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# Photodeposition Au nanoparticles on g-C<sub>3</sub>N<sub>4</sub> toward enhancing oxidation of NO

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## Abstract

The mitigation of pollution resulting from industrial waste gas emissions is a challenging academic and industrial problem. This study focused on the successful preparation of Au/g-C<sub>3</sub>N<sub>4</sub> composite material by photodeposition of Au nanoparticles onto the surface of g-C<sub>3</sub>N<sub>4</sub>. The composite catalyst exhibited robust photooxidation activity and stability in the oxidation of nitric oxide (NO) when subjected to visible light irradiation. As cocatalysts, Au nanoparticles *in-situ* grow on the surface of g-C<sub>3</sub>N<sub>4</sub>, forming a tight heterostructure with Schottky junction through van der Waals force, which enhances the SPR effect of Au nanoparticles, thereby enhancing the light absorption capacity of g-C<sub>3</sub>N<sub>4</sub> within the visible region, promoting the separation of electron-hole pairs generated during photooxidation, prolonging the lifetime of photogenerated carriers and enhancing the photooxidation capacity of the composites.

The mechanism of NO photooxidation has been proposed based on *in-situ* infrared spectroscopy and DFT calculations. This research serves as a valuable reference for the construction of semiconductor-cocatalyst systems and their behavior in NO photooxidation, contributing to the advancement of this field.

**Key words:** Carbon nitride; Au nanoparticles; Photodeposition; SPR; Photooxidation  
NO

## 1.Introduction

In recent years, as society and science have advanced, the release of industrial waste gas and water has caused serious pollution deteriorating our ecological environment [1]. As a common acid gas pollutant, NO poses numerous concerns including the generation of acid rain, depletion of the ozone layer, the formation of photochemical smog and haze, and the potential harm to human lung tissue [2-5]. Traditional methods such as the physical and chemical treatments, thermal catalytic reduction and biochemical method have obvious defects and limitations, such as high operational expenses, low efficiency, inadequate selectivity, incomplete degradation and transformation of pollutants, as well as a propensity to generate secondary pollutants [6]. Therefore, the exploration of environmentally friendly, efficient and non-secondary pollution degradation technologies has emerged as a focal point of research. Among these, semiconductor photocatalysis technology has garnered significant attention as a green, non-toxic, and sustainable degradation method.

As a typical 2D non-metallic polymer semiconductor photocatalyst, graphite-phase carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) possesses several key advantages including its affordability, robust chemical stability, and straightforward synthesis process [7]. However, single component g-C<sub>3</sub>N<sub>4</sub> has non-ignorable disadvantages such as low utilization efficiency under visible light and easy recombination of photogenerated carriers, which limits its application in photocatalysis [8]. In order to overcome the defects of g-C<sub>3</sub>N<sub>4</sub>, researchers have proposed effective strategies [9-13] to improve its photocatalytic performances. For example, Zhang et al. [14] successfully incorporated WO<sub>x</sub> layers with oxygen vacancies into Au-modified g-C<sub>3</sub>N<sub>4</sub> nanosheets to form heterojunctions with excellent CO<sub>2</sub>

photoreduction properties. Wang et al. [15] effectively promoted the separation of photogenerated electrons and holes using composite of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. However, TiO<sub>2</sub> has poor optical absorption performance in the visible range. Noble metal nanoparticles have a surface plasmonic resonance effect (SPR), wherein the localized electric field they generate enhances the absorption of composite materials to visible light. Meanwhile, noble metal nanoparticles can be used as a trap to capture photoexcited electrons in semiconductors to improve the separation efficiency of photogenerated electron-hole pairs in semiconductor catalysts [16]. Therefore, loading noble metal can improve the photocatalytic performances of semiconductors. The Pt/g-C<sub>3</sub>N<sub>4</sub> composite prepared by Zhu et al. [17] through *in-situ* photoreduction improved the photocatalytic hydrogen evolution performances, compared with pure g-C<sub>3</sub>N<sub>4</sub>. The Ag/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> and Ag/ZSM-5/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> catalysts prepared by Wang et al. [18] can significantly improve the degradation efficiency of formaldehyde. Li et al. [19] synthesized Au/g-C<sub>3</sub>N<sub>4</sub> nanocomposites by *in-situ* wet chemical reduction method. The introduction of Au NPs improved the photocatalytic nitrogen oxide removal activity of g-C<sub>3</sub>N<sub>4</sub>. Faisal et al. [20] prepared an Au/g-C<sub>3</sub>N<sub>4</sub> composite photocatalyst, which showed high photocatalytic activity for the degradation of methylene blue dye and the drug Gemefloxacin mesylate within the range of visible light. Therefore, Au nanoparticles are considered a suitable cocatalyst to improve the photocatalytic efficiency of g-C<sub>3</sub>N<sub>4</sub>.

In this study, g-C<sub>3</sub>N<sub>4</sub>-Au composite photocatalyst was synthesized by photodeposition strategy. With NO as the target pollutant, the photocatalytic performances of the composite were studied. The material structure, elemental composition, morphology, optical properties and photooxidation activity of the best composite specific photocatalyst was analyzed by a series of characterization methods. Compared with pure g-C<sub>3</sub>N<sub>4</sub>, the photooxidation removal efficiency of g-C<sub>3</sub>N<sub>4</sub>-Au-3 under visible light can reach 77.4 % within 30 min. The test results show that the SPR effect of precious metals promotes the absorption of visible light by the sample, and it is easier to generate photogenerated charge carriers. AuNPs with a particle size of about 10 nm are *in-situ* grown on the surface of g-C<sub>3</sub>N<sub>4</sub>. Thus, the Au-g-C<sub>3</sub>N<sub>4</sub> heterojunction was constructed, and the tight interface enhanced the SPR

effect of Au and helped charge transport, promotes the separation of photogenerated electron-hole pairs, prolongs the lifetime of photogenerated carriers, and significantly improves the photooxidation activity. The mechanism of NO photooxidation was preliminarily revealed by *in-situ* infrared spectroscopy. DFT calculation shows that the introduction of Au nanoparticles can promote the photooxidation reaction.

## 2. Experimental section

### 2.1 Materials

Urea ( $\text{CH}_4\text{N}_2\text{O}$ , purity $\geq$ 99.0 %), chloroauric acid ( $\text{AuCl}_3\cdot\text{HCl}\cdot 4\text{H}_2\text{O}$ , purity $\geq$ 99.0 %), ethanol ( $\text{C}_2\text{H}_6\text{O}$ , purity $\geq$ 99.7 %) are supplied by the McLean's reagent. Also, secondary distilled water is utilized for all experiments. All gas purchase from Stone Head Gas Products LLC. The NO (10 ppm) bottle contains  $\text{N}_2$  equilibrium NO.

### 2.2 Photocatalyst preparation

Preparation process of g- $\text{C}_3\text{N}_4$ : 10 g urea was put into a ceramic crucible with a lid, which was heated in a box Muffle furnace at 550 °C for 2 h at a heating rate of 2.5 °C·min<sup>-1</sup>. The crucible was cooled to room temperature and then ground to obtain light-yellow powders of g- $\text{C}_3\text{N}_4$ .

