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# Synthesis of Pd/Au bimetallic nanoparticle-loaded ultrathin graphitic carbon nitride nanosheets for highly efficient catalytic reduction of p-nitrophenol



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# G R A P H I C A L A B S T R A C T



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# ABSTRACT

Noble metal nanoparticles (NPs) applied in heterogeneous catalysis have attracted considerable attention due to their highly efficient catalytic performance. Pd/Au bimetallic NPs were successfully decorated on the ultrathin graphitic carbon nitride nanosheets (g-C<sub>3</sub>N<sub>4</sub>-N) by a facile one-pot deposition reduction method. The obtained results show that Pd/Au NPs with average diameter around 8 nm are homogeneously dispersed on the surface of unmodified g-C<sub>3</sub>N<sub>4</sub>-N. The obtained materials were characterized via transmission electron microscopy (TEM), high-resolution TEM, energy-dispersive X-ray spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). In addition, considering the large surface area and special  $\pi$ -bonded planar structure, the unique ultrathin g-C<sub>3</sub>N<sub>4</sub>-N behave as an excellent carrier and stabilizer in this synthesis. The as-synthesized Pd/Au bimetallic nanohybrids show superior catalytic performance and stability for reduction of p-nitrophenol (p-NP), which is better than either of pure Pd or Au nanohybrids. Besides, the catalytic activities of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N nanohybrids were found to be controlled by altering the Pd *versus* Au mass ratio in the preparation process.

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# 1. Introduction

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http://dx.doi.org/10.1016/j.jcis.2016.12.017 0021-9797/© 2016 Elsevier Inc. All rights reserved. Noble metal nanoparticles (NPs) (Au, Pd, Pt, etc.) have gained much attention in recent decades due to their unique optical, electronic, and catalytic properties, as well as their potential use such as surface-enhanced Raman scattering, catalysis, sensor and fuel cells [1–6]. Some bimetallic NPs, owing to their distinctive properties, better catalytic performance than either of the constituent materials, have attracted the great attentions [7–10]. However, in the practical application, free noble metal NPs can easily aggregate, leading to a considerable loss in catalytic activity. To solve this problem, a large number of supporting materials, such as polymers [11], metal-organic framework [12], mesoporous silica [13], carbon materials including graphene [14], graphene oxide [15], carbon nanotubes [16], and mesoporous carbon [17], have been used as substrates to support and stabilize NPs.

Many studies showed that Pd-based bimetallic NPs are more effective and exhibit higher catalytic performance than Pt [18]. In this context. Pd/Au bimetallic NPs become a critical point of research in the field of the heterogeneous catalysis. For example, Karatas et al. prepared a novel bimetallic nanocatalyst-Pd/Au alloy and MnO<sub>x</sub> NPs supported on 3-aminopropyltriethoxysilane functionalized silica by a combination of complimentary techniques [19]. They show superior catalytic performance in the additivefree dehydrogenation of formic acid. In addition, Darabdhara and co-workers reported the highly active Pd/Au bimetallic NPs applied to the electrochemical hydrogen generation [20]. In our previous studies, the Pd-based Pd/Fe bimetallic NPs embedded within phosphorus-doped ordered mesoporous carbons [21], magnetic multi-wall carbon nanotube nanohybrids [22], ethylenediaminemodified cross-linked magnetic chitosan resin [23], iron oxide nanoparticles-doped carboxylic ordered mesoporous carbon [24], nitrogen-functionalized magnetic ordered mesoporous carbon [25], CdS/Cu<sub>2</sub>S co-sensitized TiO<sub>2</sub> branched nanorod arrays [26] modified core-shell magnetic nanoparticles supported on carbon paste electrode [27] and disposable immunomembrane-based electrochemical sensor [28] were prepared and applied for the removal of pollutants such as 2,4-dichlorophenol, cationic dyes, chromium (VI), 2,4-dichlorophenoxyacetic, lead and phenol, enhancing the photoelectrochemical properties, using as a hydroquinone biosensor and rapid detection of Picloram. However, looking for the supporting materials to stabilize Pd/Au bimetallic NPs remains a challenge.

