Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Electrochemical measurements details

An aqueous solution of 0.5 M $Na_2SO_4$ was used as an electrolyte and the working electrode was prepared as below: 5 mg of photocatalyst was dispersed in 1 mL of ethanolic solution contained Nafion (3 v/v%) and then sonicated for 30 min to give a homogenous suspension. Then, the mixed solution was dropped on 2.5 × 2.5 cm FTO (Fluorine doped tin oxide) substrate by spin coating technique and left under the air to be dried. All electrochemical measurements were conducted under visible light irradiation provided by a 300 W Xe lamp along with a 400 nm cutoff filter. The electrochemical impedance spectra (EIS) were done at the amplitude of 5 mV and frequency ranges of 0.1-105 Hz. The acquired results vs Ag/AgCl were converted to RHE (reversible hydrogen electrode) according to Equations (1) [1]

$$E_{RHE}=E_{AgCl} + E^{0}_{AgCl} \quad (1)$$

Table S1. Values used for the entropy and zero-point energy corrections in determining the free energy of reactants, products and intermediate species adsorbed on catalysts.

| Species | Pressure/bar | Temperature/K | E(DFT)/eV | ΔG (eV) | G (eV) |
|---|---|---|---|---|---|
| $H_2$(g) | 1 | 298.15 | | | -9.91 |
| $O_2$(g) | 1 | 298.15 | -6.78 | -0.022 | -6.80 |
| $H_2O$(l) | 0.035 | 298.15 | -14.20 | -0.024 | -14.22 |

Table S2. Adsorption free energies of *OH, *O, and *OOH on different active sites over catalysts.

| atalysts Species | *O | *OH | *OOH |
|---|---|---|---|
| Au/CN-150 ($Au_4$) | 2.82 | 1.56 | 3.71 |
| Au/CN-100($Au_8$) | 1.67 | 1.39 | 4.49 |
| Au/CN-50($Au_{12}$) | 2.27 | 0.86 | 4.22 |

Table S3. Reaction free energy (vs. RHE) of elementary step for 4e- transfer ORR at $U_{RHE}$ = 0 V on different catalysts.

| Catalysts | $\Delta G_1$ (eV) | $\Delta G_2$ (eV) | $\Delta G_3$ (eV) | $\Delta G_4$ (eV) |
|---|---|---|---|---|
| Au/CN-150 ($Au_4$) | -1.21 | -0.89 | -1.26 | -1.56 |
| Au/CN-100 ($Au_8$) | -0.43 | -2.82 | -0.28 | -1.39 |
| Au/CN-50 ($Au_{12}$) | -0.7 | -1.95 | -1.41 | -0.86 |

Table S4. Reaction free energy (vs. RHE) of elementary step for 2e- transfer ORR at $U_{RHE}$ = 0 V on different catalysts.

| Catalysts | $\Delta G_5$ (eV) | $\Delta G_6$ (eV) |
|---|---|---|
| Au/CN-150 ($Au_4$) | -1.21 | -0.19 |
| Au/CN-100 ($Au_8$) | -0.43 | -0.97 |
| Au/CN-50 ($Au_{12}$) | -0.80 | -0.60 |

Table S5. Reaction free energy for potential determining step at equilibrium potential (ΔGmax) for ORR, reaction free energy of potential determining step for 4e- ORR ($\Delta G_{H2O}$). reaction free energy of potential determining step for 2e- ORR ($\Delta G_{H2O2}$).

| Catalysts | $\Delta G_{H2O}$ (eV) | $\Delta G_{H2O2}$ (eV) | $\Delta G_{H2O}$ -$\Delta G_{H2O2}$ (eV) |
|---|---|---|---|
| Au/CN-150 ($Au_4$) | -0.89 | -0.19 | -0.70 |
| Au/CN-100 ($Au_8$) | -0.28 | -0.43 | 0.15 |
| Au/CN-50 ($Au_{12}$) | -0.70 | -0.60 | -0.10 |