Preparation process of g- $\text{C}_3\text{N}_4$ -Au: g- $\text{C}_3\text{N}_4$ -Au were prepared by photo-deposition method. In a typical process ,0.5 g prepared g- $\text{C}_3\text{N}_4$  were dispersed to 100 ml secondary distilled water by ultrasonic treatment for 30 min, a certain amount of chloroauric acid (0.025 mol·L<sup>-1</sup>) were added into the suspension drop by drop under magnetic stirring, and continue stirring for 60 min. At room temperature, the mixed solution was stirred under xenon lamp with 350 W and illuminated for 1.5 h, the product was centrifuged at 8000 rpm for 10 min and washed repeatedly with deionized water and ethanol, then dried in 333 K constant temperature oven for 24 h. The g- $\text{C}_3\text{N}_4$ -Au composites with mass fraction of Au about 1 %, 3 % and 5 % were named g- $\text{C}_3\text{N}_4$ -Au-1, g- $\text{C}_3\text{N}_4$ -Au-3 and g- $\text{C}_3\text{N}_4$ -Au-5, respectively.

### 2.3 Characterizations

Phase analysis was performed by X-ray diffractometer (D8, Bruker AXS GmbH, Germany). The Cu target is the radiation source ( $\lambda= 0.15418$  nm), the voltage is 40

kV, the current is 40 mA, and the  $2\theta$  range of X-ray diffraction detection is  $10^\circ$ - $80^\circ$ . Scanning electron microscopy (SEM, JSM 7401F, JEOL, Japan) and transmission electron microscopy (TEM, Tecnai G2 TF30, FEI, USA) were used to characterize the micromorphology of the composites. The elemental composition of the composites was analyzed by energy dispersive X-ray spectrometer (EDS) equipped with transmission electron microscope. The surface compositions, chemical valence states and valence band spectrum of the composites were analyzed by X-ray photoelectron spectroscopy (XPS, XSAM-800). The composites were diluted with potassium bromide powder, and the changes of functional groups of the photocatalysts were analyzed by Fourier Transform infrared spectrometer (FT-IR, Tensor27, Bruker) at the wave number of  $400$ - $4000\text{ cm}^{-1}$ . Photoluminescence (PL) spectra were measured using a fluorescence spectrometer (F-7000 FL, Hitachi, Japan) with an excitation wavelength of 325 nm. The UV-visible diffuse reflectance spectrum (DRS) of the photocatalyst was measured by UV-2550, Shimadzu, Japan. After the composites were degassed at  $200^\circ\text{C}$  for 6 h, the  $\text{N}_2$  adsorption-desorption isotherm was measured by adsorption analyzer (Mike ASAP2460). Electron spin resonance (ESR) spectra were obtained using A300 spectrometers ( Bruker, Germany) for the detection of free radical active species. The electrochemical characteristics of the composites were analyzed on CHI 604E electrochemical analyzer (CH Instruments Inc.). Platinum wire was used as the counter electrode, calomel reference electrode and working electrode. Using  $0.5\text{ mol/LNa}_2\text{SO}_4$  as electrolyte, the photoelectric response was tested by turning on and off the light source regularly.

## **2.4. Photocatalytic performance test**

### **2.4.1 Photooxidation NO Oxidation**

NO gas was oxidized in a quartz tube reactor at room temperature in order to evaluate the photocatalytic activity of the prepared composites. A 300 W xenon lamp was used to simulate a visible light source, in which the UV was cut off by a filter ( $\lambda > 420\text{ nm}$ ) placed vertically above the reactor. An on-line NO<sub>x</sub> detector (Model HNAG1000-4ST, Honeyeagle) was used to continuously record the concentration of NO at the reactor outlet. The specific experimental reaction system is shown in S1. The

0.025 g photocatalyst was weighed and placed in the quartz tube, the flow rate of compressed air and NO was controlled at 350 mL·min<sup>-1</sup> and 70 mL·min<sup>-1</sup>, respectively, by a mass flow controller. NO/Air flow passes through the reactor after complete premix through the humidification chamber. After the adsorption and desorption equilibrium is completed and the concentration of mixed gas was stable to 300 ppb, light is turned on for photooxidation reaction. The concentration of NO at the outlet of the reactor was continuously recorded by NO detector, and the removal ratio of NO oxidation was calculated as Eq. (1):

$$\eta (\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Where  $\eta$  is the removal ratio of NO oxidation,  $C_0$  is the initial concentration of NO, ppb;  $C$  is the final concentration of NO, ppb.

#### 2.4.2 Capture experiment

The mechanism of photocatalysis was studied by the trapping experiment of active components. P-benzoquinone (BQ), disodium ethylenediamine tetraacetate (EDTA-2Na), and isopropanol (IPA) are used as inhibitors of  $\bullet\text{O}_2^-$ ,  $h^+$ , and  $\bullet\text{OH}$  produced in photooxidation reactions. Under the same conditions, the 0.025g photocatalyst was ultrasonically dispersed in 10 mL H<sub>2</sub>O with 0.001 mol of BQ, EDTA-2Na or IPA, respectively. It was dried at 60 ° C until the moisture was completely removed, and samples were collected for oxidative removal of 300 ppb of NO under visible light.

#### 2.4.3 *In-situ* infrared spectroscopy study of photoinduced NO oxidation process

The photooxidation pathway and reaction mechanism of NO under visible light were studied by *in-situ* Fourier transform infrared spectroscopy. The TENSOR II FT-IR spectrometer (Brüker) was tested alongside a high-temperature reaction chamber (HVC) and an *in-situ* diffuse reflection unit (Harrick). The 0.5 g sample was put into the reaction chamber and heat-treated at 110 °C for 1 h to drain the residual gas. The infrared diffuse reflection spectrum was used as the background, and the baseline was collected under dark conditions. Then the NO mixed gas was first passed through the humidification chamber and then into the reaction chamber (10 ppm NO cylinder, nitrogen as carrier gas, air mixing diluted NO concentration to 5 ppm). After adsorption