Recently, many carbon materials with graphite-like structure, such as graphene and graphene oxide, have become the focus of many research [29-32]. As a graphene-like material, graphitic carbon nitrides (g-C<sub>3</sub>N<sub>4</sub>) have also achieved tremendous attention due to their distinctive structure and optical nature. Owing to the incorporation of nitrogen atoms in the carbon skeleton, the g-C<sub>3</sub>N<sub>4</sub> gains much better properties than carbon materials, such as electrical, chemical and functional properties. Considering their thermal and chemical stability, the g-C<sub>3</sub>N<sub>4</sub> can be directly used in heterogeneous catalysis [33–35]. For example, the work of Zhang et al. markedly demonstrated that the in situ ion exchange method was successfully applied to fabricate Ag/AgCl NPs on the exfoliated  $g-C_3N_4$  nanosheets with 2D morphology [36]. The as-prepared nanohybrid exhibited excellent photocatalytic performance to degrade rhodamine B. However, bulk g-C<sub>3</sub>N<sub>4</sub> usually shows worse catalytic performance than the corresponding g-C<sub>3</sub>N<sub>4</sub> nanosheets [37,38]. This provides a clue that the ultrathin 2D materials of g- $C_3N_4$  nanosheets may be an excellent choice as a support to avoid the aggregation and migration of metal NPs. To date, many studies have been conducted about preparation of Ag NPs as a decent cocatalyst loaded on g-C<sub>3</sub>N<sub>4</sub> and application in photocatalytic utilizations [36,39,40]. To the best of our knowledge, few reports are focused on preparation and application of Pd/Au bimetallic NPs supported on the ultrathin g-C<sub>3</sub>N<sub>4</sub> nanosheets so far.

Herein, we demonstrate that the well-dispersed Pd/Au NPs can be successfully decorated on the ultrathin  $g-C_3N_4-N$  (Pd/Au@  $g-C_3N_4-N$ ) via simultaneous chemical reduction of the bimetallic precursors, and g-C<sub>3</sub>N<sub>4</sub>-N with sodium borohydride (NaBH<sub>4</sub>) as reductant, and sodium citrate as capping agent under mild reaction conditions. The ultrathin g-C<sub>3</sub>N<sub>4</sub>-N used in my study, a kind of twodimensional (2D) sheet-like material, is readily obtained by a twopot thermal oxidation method. Considering the large surface area and special  $\pi$ -bonded planar structure, the ultrathin g-C<sub>3</sub>N<sub>4</sub>-N plays a vital role as a support and stabilizer in this synthesis. Moreover, we found that the resultant nanohybrid is finely dispersible in aqueous solution under ultrasonic-assisted condition, finally forming a homogeneous solution, which can facilitate the heterogeneous catalysis. The catalytic performance of the nanohybrid was assessed by the reduction reaction of p-nitrophenol (p-NP) to p-aminophenol (p-AP). The results revealed that Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N show better catalytic performance than either of the constituent materials.

## 2. Methods and material

# 2.1. Materials

HAuCl<sub>4</sub>, PdCl<sub>2</sub> and p-NP ( $C_6H_5NO_3$ ), melamine ( $C_3N_6H_6$ ), were purchased from Sigma-Aldrich (USA) and used as received. All other regents, such as sodium borohydride (NaBH<sub>4</sub>), ethanol, and HCl, were of analytical grade and used as received without further purification. Moreover, High-purity water (18.25 MΩ/cm, Milli-Q) was used in all experiment.