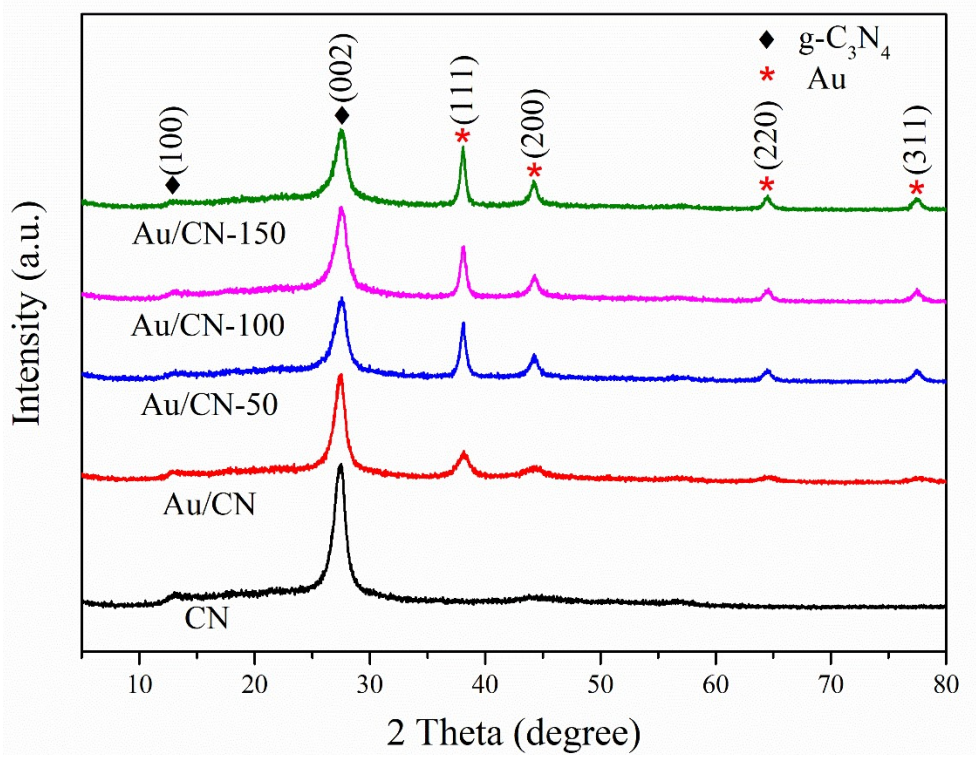


Figure S1. XRD pattern of different samples.