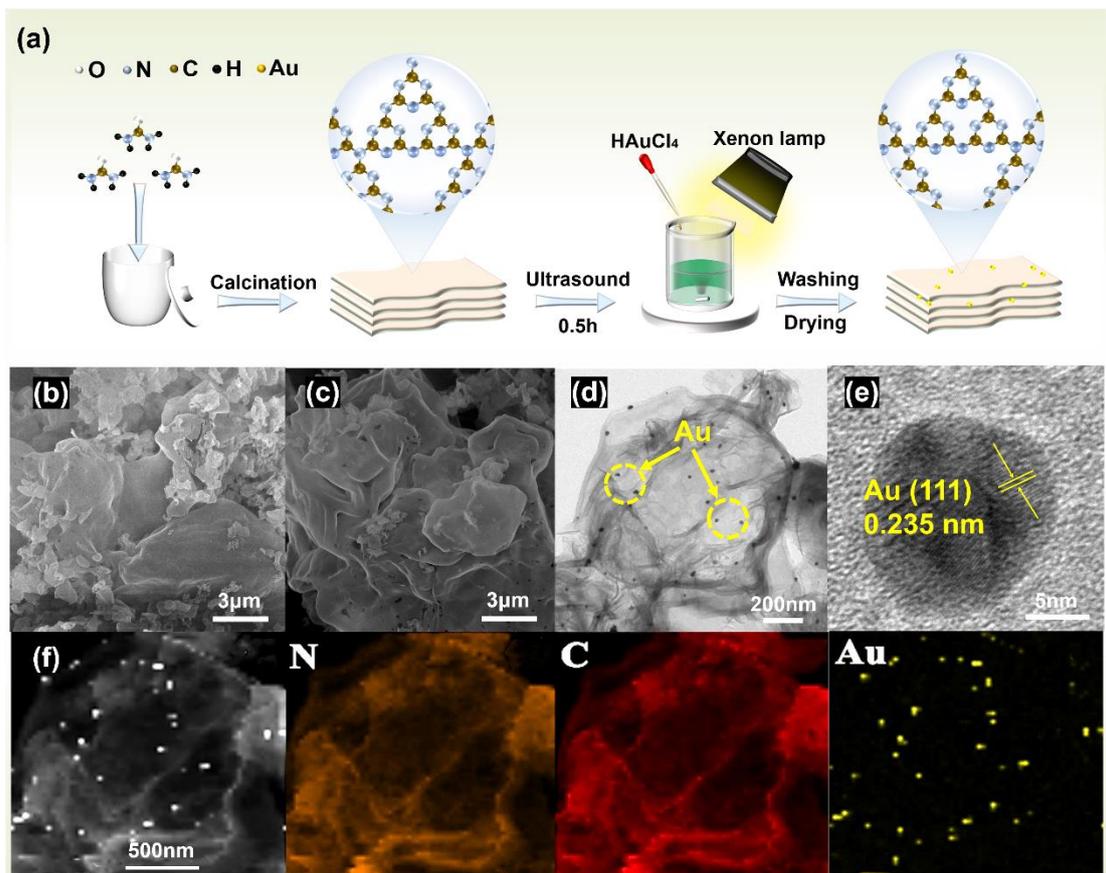
for 30 min, the visible light source 300 W xenon lamp ( $> 420$  nm filter) is open, and irradiates the photocatalyst, the infrared spectral data is record every 2 min, and scan in the range of  $4000\text{-}800\text{ cm}^{-1}$  [19].

#### 2.4.4 DFT Computational Details

All the density functional theory calculations were performed by using the Vienna ab initio Simulation Program (VASP) [21, 22]. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form and a cutoff energy of 500 eV for planewave basis set were adopted [23]. A  $3 \times 3 \times 1$  Monkhorst-Pack grid was used for sampling the Brillouin zones at structure optimization [24]. The ion-electron interactions were described by the projector augmented wave (PAW) method [25]. The convergence criteria of structure optimization were chosen as the maximum force on each atom less than  $0.01\text{ eV}/\text{\AA}$  with an energy change less than  $1 \times 10^{-5}$  eV. The DFT-D3 semiempirical correction was described via Grimme's scheme method [26].

### 3. Results and discussion

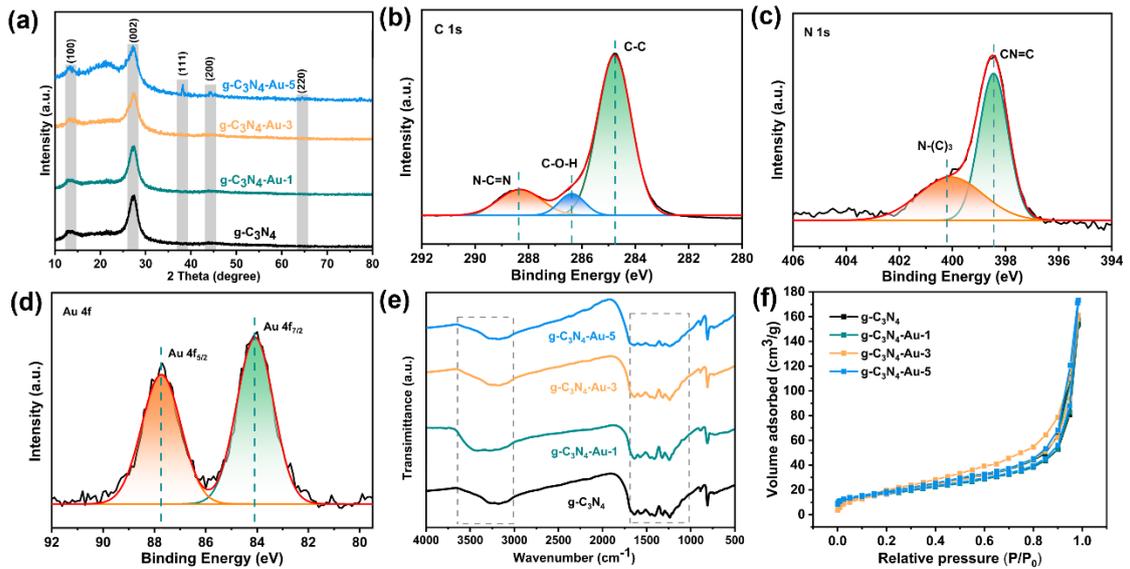
The g-C<sub>3</sub>N<sub>4</sub>-Au photocatalyst was successfully prepared by photo-deposition method (Fig. 1(a)). From Fig. 1(b), g-C<sub>3</sub>N<sub>4</sub> shows an obvious sheet stacking structure with no obvious change after the introduction of Au (Fig. 1(c)). Further observations of the composites by transmission electron microscopy (TEM) show that Au nanoparticles with a size of about 10 nm are well distributed on the surface of g-C<sub>3</sub>N<sub>4</sub> (Fig. 1(d)). The high-resolution transmission electron microscopy (HR-TEM) image (Fig 1(e)) reveals a lattice spacing of 0.235 nm, which corresponds to the crystal plane of face-centered cubic Au (1 1 1) [27]. The element mapping (Fig. 1(f)) shows the uniform distribution of C, N and Au in the catalyst [28].



**Fig. 1** Preparation process and microstructure of samples: (a) synthesis of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au, (b, c) SEM patterns of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au nanocomposites, (d) TEM image of g-C<sub>3</sub>N<sub>4</sub>-Au-3 nanocomposites, (e) HR-TEM image, (f) the elemental mapping images

As shown in Fig. 2(a), all materials show characteristic diffraction peaks at 13.3° and 27.4° of (1 0 0) and (0 0 2) lattice planes of g-C<sub>3</sub>N<sub>4</sub>, respectively, reflecting the in-plane structure stacking motif and the interlayer structure stacking [29]. As the loading percentage of Au nanoparticles (AuNPs) on g-C<sub>3</sub>N<sub>4</sub> increases to 5 %, the X-ray diffraction (XRD) pattern exhibits distinct peaks at 38.23°, 44.24°, and 64.73° corresponding to the crystallographic planes of (1 1 1), (2 0 0), and (2 2 0) of the Au nanoparticles, respectively [30]. The chemical state of the composite surface was studied by X-ray photoelectron spectroscopy (XPS). Fig 2b shows the characteristic peaks at 284.8 eV, 286.4 eV and 288.2 eV in the C 1s high-resolution map of the composite, which are attributed to the C-C, C-O-H and N-C=N in g-C<sub>3</sub>N<sub>4</sub>, respectively [14]. The N 1s spectrum contains peaks at 398.8 eV and 400.5 eV corresponding to sp<sup>2</sup> hybrid

