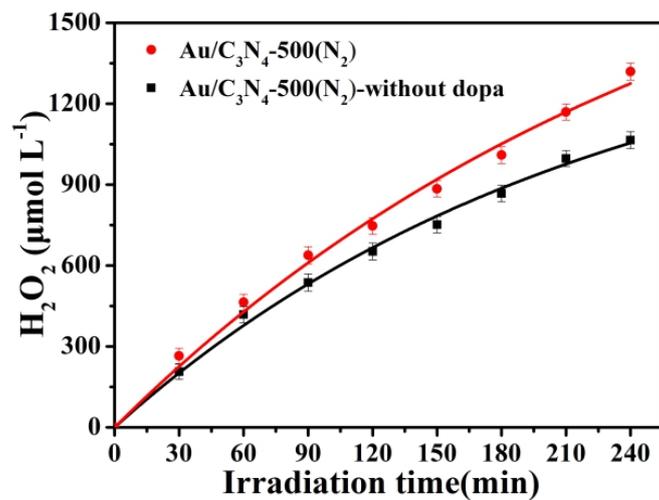
**Figure S2.** The light-driven H<sub>2</sub>O<sub>2</sub> generation over Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>) under light irradiation with a 420 nm cut-off filter. The experimental conditions were as follows: 1g/L of photocatalyst, 5vol% of 2-propanol, pH = 3.0, and O<sub>2</sub>-saturated condition.



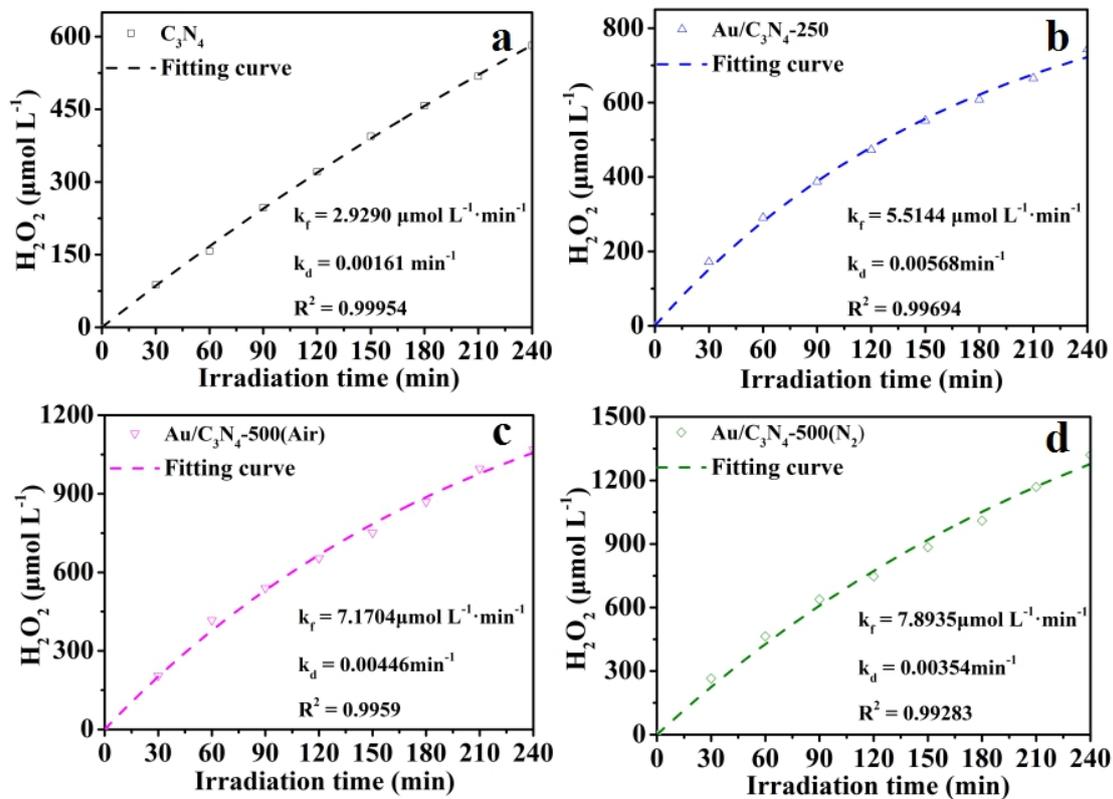
**Figure S3.** The light-driven H<sub>2</sub>O<sub>2</sub> generation over C<sub>3</sub>N<sub>4</sub> and Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>) under light irradiation using a 510 nm cut-off filter. The experimental conditions were as follows: 1g/L of photocatalyst, 5vol% of 2-propanol, pH = 3.0, and O<sub>2</sub>-saturated condition.



**Figure S4.** The light-driven H<sub>2</sub>O<sub>2</sub> generation over 1%, 2% and 3% Au-supported catalysts. The experimental conditions were as follows: 1g/L of photocatalst, 5vol% of 2-propanol, pH = 3.0, illumination intensity is 100 mW/cm<sup>2</sup> and O<sub>2</sub>-saturated condition.