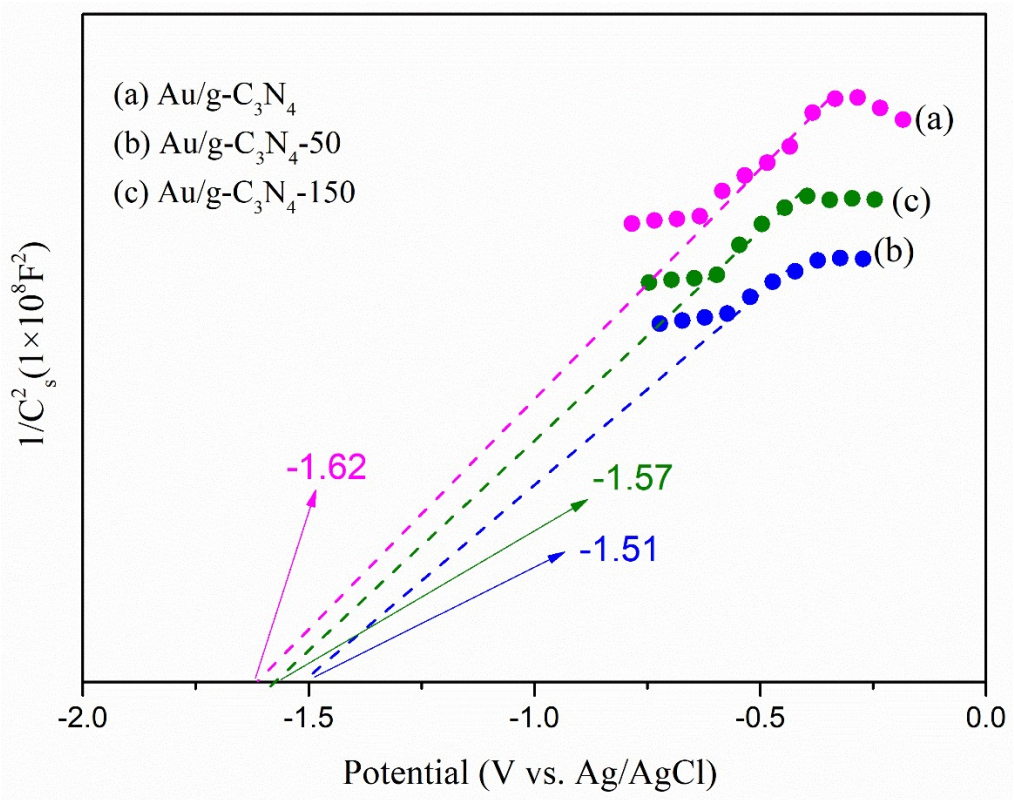


Figure S2. Mott-Schottky polt of of Au/CN, Au/CN-50 and Au/CN-150

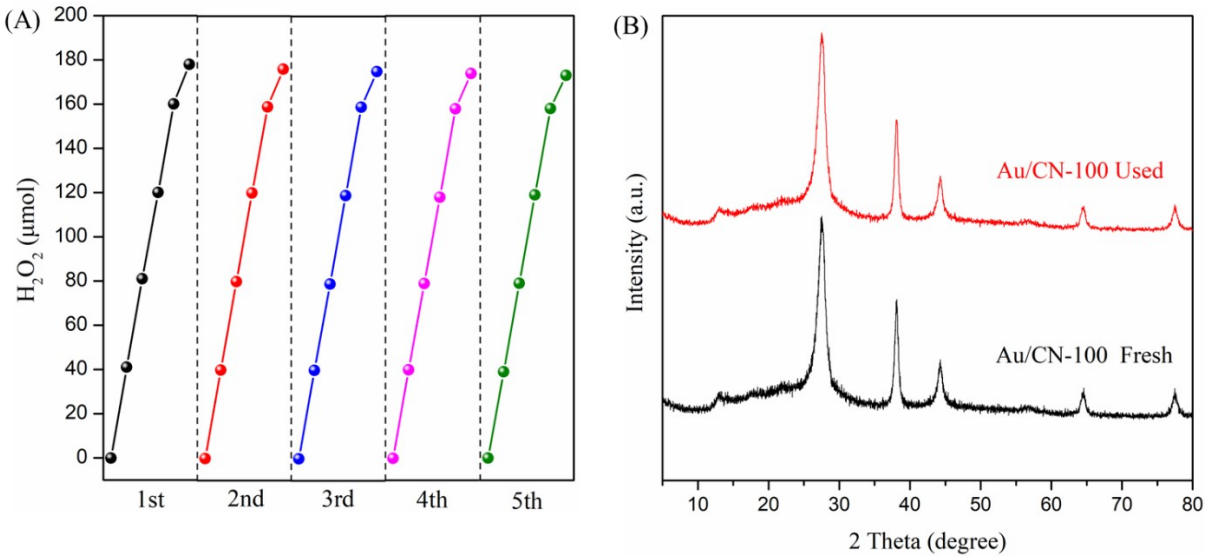


Figure S3. (A) Reusability of Au/CN-100 in the production of $H_2O_2$;(B) XRD patterns of Au/CN-100 photocatalytic reaction before and after.