nitrogen (CN=C) and  $sp^3$  bonded nitrogen N-(C)<sub>3</sub>, respectively. Fig. 2(d) displays that the Au 4f high-resolution map of the composite material has two symmetric peaks near 84.2 eV and 87.8 eV, corresponding to Au 4f<sub>7/2</sub> and Au 4f<sub>5/2</sub>, which is consistent with the standard binding energy of zero-valence Au [31]. This indicates that Au nanoparticles are successfully loaded on g-C<sub>3</sub>N<sub>4</sub> matrix [32]. FTIR was used to study the surface functional groups and structural changes of the composites. The FTIR spectra of pure g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au composites are shown in Fig. 2(e). The peak of all composites at 810 cm<sup>-1</sup> corresponds to the respiratory vibration of the tri-s-triazine ring in g-C<sub>3</sub>N<sub>4</sub>. Peaks in the 1200-1650 cm<sup>-1</sup> range (located at 1238, 1317, 1404, 1572 and 1637 cm<sup>-1</sup>) are caused by vibrations of aromatic C-N heterocyclic rings. The peaks of the sample in the range of 3100~3600 cm<sup>-1</sup> are attributed to the signals of O-H or N-H vibrations [33, 34].



**Fig. 2** Phase structure and chemical composition of samples: (a) XRD spectra of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au nanocomposites, XPS spectra of g-C<sub>3</sub>N<sub>4</sub>-Au-3 nanocomposites: (b) C 1s, (c) N 1s, (d) Au 4f, (e) FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au nanocomposites, (f) the N<sub>2</sub> adsorption–desorption isotherms

The N<sub>2</sub> adsorption-desorption isotherms and the pore size distribution curve depicted in Fig. 2(f) were utilized for assessing the pore structure of the composites. By employing the Brunauer-Deming-Deming-Teller (BDDT) classification, it was determined that both pure g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au composites exhibited IV-type curves

and displayed H3 hysteresis rings. These characteristics indicate the presence of mesoporous pores in the composites, which are formed between sheets of g-C<sub>3</sub>N<sub>4</sub>.<sup>[35, 36]</sup> This is consistent with the g-C<sub>3</sub>N<sub>4</sub> morphology observed by SEM in Fig. 1(a).

To assess the photooxidation properties of the composites under visible light, g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>-Au-1, g-C<sub>3</sub>N<sub>4</sub>-Au-3 and g-C<sub>3</sub>N<sub>4</sub>-Au-5 were used for oxidation of NO gas at a concentration of 300 ppb. Under visible light irradiation, the photocatalytic conversion rate of NO decreases rapidly within the first 5 min to stable catalytic activity. As shown in Fig. 3(a), g-C<sub>3</sub>N<sub>4</sub> modified with Au NPs enhanced the NO oxidation activity. The highest conversion rate of NO is observed over g-C<sub>3</sub>N<sub>4</sub>-Au-3 at 77.4 %, while the conversion rate of a pure g-C<sub>3</sub>N<sub>4</sub> under the same conditions is only 33.2 %, When the content of Au reached 5 %, the conversion ratio of NO decreased to 54.4 %, which indicated that a proper amount of AuNPs doping could improve the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> for NO removal, this may be due to photodeposition forming tight Au-g-C<sub>3</sub>N<sub>4</sub> heterostructures on the g-C<sub>3</sub>N<sub>4</sub> surface, enhances the charge transfer, improves the separation efficiency of electron-hole pairs, and prolongs the life of photogenerated carriers, which is conducive to improve the photocatalytic activity<sup>[37]</sup>.

The catalytic results can be fitted by (Fig. 3(b)) the first-order kinetic model<sup>[38]</sup> (Eq.2)

$$\ln(C/C_0) = kt \quad (2),$$

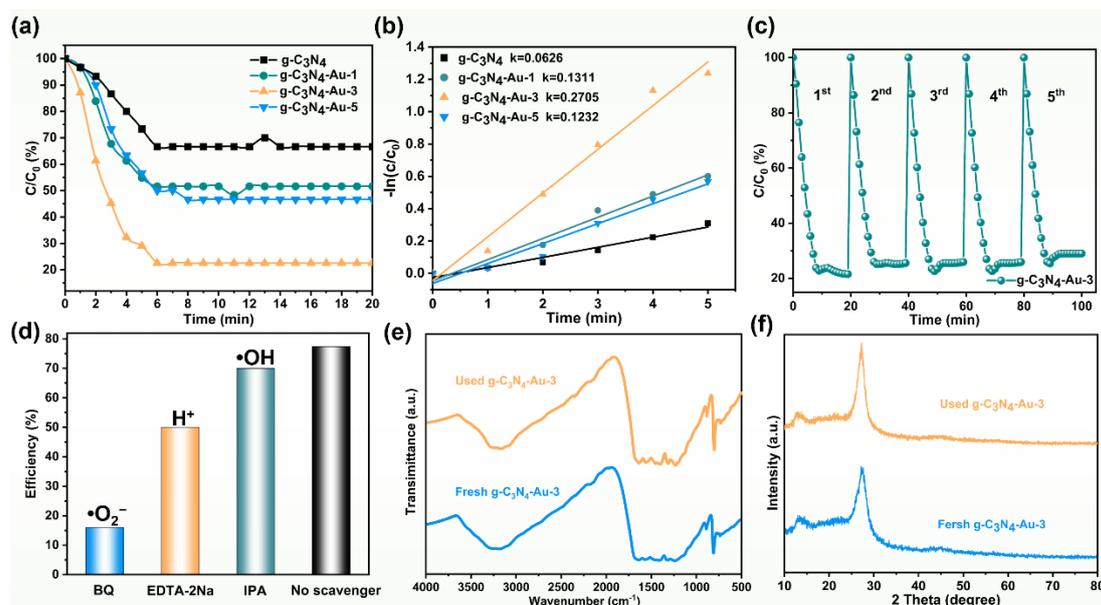
The kinetic constants decrease in the row g-C<sub>3</sub>N<sub>4</sub>-Au-3 (0.02705 min<sup>-1</sup>)> g-C<sub>3</sub>N<sub>4</sub>-Au-1 (k = 0.1232 min<sup>-1</sup>) ≈ g-C<sub>3</sub>N<sub>4</sub>-Au-5 (k = 0.1311 min<sup>-1</sup>)> g-C<sub>3</sub>N<sub>4</sub>. The kinetic results further indicate that the introduction of Au nanoparticles plays a key role in enhancing the performance of photooxidation capacity.

The catalyst stability is an important factor for practical applications. To test this, we reused g-C<sub>3</sub>N<sub>4</sub>-Au-3 and exposed it to visible light for five cycles. Fig. 3(c) shows that while the activity of g-C<sub>3</sub>N<sub>4</sub>-Au-3 decreased slightly, it remained mostly unchanged. This suggests that it has good photostability and can be used again.