**Figure S5.** The light-driven H<sub>2</sub>O<sub>2</sub> generation over Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>) and Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>)-without dopa. The experimental conditions were as follows: 1g/L of photocatalst, 5vol% of 2-propanol, pH = 3.0, illumination intensity is100 mW/cm<sup>2</sup> and O<sub>2</sub>-saturated condition.



**Figure S6 .** Kinetic fitting curves of the samples: (a)  $\text{C}_3\text{N}_4$ , (b)  $\text{Au/C}_3\text{N}_4\text{-250}$ , (c)  $\text{Au/C}_3\text{N}_4\text{-500(Air)}$ , (d)  $\text{Au/C}_3\text{N}_4\text{-500(N}_2\text{)}$ .

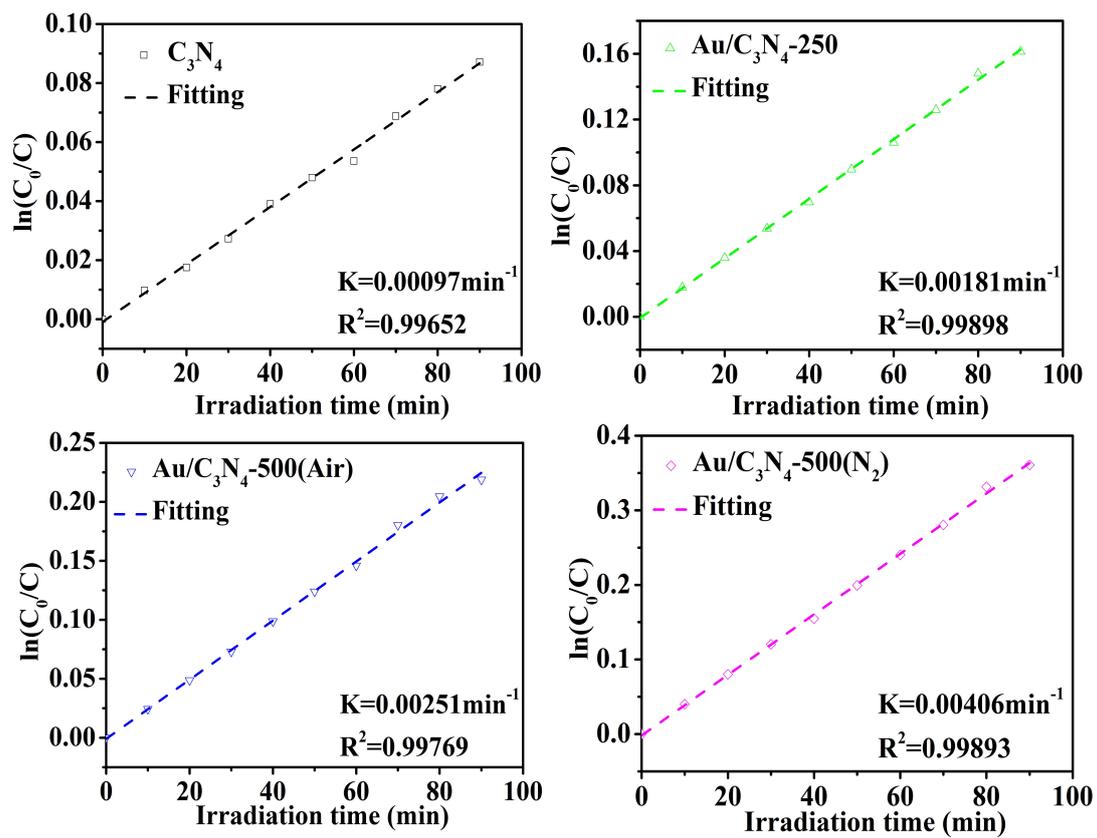


Figure S7. The fitting curves of  $\text{H}_2\text{O}_2$  decomposition, following first-order kinetic equation.