# 2.2. Synthesis of $g-C_3N_4-N$

The g-C<sub>3</sub>N<sub>4</sub>-N was prepared by two-pot successive heating method according to the procedures of reported literature [37]. Firstly, 5 g of melamine was added into a crucible with a cover, then heated in muffle furnace at 500 °C for 2 h at a rate of 2 °C/min. Subsequently, further heat treatment was conducted at 520 °C for another 2 h remaining the same heating rate. The asobtained material was ground in a mortar and was used in the next experiment. Last but not least, 1 g of the obtained bulk g-C<sub>3</sub>N<sub>4</sub> was added into an open crucible and heated at 2 °C/min up to 520 °C, and then keeping the temperature for 4 h. The g-C<sub>3</sub>N<sub>4</sub>-N was obtained with color of light yellow for further use.

# 2.3. Synthesis of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N, Pd@g-C<sub>3</sub>N<sub>4</sub>-N and Au@g-C<sub>3</sub>N<sub>4</sub>-N

 $Pd/Au@g-C_3N_4-N$  1 wt% with a Pd-to-Au mass ratio of 1:1 (Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1)) was fabricated through a deposition coreduction method using g-C<sub>3</sub>N<sub>4</sub>-N as support and HAuCl<sub>4</sub> and PdCl<sub>2</sub> as the gold and palladium source, respectively [41]. Typically, 50 mg of g-C<sub>3</sub>N<sub>4</sub>-N was re-dispersed in 20 mL of high-purity water, and the mixture was treated under ultrasonic-assisted condition for 30 min, and then 52 µL of HAuCl<sub>4</sub> (24.28 mM) aqueous solution and 209 µL of PdCl<sub>2</sub> (11.28 mM) HCl solution were put into the above prepared suspension under stirring for 5 min. Afterward, 0.5 mL of 0.05 M sodium citrate solution was added dropwise into the suspension under the same stirring for 20 min. Then, 0.5 mL of 0.05 M freshly fabricated NaBH<sub>4</sub> solution was added quickly to the above solution, followed by continuously vigorous stirring (1000 rpm) for 40 min. Subsequently, the as-obtained nanohybrid materials was washed with high-purity water and recovered by centrifugation, and then dried at 60 °C in a vacuum oven for all night. Finally, the as-prepared nanomaterial, Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1), was collected for further use. Other Pd/Au mass ratio (1:3, 1:2, 2:1, 3:1) bimetallic materials (the total metal quantity is 1 wt%) were prepared according to the aforementioned same procedures except for adjusting the addition volumes of PdCl<sub>2</sub> (11.28 mM) HCl solution and HAuCl<sub>4</sub> (24.28 mM) aqueous solution. Similarly,  $Pd@g-C_3N_4-N 0.5 wt\%$  and  $Au@g-C_3N_4-N 0.5 wt\%$  were obtained with the same procedure except for adding 417  $\mu$ L PdCl<sub>2</sub> (11.28 mM) HCl solution and 104.5  $\mu$ L HAuCl<sub>4</sub> (24.28 mM) aqueous solution.

# 2.4. Characterization instruments

The ultraviolet-visible (UV-Vis) absorbance of p-NP was measured on a SHIMADZU 2550 UV-Vis spectrophotometer. The wavelength was set between 250 nm and 500 nm for all the reaction processes. Morphologies and structures of samples were examined by scanning electron microscopy (SEM, JEOL JSM-6700) at an acceleration voltage of 5.0 kV and transmission electron microscopy (Tecnai G2 F20 S-TWIN), high-resolution TEM (HR-TEM) with an acceleration voltage of 200 kV. To further identify the state of Pd and Au in the nanohybrid,  $Pd/Au@g-C_2N_4-N$  (1:1) was observed by high-angle annular dark-field scanning TEM (HAADF-STEM) and Energy dispersive X-ray spectroscopy (EDX) mapping analysis. The X-ray powder diffraction (XRD) patterns were made using a Bruker D8 ADVANCE X-ray diffractometer with Cu Ka (1.541 Å) radiation (40 kV, 30 mA). The surface elemental composition of the Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) were obtained by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, UK), and the binding energies were referenced to the C 1s peak at 284.8 eV of adventitious carbon.