In order to explore the photooxidation removal mechanism of NO by g-C<sub>3</sub>N<sub>4</sub>-Au, trapping experiments were conducted to determine the formation of active free radicals

involved in the oxidation removal of NO. P-benzoquinone (BQ), disodium ethylenediamine tetraacetate (EDTA-2Na), and isopropyl alcohol (IPA) were used as scavengers of  $\bullet\text{O}_2^-$ ,  $\text{h}^+$ , and  $\bullet\text{OH}$  produced in photocatalytic reactions. As can be seen from Fig. 3(d), the photooxidation efficiency of g-C<sub>3</sub>N<sub>4</sub>-Au-3 composite decreases from 77.4 % to 6 %, 50 % and 70 %, respectively, after the addition of BQ, EDTA-2Na and IPA. The results show that  $\bullet\text{O}_2^-$  is the main active radical in the photooxidative degradation of NO.  $\bullet\text{O}_2^-$  can be obtained by photogenerative electron reduction of O<sub>2</sub> adsorbed on the surface of the composite. Meanwhile,  $\text{h}^+$  at the VB of g-C<sub>3</sub>N<sub>4</sub>-Au cannot oxidize H<sub>2</sub>O to  $\bullet\text{OH}$  due to potential differences. Therefore, we speculate that  $\text{h}^+$  generated by photocatalysis can directly oxidize NO and enhance the photooxidation performance to a certain extent [39].

We analyzed the FTIR patterns and XRD patterns of the materials before and after recycling. Fig. 3(e, f) illustrates that the surface functional groups and crystal structure of the catalysts remained largely unchanged after cycling. Additionally, Table 1 provides a comparison of the NO removal performance of g-C<sub>3</sub>N<sub>4</sub>-Au-3 with other photocatalysts reported in previous studies. Li et al. [19] successfully loaded Au nanoparticles on g-C<sub>3</sub>N<sub>4</sub>-Au by reducing chloroauric acid with sodium borohydride, and the degradation rate reached 41% by using NO gas flow of 500 ppb. In this work, g-C<sub>3</sub>N<sub>4</sub> was excited under visible light to generate reducing electrons to effectively reduce chloroauric acid, and the deposited Au NPs had good dispersion and stability, which made the formation of a tight heterostructure between AuNPs and g-C<sub>3</sub>N<sub>4</sub>, which can improve the photooxidation activity of NO.



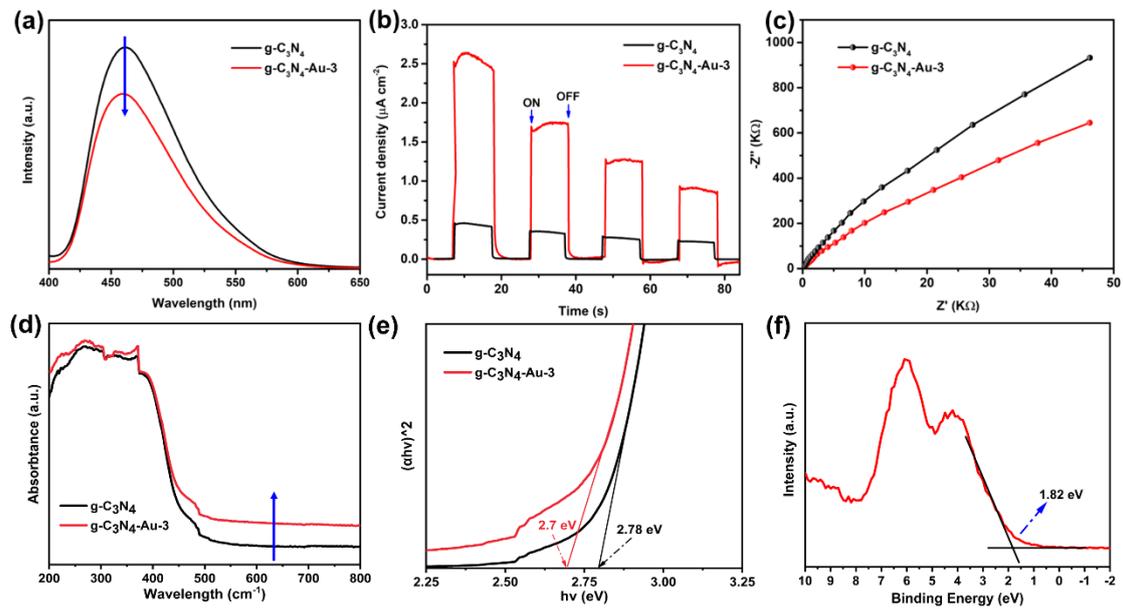
**Fig. 3** Performance and stability analysis of samples: (a) time-dependent oxidation removal of NO, (b) first-order kinetic curves of NO oxidation removal, (c) catalytic stability test for the g-C<sub>3</sub>N<sub>4</sub>-Au-3 photocatalyst, (d) effect of the trapping reagent on the oxidation removal of NO, (e) FTIR spectra and (f) XRD spectra of fresh and used g-C<sub>3</sub>N<sub>4</sub>-Au-3 composite

Table 1 NO removal performance of g-C<sub>3</sub>N<sub>4</sub>-Au-3 compared with other photocatalysts reported in the reference.

Photocatalyst	Initial concentration of NO	Oxidation removal ratio	light source	references
Pd/g-C <sub>3</sub> N <sub>4</sub>	2.2 ppm	56.30%	A 300W Xe lamp	[40]
S-doped g-C <sub>3</sub> N <sub>4</sub>	600 ppm	53%	A 150 W visible light LED lamp with filter ( $\lambda > 400$ nm)	[13]
Au/g-C <sub>3</sub> N <sub>4</sub>	500 ppb	41%	A 150 W commercial halogen tungsten lamp with filter ( $\lambda > 420$ nm)	[19]
Pd/g-C <sub>3</sub> N <sub>4</sub>	12 ppm	83%	A 300 W xenon lamp with filter ( $\lambda > 380$ nm)	[41]
WO <sub>x</sub> /Au/g-C <sub>3</sub> N <sub>4</sub>	600 ppb	61%	A 500 W Xe lamp	[14]
Ag/Bi <sub>2</sub> S <sub>3</sub>	500 ppb	31.12%	A 300 W solar lamp with filter ( $\lambda > 300$ nm)	[4]
Ag <sub>3</sub> PO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	2 ppm	41.76%	A mercury lamp with filter (>290 nm)	[42]
black P/g-C <sub>3</sub> N <sub>4</sub>	600 ppb	74%	Two 300 W Xe lamps with filter ( $\lambda > 420$ nm)	[43]
Graphene quantum dots/g-C <sub>3</sub> N <sub>4</sub>	20 ppm	87%	A 300 W Xe lamp with filter ( $\lambda > 380$ nm)	[44]
Au/ZnIn <sub>2</sub> S <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	600 ppb	59.70%	A 300 W Xe lamp	[45]
TiO <sub>2</sub> /C/g-C <sub>3</sub> N <sub>4</sub>	100 ppm	94%	A 500 W Xe lamp with filter ( $\lambda > 420$ nm)	[46]
NiCoP/g-C <sub>3</sub> N <sub>4</sub>	600 ppb	78%	A 500 W Xe lamp	[47]
AgVO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	600 ppb	65%	A 300 W Xe lamp	[48]
Au/g-C <sub>3</sub> N <sub>4</sub>	300 ppb	77.4%	A 300 W Xe lamp ( $\lambda > 420$ nm)	This work