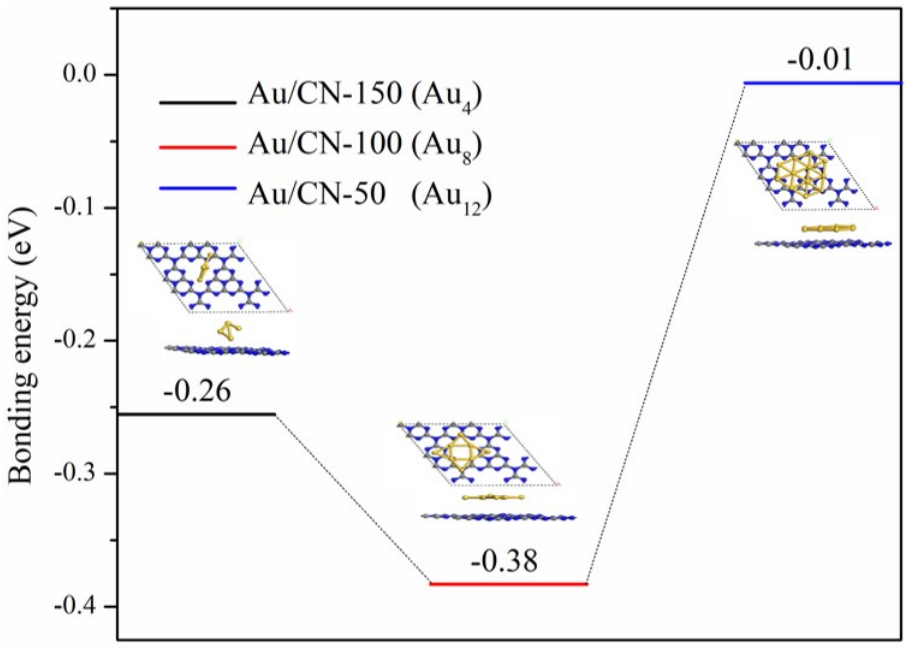


Figure S4. Optimized structures and the free energies of CN combine with $Au_4$, $Au_8$ and $Au_{12}$.

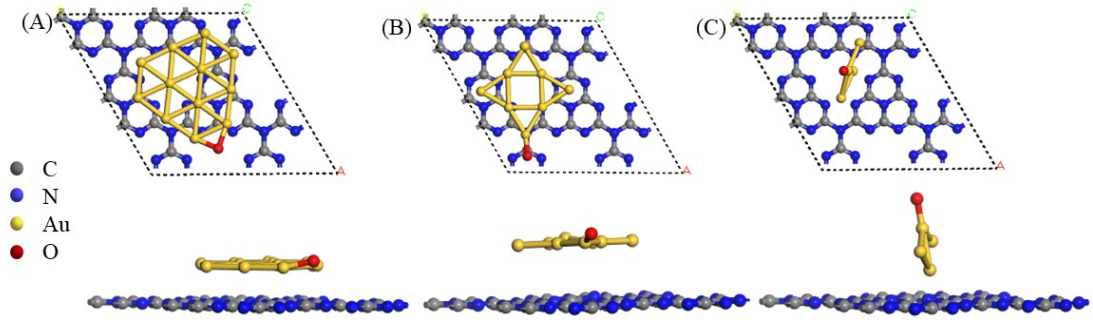


Figure S5. Top and side views of the optimized *O adsorption stability model for (A)Au/CN-50($Au_{12}$), (B)Au/CN-100($Au_8$), (C) Au/CN-150($Au_4$) structures

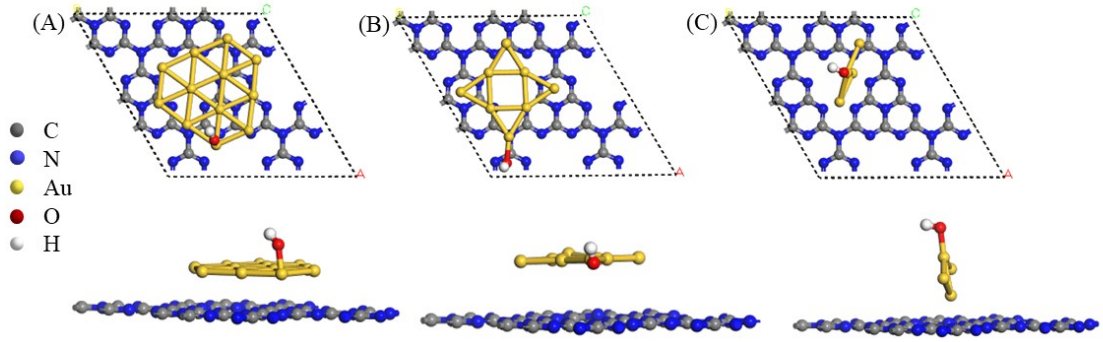


Figure S6. Top and side views of the optimized *OH adsorption stability model for (A)Au/CN-50($Au_{12}$), (B)Au/CN-100($Au_8$), (C) Au/CN-150($Au_4$) structures