#### 2.5. Catalysis experiments

The catalytic reduction of p-NP in the presence of NaBH<sub>4</sub> was carried out in 50 mL conical flasks containing 20 mL 100 mg/L p-NP and a certain quantity of NaBH<sub>4</sub> (the mole ratio of p-NP:  $NaBH_4$  is 1/100) at 300 rpm rate. On adding the fresh  $NaBH_4$ , the color of the reaction solution immediately changed from light yellow to bright yellow. And then, 100 µL of 2.5 mg/mL bimetallic catalyst Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (with the Pd/Au mass ratio of 1/3, 1/2, 1/1, 2/1, 3/1) was added, as a contrast,  $200 \,\mu\text{L}$  of  $2.5 \,\text{mg/mL}$ monometallic catalyst (Pd@g-C<sub>3</sub>N<sub>4</sub>-N 0.5 wt%, Au@g-C<sub>3</sub>N<sub>4</sub>-N 0.5 wt%) or the equal quality of pure g-C<sub>3</sub>N<sub>4</sub>-N was added. Subsequently, we found that the bright yellow solution gradually faded with the reaction proceeded. Immediately after that, the residual solution of p-NP was measured by UV-Vis spectroscopy at a maximum absorbing wavelength ( $\lambda = 400 \text{ nm}$ ) in alkaline atmosphere [42]. Additionally, the UV-vis spectrums with a measuring interval of 2 min were recorded from 250 to 500 nm using NaOH solution with the same concentration. Each catalytic experiment was repeated three times.

For the recycle and anti-oxidation experiments, typically, the antioxidant test was conducted to expose the Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N 1 wt% in the air for 0 or 30 days, respectively. Then, the catalytic activity of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N 1 wt% (0 and 30 days) was examined through four cycles. For the first reaction, 100  $\mu$ L of 2.5 mg/mL bimetallic catalyst Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N 1 wt% was added to 20 mL



**Fig. 1.** (a) Typical SEM image of pure g-C<sub>3</sub>N<sub>4</sub>-N; (b) representative TEM image of pure g-C<sub>3</sub>N<sub>4</sub>-N; (c) tri-s-triazine-based connection patterns of g-C<sub>3</sub>N<sub>4</sub>; (d) XRD patterns of Au@g-C<sub>3</sub>N<sub>4</sub>-N-a, Pd@g-C<sub>3</sub>N<sub>4</sub>-N-b, Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) and pure g-C<sub>3</sub>N<sub>4</sub>-N-d; (e) the local magnification of (b).

multicomponent system containing p-NP (1 mL, 14.37 mM) and fresh NaBH<sub>4</sub> (1 mL, 1.43 M) as described above. The UV-vis spectrum data were recorded after the reaction. Then, the first run was conducted by adding 28.8  $\mu$ L of 0.5 M p-NP and 0.23 mL of 6 M fresh NaBH<sub>4</sub> solution into the above reaction system and the same process for the next run. This recycle text was repeated four times in all.

# 3. Results and discussion

# 3.1. Synthesis and characterization of catalysts

In the present study, the g-C<sub>3</sub>N<sub>4</sub>-N was easily obtained by two-pot thermal oxidation etching method. The morphology and structure of g-C<sub>3</sub>N<sub>4</sub>-N were characterized by means of SEM and TEM techniques. The representative SEM picture in Fig. 1(a) and TEM picture in Fig. 1(b) reveal that the  $g-C_2N_4-N$  possess a twodimensional ultrathin sheet-like structure with thickness of several nanometers and length from 200 nm to several micrometers. Because of its superior structural properties such as the large surface area and special  $\pi$ -bonded planar structure, the g-C<sub>3</sub>N<sub>4</sub>-N are potentially suitable as excellent substrate to immobilize noble metal NPs, which can keep the good dispersity of the NPs and hinder the aggregation. Also, some groups have done many similar researches about g-C<sub>3</sub>N<sub>4</sub> sheet-like materials [36,38,43-45]. For example, Niu and co-workers successfully developed a highly anisotropic 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets by facile thermal oxidation etching method applied as photocatalysts to improve the photocatalytic activities. As the most stable allotrope among carbon nitride materials, g-C<sub>3</sub>N<sub>4</sub> composed of tri-s-triazine in Fig. 1(c) as tectonic units can be considered as the most stable local connection pattern [46]. Importantly, the elemental analysis data of the pure g-C<sub>3</sub>N<sub>4</sub>-N show that the surface atomic ratio of C/N is as high as 0.85 for the nanosheets, which is in accordance with the previous study [43]. Through the analysis of XRD in Fig. 1(d), the characteristic diffraction peak related to the (002) interlayer reflection of the pure g-C<sub>3</sub>N<sub>4</sub>-N is found at 27.7°, [37,43] further suggesting that the as-obtained material exhibits ultrathin sheet structure.