PL spectra were used to characterize the separation and recombination of electron-hole pairs in composites [49]. The fluorescence intensity serves as an indicator of the separation rate of photogenerated carriers, with higher intensity indicating lower separation. In Fig. 4(a), it is observed that the fluorescence emission peak intensity of g-C<sub>3</sub>N<sub>4</sub>-Au-3 composites is significantly weaker compared to pure g-C<sub>3</sub>N<sub>4</sub>. This suggests that the introduction of Au effectively inhibits the recombination of photogenerated electron-hole pairs, thereby extending the lifespan of the photogenerated carriers. Furthermore, the photocurrent response and electron migration rate were analyzed using photocurrent and electrochemical impedance spectroscopy (EIS). In Fig. 4(b), it can be observed that the photocurrent response intensity of the composite is notably greater compared to pure g-C<sub>3</sub>N<sub>4</sub>. This indicates that the migration rate of photogenerated carriers in this sample is higher, which is advantageous for facilitating efficient photocatalytic reactions [50]. Furthermore, as depicted in Fig. 4(c), a smaller radius of curvature observed in the electrochemical impedance spectroscopy (EIS) indicates a lower impedance for the composite material [51]. This reduced impedance is favorable for the transmission of photogenerated carriers, aligning with the results obtained from the photocurrent tests. The photochemical characterization results demonstrate that the introduction of Au nanoparticles effectively enhances the separation of photogenerated electron-hole pairs, prolongs the lifetime of photogenerated carriers, reduces the resistance for carrier migration, and improves the photocatalytic performance. The optical properties of the samples were assessed using UV-vis measurements. Fig. 4(d) illustrates that the composite material exhibits significantly enhanced light absorption capacity within the visible light wavelength range compared to pure g-C<sub>3</sub>N<sub>4</sub>. This enhancement suggests that the surface plasmon resonance (SPR) effect of the noble metal (Au) improves the sample's response to visible light and enhances its photocatalytic performance [46]. In Fig. 4(e), the tauc diagram represents the band gap width spectrum of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au-3, calculated using the Kubelka-Munk formula. The tangents intersecting the X-axis indicate band gap widths of 2.7 eV and 2.78 eV for the g-C<sub>3</sub>N<sub>4</sub>-Au-3 and g-C<sub>3</sub>N<sub>4</sub>, respectively. Narrowing the band gap width allows for a broader range of light response,

thereby generating more excited electrons, which is beneficial for enhancing photocatalytic activity [52]. Apart from the number of surface holes and electrons, the photocatalytic activity of a photocatalyst is also influenced by the redox potential of surface holes and electrons. Therefore, the XPS valence band spectrum was measured to analyze the valence band potential of g-C<sub>3</sub>N<sub>4</sub>-Au-3. As shown in Fig. 4(g), the valence band potential of g-C<sub>3</sub>N<sub>4</sub>-Au-3 is 1.82 eV, and its band gap is 2.7 eV, as depicted in the tauc diagram. The conduction band potential (Ec) can be calculated using the formula  $E_g = E_v - E_c$ .

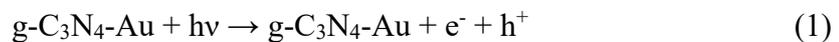


**Fig. 4** Analysis of charge separation, charge transfer and light adsorption: (a) the photoluminescence spectra, (b) the transient photocurrent response and (c) electrochemical resistance spectra of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au -3 nanocomposites, (d) UV-vis absorbance spectra, (e)  $E_g$  of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au -3 nanocomposites and (f) the XPS valence band spectrum

EPR was utilized to detect the reactive species produced during the photooxidation reaction under irradiation of visible light. 5, 5-dimethyl-1-pyrrolin-n-oxide (DMPO) acts as a trapping agent to trap  $\bullet\text{O}_2^-$  and  $\bullet\text{OH}$  [53]. It can be seen from Fig. 5(a, b), the composites exhibit obvious  $\bullet\text{OH}$  and  $\bullet\text{O}_2^-$  characteristic signals under visible light irradiation. Compared with pure g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>-Au-3 has a higher signal intensity, which indicates that g-C<sub>3</sub>N<sub>4</sub>-Au-3 can produce more  $\bullet\text{O}_2^-$  and

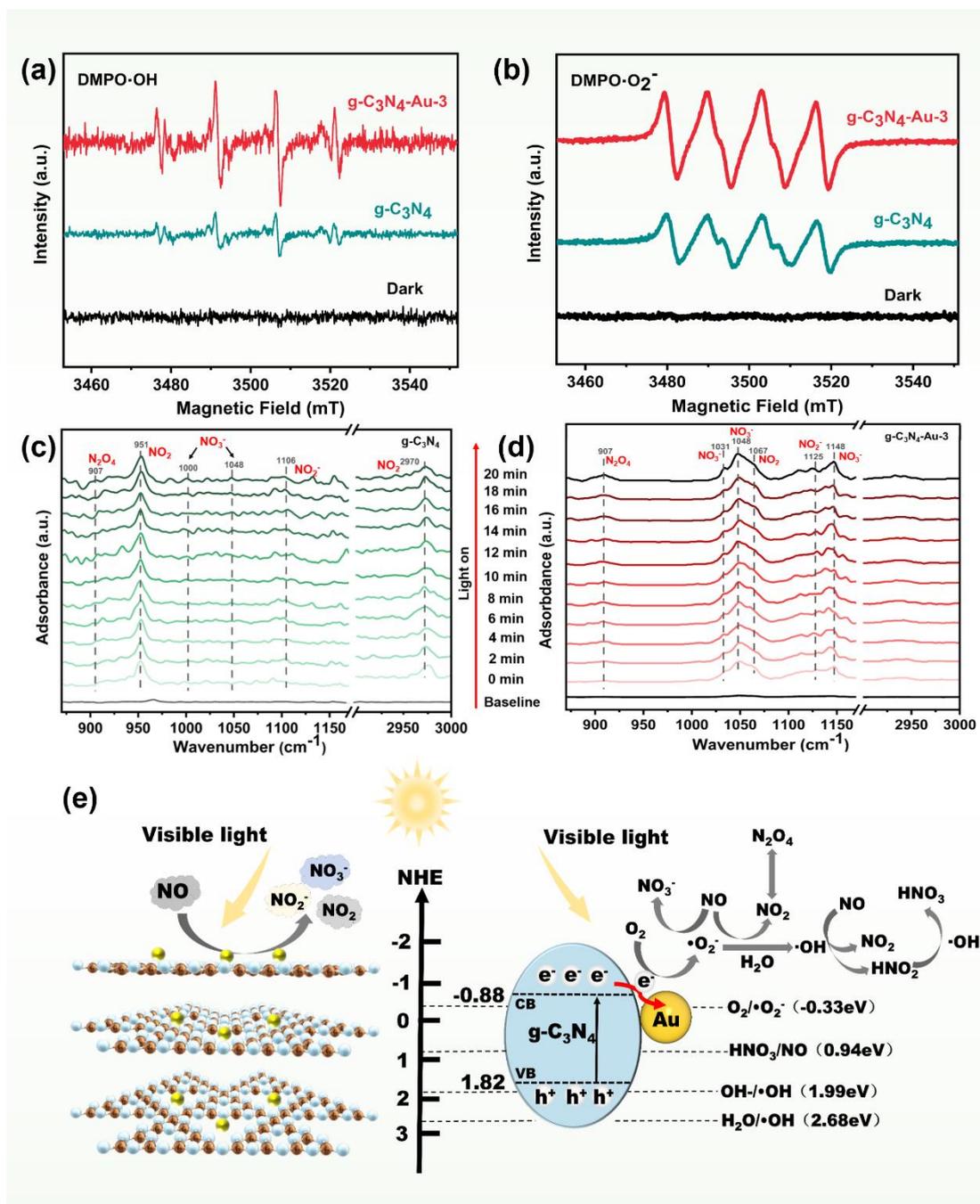
•OH to participate in the photocatalytic reaction. This is consistent with the results of PL and photochemical characterizations. The introduction of Au NPs promote the separation of photogenerated electron-hole pairs, extends the life of the carrier, and shows better photooxidation activity. Combined with the experimental results of free radical capture (Fig. 5(d)), as the signal of •OH detected by EPR, it can be inferred that •O<sub>2</sub><sup>-</sup>, as the main active free radical in the photocatalytic reaction process, can oxidize H<sub>2</sub>O to obtain •OH, thus enhancing the photooxidation activity.