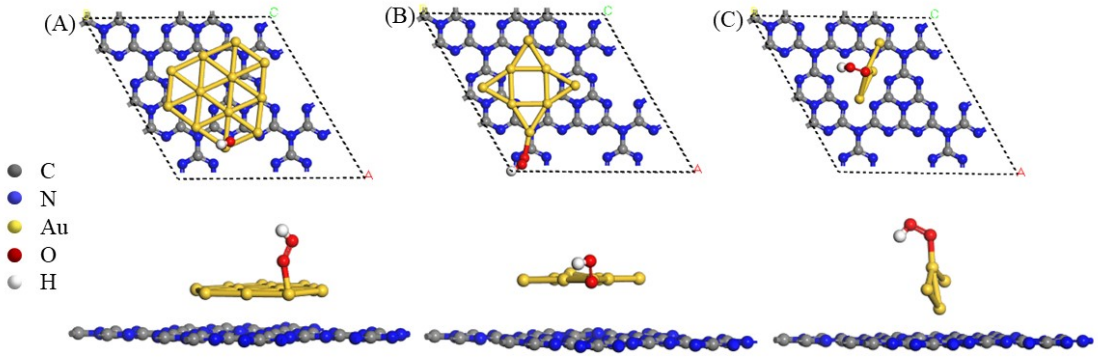


Figure S7. Top and side views of the optimized ·OOH adsorption stability model for (A)Au/CN-50($Au_{12}$), (B)Au/CN-100($Au_8$), (C) Au/CN-150($Au_4$) structures

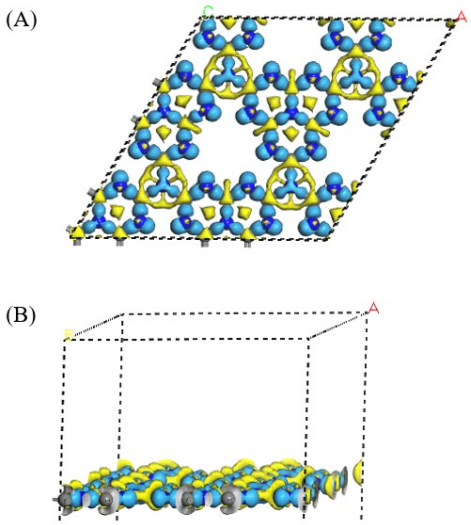


Figure S8. Charge density difference of Au/CN-100 Top(A) and side(B)