Pd/Au bimetallic NPs were deposited onto the g-C<sub>3</sub>N<sub>4</sub>-N by a one-pot deposition co-reduction method using HAuCl<sub>4</sub> and PdCl<sub>2</sub> as the gold and palladium source respectively at ambient conditions. The obtained representative TEM and HRTEM images of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) are shown in Fig. 2(a) and (b), respectively. As can be seen from Fig. 2(a), the Pd/Au NPs are well dispersed on the surfaces of g-C<sub>3</sub>N<sub>4</sub>-N. On the analysis of the size distribution histogram (Fig. S1), we can know that the particle size mainly concentrates in the distribution ranges from 6 nm to10 nm, and the mean diameter is around 8 nm. The typical HRTEM image of Pd NPs (Fig. 2(c)) and Au NPs (Fig. 2(d)) shows that the (111) lattice interfringe distance of 0.223 nm belongs to the (111) plane of face-centered cubic (fcc) Pd NPs. and an interfringe distance of 0.234 nm is assigned to the (111) plane of fcc Au NPs, respectively. Most importantly, Fig. 2(b) shows the typical HRTEM image of Pd/Au NPs with the (111) lattice interfringe distance of 0.229 nm, which is located in the range of 0.234 nm and 0.223 nm corresponding to the (111) plane of fcc lattice structure of Au and Pd, respectively.

Furthermore, the elemental composition of the Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N nanohybrid was further investigated by the HAADF-STEM technique (Fig. 3). The STEM-EDX mapping results confirm that C, N, Pd and Au elements are apparently observed in Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N. However, it is worth pointing out that the Pd/Au NPs may slightly aggregate in the process of the HAADF-STEM measurements. Therefore, some unsharp image of Pd/Au NPs with large size can



Fig. 2. (a) Representative TEM images of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1); (b)-(d) typical HRTEM images of Pd/Au alloy NPs (b), Pd NPs (c) and Au NPs (d) in the as-obtained Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1).

be found by the HAADF-STEM measurements. A similar phenomenon has occurred in the previous study [9]. As shown in Fig. 3(d) and (e), a homogeneous distribution of both Pd element and Au element is found, indicating the formation of Pd/Au alloy on the surface of the g-C<sub>3</sub>N<sub>4</sub>-N. To further prove the formation of Pd/Au alloyed structure rather than other structures, the XRD patterns in Fig. 1(d) and (e) of as-obtained catalysts were investigated. For comparison, Fig. 1(d) shows the XRD patterns of these materials containing Au@g-C<sub>3</sub>N<sub>4</sub>-N, Pd@g-C<sub>3</sub>N<sub>4</sub>-N, Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N and pure g-C<sub>3</sub>N<sub>4</sub>-N, respectively. Fig. 1(e) illustrates the XRD image shown in Fig. 1(d) in the form of local amplification, in which the different distinct diffraction peaks of the Pd (111) and Au (111)