The photo-oxidation of NO using g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au-3 photocatalysts under visible light, as well as the reaction mechanism, were further investigated through *in-situ* Fourier transform infrared spectroscopy. In Fig. 5(c), the bands at 951 cm<sup>-1</sup> and 2970 cm<sup>-1</sup> correspond to nitrogen dioxide (NO<sub>2</sub>) after illumination. The peak position of 907 cm<sup>-1</sup> corresponds to N<sub>2</sub>O<sub>4</sub>, NO<sub>2</sub><sup>-</sup> is represented at 1106 cm<sup>-1</sup>, and (NO<sub>3</sub><sup>-</sup>) are observed at 1000 cm<sup>-1</sup> and 1048 cm<sup>-1</sup>. During this time, NO is primarily adsorbed on the catalyst's surface, and oxidation results in the formation of NO<sub>2</sub>. Pure g-C<sub>3</sub>N<sub>4</sub> exhibits high photogenerated electron-hole pair recombination efficiency, low visible light absorption capacity, and fewer active free radicals, leading to a single product and poor photocatalytic activity. Upon the introduction of Au nanoparticles, a new characteristic peak appears in the *in-situ* infrared spectrum of g-C<sub>3</sub>N<sub>4</sub>-Au-3, as shown in Fig. 5(d). This includes N<sub>2</sub>O<sub>4</sub> (907 cm<sup>-1</sup>), NO<sub>2</sub> (1067 cm<sup>-1</sup>), NO<sub>2</sub><sup>-</sup> (1125 cm<sup>-1</sup>), and NO<sub>3</sub><sup>-</sup> (1031 cm<sup>-1</sup>, 1048 cm<sup>-1</sup>, 1148 cm<sup>-1</sup>). Notably, compared to Fig. 5(c), the addition of AuNPs increases the peak intensity attributed to nitrate ions at 1048 cm<sup>-1</sup>, and new characteristic peaks of nitric acid at 1031 cm<sup>-1</sup> and 1148 cm<sup>-1</sup> emerge. Furthermore, the strong peak of NO<sub>2</sub> at 951 cm<sup>-1</sup> disappears in Fig. 5(d). It is speculated that the presence of AuNPs facilitates the oxidation and conversion of NO<sub>2</sub> to nitrate. The formation of new intermediates contributes to a more complex photocatalytic reaction process. Equation (1-9) is a proposed representation of the photooxidation removal pathway of NO:





According to the above-mentioned experiment results, the photocatalytic mechanism is proposed in Fig. 5(e). Under the irradiation of visible light, g-C<sub>3</sub>N<sub>4</sub> generates photogenerated electron-hole pairs, which are concentrated in the conduction band and valence band of g-C<sub>3</sub>N<sub>4</sub>. Au nanoparticles are anchored on the carbon nitride surface *in-situ* by photodeposition, and the contact surface form a heterojunction with Schottky junction due to the difference in the Fermi level, and excited electrons at the conduction band of g-C<sub>3</sub>N<sub>4</sub> are easily transferred to Au nanoparticles, which act as a trap for photogenerated electrons to promote electron transfer and improve the photogenerated carrier separation efficiency of semiconductor catalysts [54]. More importantly, as a cocatalyst, Au nanoparticles directly in contact with g-C<sub>3</sub>N<sub>4</sub> experience SPR under certain wavelength of light excitation, generate "hot electrons" that can cross the Schottky junction, and are injected into the conduction band of g-C<sub>3</sub>N<sub>4</sub> to participate in the photocatalytic reaction, as a result, the band gap energy decreases from 2.78 eV to 2.7 eV, which promotes the absorption of visible light by the composite, thus the photocatalytic efficiency of the photocatalyst is improved. Electrons can reduce the surface chemisorbed O<sub>2</sub> to  $\cdot\text{O}_2^-$ , and then react with H<sub>2</sub>O to generate  $\cdot\text{OH}$ . Due to potential differences,  $\cdot\text{OH}$  cannot be generated at the valence band of g-C<sub>3</sub>N<sub>4</sub> [55]. Therefore, the main active free radicals in this reaction is  $\cdot\text{O}_2^-$ , which NO can be oxidized to NO<sub>2</sub>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> and accumulate on the surface of the composites [42, 48].



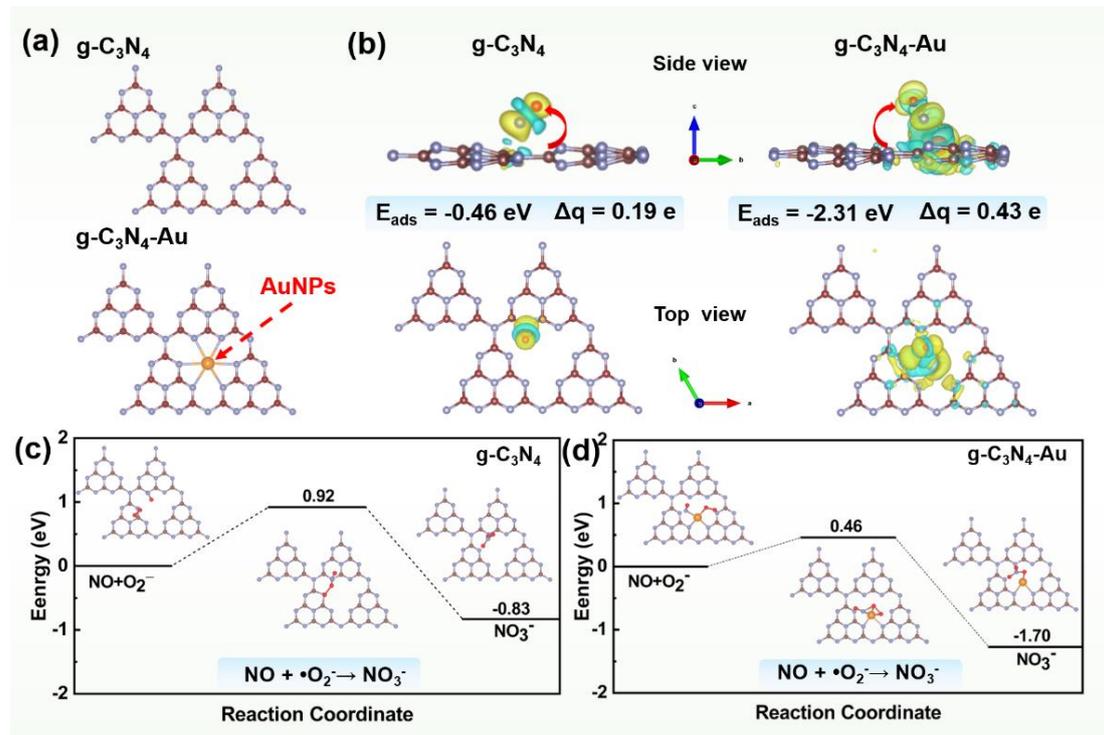
**Fig 5.** Radicals monitoring and simulation and photocatalysis reaction process: EPR spectra of (a) DMPO•OH and (b) DMPO•O<sub>2</sub><sup>-</sup> over the g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au -3 nanocomposites, *in-situ* DRIFTS spectra of NO removal by photooxidation of (c) g-C<sub>3</sub>N<sub>4</sub> and (d) g-C<sub>3</sub>N<sub>4</sub>-Au (e) photocatalytic mechanism diagram of g-C<sub>3</sub>N<sub>4</sub>-Au composite