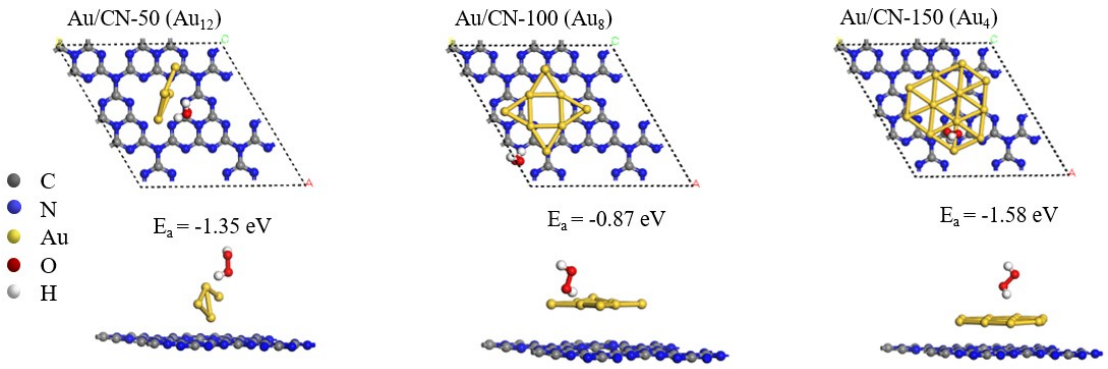


Figure S9. Top and side views of the optimized $H_2O_2$ adsorption structures

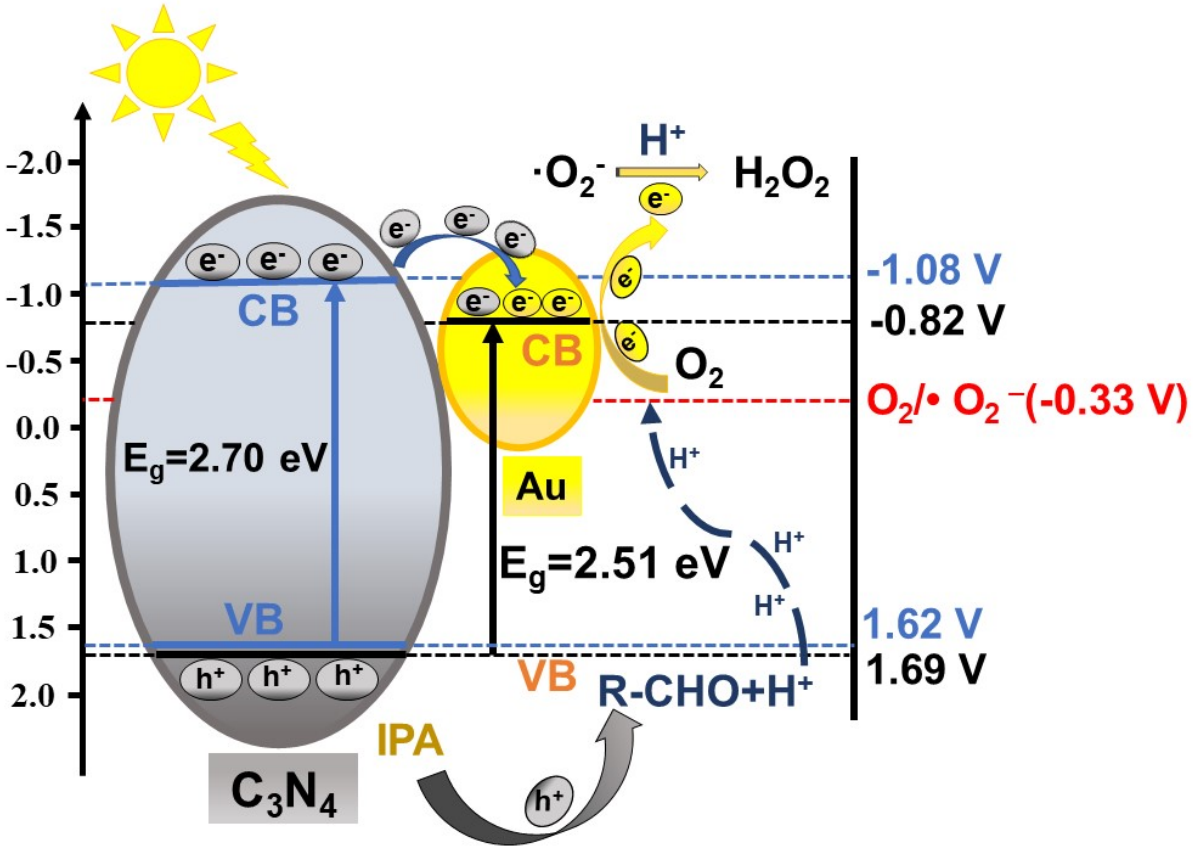


Figure S10. Reaction mechanism on Au/CN-100

[1] Tang, R.; Gong, D.; Zhou, Y.; Deng, Y.; Feng, C.; Xiong, S.; Huang, Y.; Peng, G.; Li, L.; Zhou, Z., Unique g-$C_3N_4$/PDI-g-$C_3N_4$ homojunction with synergistic piezo-photocatalytic effect for aquatic contaminant control and $H_2O_2$ generation under visible light. *Appl. Catal. B: Environ.* 2022, 303, 120929.