are clearly seen at 40.05° and 38.13°, respectively. The Pd and Au diffraction peaks are very weak compared with the Pd/Au alloy, owing to the formation of the small sizes of Pd and Au NPs [12]. In addition, for the Pd/Au bimetallic NPs, the peaks at 39.39° diffract from the (111) planes. Compared to the (111) diffraction peak of Au@g-C<sub>3</sub>N<sub>4</sub>-N, the diffraction peak of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N are slightly shifted to higher 20 values because of the replacement by Pd atoms. On the above analysis, we can conclude that Pd/Au bimetallic NPs exist in the form of alloy rather than core-shell NPs and have a high alloyed level. Other researchers also reported similar phenomenon about the formation of Pd/Au alloy NPs [9,47,48].



Fig. 3. (a) HAADF-STEM images of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1); EDX mapping of C element (b), N element (c), Pd element (d) and Au element (e).

Additionally, further investigation was carried out to analyze the structure and properties of the Pd/Au NPs by comparison with the corresponding Pd and Au monometallic NPs. The morphologies of Pd@g-C<sub>3</sub>N<sub>4</sub>-N and Au@g-C<sub>3</sub>N<sub>4</sub>-N nanohybrids were characterized by using TEM and HRTEM. Typical TEM images show that well-dispersed Pd NPs (mean diameter about 5.22 nm) and Au NPs (mean diameter around 4.98 nm) have been successfully synthesized in the ultrathin g-C<sub>3</sub>N<sub>4</sub>-N (Fig. S2).

The X-ray photoelectron spectroscopy (XPS) measurements (Fig. 4) have demonstrated the chemical compositions of Pd/ Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1), including C, N, Pd, Au elements. Therefore, we can conclude that Pd/Au bimetallic NPs have been successfully supported on g-C<sub>3</sub>N<sub>4</sub>-N structure. As observed from Fig. 4a, the high-resolution C 1s spectrum can be divided into two peaks at 284.8 eV and 288.1 eV, attributed to the graphitic carbon in g- $C_3N_4$ -N and the sp<sup>2</sup>-bond carbon atoms (N–C=N), respectively [37,49]. The high-resolution N 1s spectrum in Fig. 4b can be fitted into two main peaks at 398.7 eV and 400.1 eV, ascribable to sp<sup>2</sup>hybridized N atoms bonded to carbon in an aromatic ring (C–N=C) at 398.7 eV and tertiary N bonded to carbon atoms in the form of  $N-(C)_3$  at 400.1 eV, respectively [37,49]. Fig. 4(d) exhibits the XPS spectra of the Au 4f doublet (4f  $_{7/2}$  and 4f $_{5/2}$ ). The Au 4f  $_{7/2}$ and  $4f_{5/2}$  peaks are at 83.24 and 86.89 eV, respectively. The high resolution Pd 3d spectra shown in Fig. 4(c) can be divided into four main peaks located at 334.97, 337.52, 340.28 and 342.86 eV, respectively. Among these peaks, two peaks centered at 334.97 and 340.28 eV are respectively assigned to the doublets 3d<sub>5/2</sub> and  $3d_{3/2}$  binding energies of Pd<sup>0</sup>, and another two peaks located at 337.52 and 342.86 eV belong to the Pd<sup>2+</sup> species. Hence, we can know the existence of both  $Pd^{2+}$  and  $Pd^{0}$  on g-C<sub>3</sub>N<sub>4</sub>-N, and the atomic ratio of Pd<sup>2+</sup> and Pd<sup>0</sup> is 3/2. Through all the above analyses, we reach the following conclusion: the Pd/Au alloy structure is formed on the surface of g-C<sub>3</sub>N<sub>4</sub>-N. On the other hand, the XPS peaks of Au 4f shift 0.76 eV to lower binding energies compared with the standard characteristic metallic Au<sup>0</sup> peaks, while for Pd 3d<sub>5/2</sub> peak, there are slight shifts of 0.27 eV to higher binding energies compared with the standard characteristic metallic Pd<sup>0</sup> 3d<sub>5/2</sub> peak. Therefore, we can make reasonable speculation that electron transfer may take place not only between Pd/Au bimetallic NPs and  $g-C_3N_4-N$ , but also between Au and Pd NPs [8.47.50].