2.3. Stability of the photocatalysts

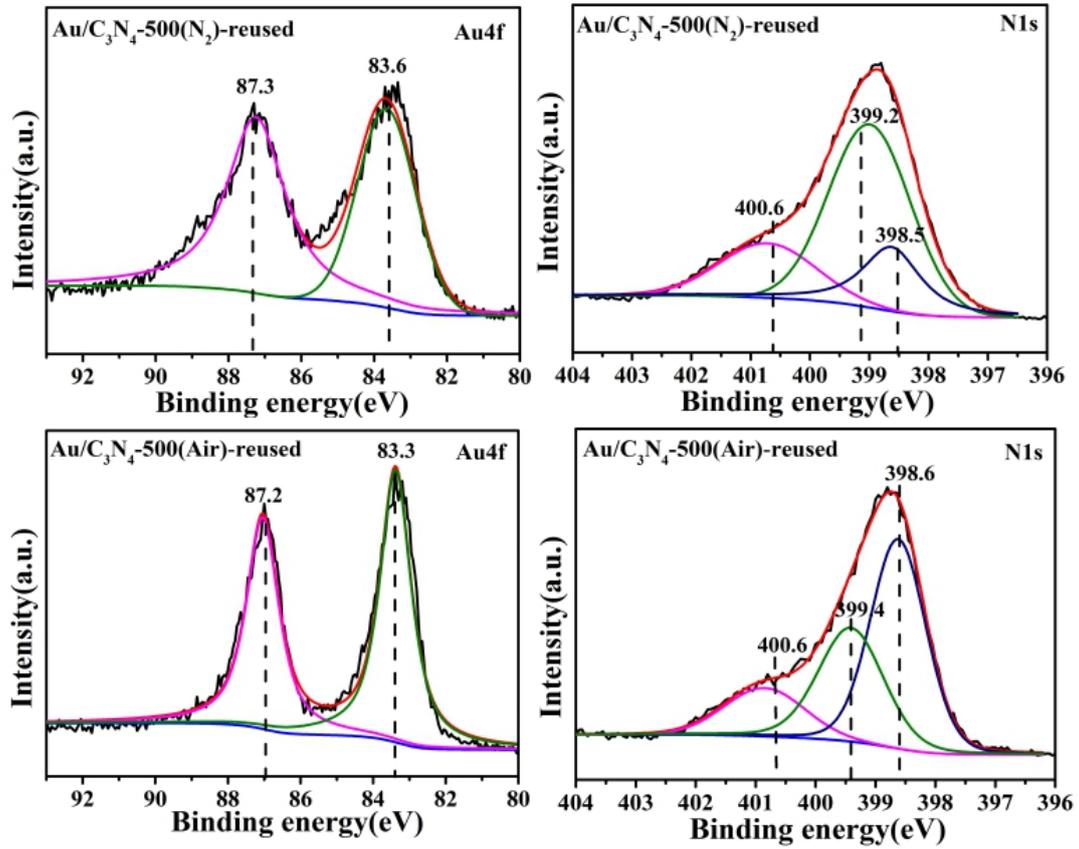
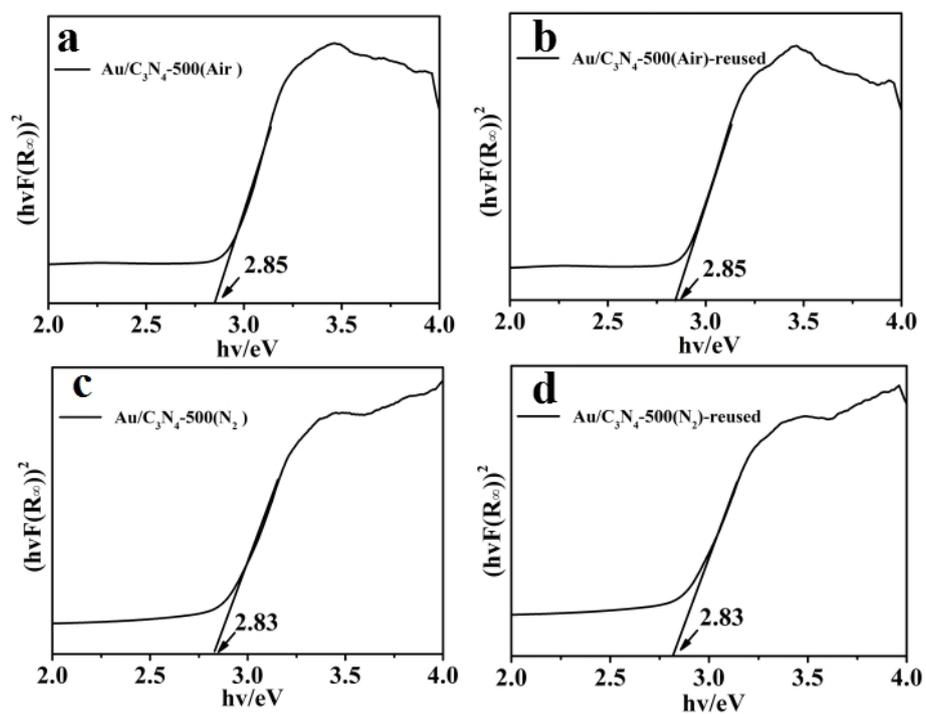


Figure S8. XPS core level spectra of Au4f , N1s in  $\text{Au/C}_3\text{N}_4\text{-500(N}_2\text{)-reused}$  and  $\text{Au/C}_3\text{N}_4\text{-500(Air)-reused}$ .



**Figure S9.** Tauc plots of (a) Au/C<sub>3</sub>N<sub>4</sub>-500(Air); (b) Au/C<sub>3</sub>N<sub>4</sub>-500(Air)-reused; (c) Au/C<sub>3</sub>N<sub>4</sub>-500(N<sub>2</sub>); (d) Au/C<sub>3</sub>N<sub>4</sub>-500 (N<sub>2</sub>)-reused .