**Table 3** Assignments of the IR bands during photooxidation of NO process during visible-light irradiation

Wavenumbers (cm <sup>-1</sup> )	Assignment	References
907	N <sub>2</sub> O <sub>4</sub>	[3]
951	NO <sub>2</sub>	[56]
1000	bridging nitrates	[57]
1031	NO <sub>3</sub> <sup>-</sup>	[56]
1048	NO <sub>3</sub> <sup>-</sup>	[58]
1067	NO <sub>2</sub>	[39]
1106	bi/monodentate nitrites	[56]
1125	NO <sub>2</sub> <sup>-</sup>	[39]
1148	monodentate nitrates	[57]
2970	NO <sub>2</sub>	[59]

In order to explore the effect of the introduction of AuNPs on the adsorption activation of NO by g-C<sub>3</sub>N<sub>4</sub>, charge density difference (CDD), adsorption energy of NO and effective charge of Bader were simulated based on DFT. Fig. 6(a) shows the g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au models constructed for calculation. Fig. 6(b) shows the charge difference distribution of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au, with yellow areas indicating charge depletion and blue areas indicating charge accumulation. The change of charge in g-C<sub>3</sub>N<sub>4</sub> indicates that there is NO obvious electron transfer between the photocatalyst and NO, while there is obvious charge accumulation and charge consumption on g-C<sub>3</sub>N<sub>4</sub>-Au. The calculated Bader charge difference is used to study the charge conversion and electron redistribution between NO and photocatalysts. The accepted electron of NO increased from 0.19 e (g-C<sub>3</sub>N<sub>4</sub>) to 0.43 e (g-C<sub>3</sub>N<sub>4</sub>-Au), while the adsorption energy of NO molecule ( $E_{\text{ads}}$ ) decreased from -0.46 eV on g-C<sub>3</sub>N<sub>4</sub> to -2.31 eV on g-C<sub>3</sub>N<sub>4</sub>-Au. This indicates that NO, as an electron acceptor, is more likely to acquire electrons from g-C<sub>3</sub>N<sub>4</sub>-Au for adsorption and activation [13, 56]. The introduction of AuNPs not only reduces the band gap, but also facilitates the adsorption of NO, promotes electron transfer and thus promotes the photooxidation reaction. Fig. 6(c) and Fig. 6(d) show the calculated results of the main reaction pathways. We chose one main reaction:  $\text{NO} + \cdot\text{O}_2^- \rightarrow \text{NO}_3^-$ , and the Gibbs free energy of the lowest transition state ( $\Delta G_{\text{TS}}$ ) and Gibbs free energy of the reaction ( $\Delta G_{\text{rea}}$ ) in the photocatalytic reaction on g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au were

calculated. Fig. 6(c) shows that the  $\Delta G_{TS}$  and  $\Delta G_{rea}$  in the reaction are 0.92 eV and -0.83 eV, respectively. The  $\Delta G_{TS}$  and  $\Delta G_{rea}$  of the reaction on g-C<sub>3</sub>N<sub>4</sub>-Au are 0.46 eV and -1.70 eV, indicating that the reaction requires a lower activation energy barrier and is more likely to occur. The negative  $\Delta G_{rea}$  indicates that the reaction can occur spontaneously, and the more negative the reaction is, the more likely it is to occur, and the energy release process exists in the reaction path. The calculation results proved that the reaction (7) on the photocatalyst surface was easier to carry out after the introduction of AuNPs, so more nitrate ions were generated and the photocatalytic activity of the catalyst was improved [41].



**Fig. 6** Analysis of the adsorption process of reactant molecules and reaction process: (a) the geometric structure of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au; red, blue, brown and yellow spheres represent O, N, C and Au atoms respectively; (b) the charge difference distribution when g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-Au adsorb NO, where yellow represents charge depletion, blue indicates charge build-up.  $E_{ads}$  and  $\Delta q$  represent the calculated results of adsorption energy and Bader electron, respectively, (c, d) the calculated results of the main reaction pathways

#### 4. Conclusion

In this study, the g-C<sub>3</sub>N<sub>4</sub>-Au composite photocatalyst was successfully prepared

by photo-deposition method. Due to the SPR effect of Au nanoparticles, the visible light absorption capacity of the composites was significantly improved. By introducing Au nanoparticles to construct a heterojunction between Au nanoparticles and carbon nitride, a tight interface is formed between metal and semiconductor, promoting the SPR effect of Au, then enhanced the transfer of charge, improved the separation efficiency of electron-hole pairs, and prolonged the life of photogenerated carriers, so that the efficiency of NO oxidation removal was significantly improved. In addition, the main active species of catalytic oxidation process was confirmed by capture experiment as  $\bullet\text{O}_2^-$ . By optimizing the loading capacity of Au nanoparticles, under visible light irradiation, the oxidation removal ratio of NO remained 77.4 %, and the kinetic ratio constant was 4.32 times that of g-C<sub>3</sub>N<sub>4</sub>. In addition, g-C<sub>3</sub>N<sub>4</sub>-Au-3 composites still maintain high oxidation activity, indicating that it has excellent stability. after four cycles. In addition, *in-situ* infrared spectroscopy and DFT calculation were used to explore the oxidation pathway of NO. The results indicate that the introduction of Au nanoparticles reduced the activation energy of the oxidation reaction, made the reaction easier to proceed, and the intermediate products were reduced, and most of NO was eventually converted into nitrate, and accumulated on the surface of the composites.

#### **CRedit authorship contribution statement**

**Yanzhi Liu and Cheng Xie:** Writing - original draft, Methodology, Investigation.  
**Lei Xu:** Writing- Reviewing and Editing, Supervision, Funding acquisition. **Qianjun Ye:** Validation. **Bochuan Zhang:** Validation. **Mickael Capron and Vitaly Ordonsky:** Reviewing and Editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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