## 3.2. Catalytic properties of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N

The catalytic reduction of p-NP in the presence of excess NaBH<sub>4</sub> to generate p-aminophenol (p-AP) was selected as a model reaction to assess the catalytic properties of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N at room temperature. As is known to all, the reaction route of p-NP to p-AP can be achieved by various noble metals in the presence of NaBH<sub>4</sub>,



Fig. 4. X-ray photoelectron spectra of (a) C 1s, (b) N 1s, (c) Pd 3d and (d) Au 4f in Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1).



**Fig. 5.** Typical time-dependent evolutions of UV–Vis spectra of (a) Pd/Au@g-C<sub>3</sub>N<sub>4</sub>–N (1:1), (b) Pd@g-C<sub>3</sub>N<sub>4</sub>–N and (c) Au@g-C<sub>3</sub>N<sub>4</sub>–N; (d) plot of  $C_t/C_0$  versus reaction time for the reduction of p-NP over Pd/Au@g-C<sub>3</sub>N<sub>4</sub>–N with different Pd-to-Au mass ratio; plot of  $\ln(C_t/C_0)$  versus reaction time for the reduction of p-NP over (e) Pd/Au@g-C<sub>3</sub>N<sub>4</sub>–MN (1:1) and corresponding monometallic counterparts and (f) Pd/Au@g-C<sub>3</sub>N<sub>4</sub>–N with different Pd-to-Au mass ratio.

which can be widely regarded as an environment friendly and practical conversion route. In the presence of catalysts, the typical UV–Vis absorption change of the reaction mixture is shown in Fig. 5(a)-(c). Apparently, the characteristic absorption at 400 nm (assigned to p-NP ions) decreases with the concomitant increase of absorption at 303 nm (ascribed to p-AP) under ambient

conditions [9]. With the addition of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1), the bright yellow color of the p-NP solution thoroughly fades in 4 min, suggesting the finish of the mixture reaction. However, the UV–Vis spectra of the mixture reaction exhibit only a characteristic absorption at 400 nm and remain unchanged with time in the case of lacking of any catalysts or adding pure g-C<sub>3</sub>N<sub>4</sub>-N (Fig. S3),

#### Table 1

Summary of the pseudo-first-order model parameters containing the rate constants of the reaction ( $k(min^{-1})$ ) and correlation coefficients ( $R^2$ ) for p-NP removal by different Pd/Au mass ratio and the Pd or Au monometallic counterpart (the amount of each catalyst was controlled at 0.25 mg).

Sample	Pd (wt%)	Au (wt%)	$K(\min^{-1})$	Correlation coefficients (R <sup>2</sup> )
0.5 wt% Pd@g-C <sub>3</sub> N <sub>4</sub> -N	0.50	0.00	0.3807	0.9971
1 wt% Pd/Au@g-C <sub>3</sub> N <sub>4</sub> -N (3:1)	0.75	0.25	0.5310	0.9811
1 wt% Pd/Au@g-C <sub>3</sub> N <sub>4</sub> -N (2:1)	0.67	0.33	0.5691	0.9819
1 wt% Pd/Au@g-C <sub>3</sub> N <sub>4</sub> -N (1:1)	0.50	0.50	0.7907	0.9945
1 wt% Pd/Au@g-C <sub>3</sub> N <sub>4</sub> -N (1:2)	0.33	0.67	0.3875	0.9744
1 wt% Pd/Au@g-C <sub>3</sub> N <sub>4</sub> -N (1:3)	0.25	0.75	0.6425	0.9940
0.5 wt% Au@g-C <sub>3</sub> N <sub>4</sub> -N	0.00	0.50	0.3522	0.9935



Fig. 6. The reusability of Pd/Au@g-C\_3N\_4-N (1:1) (0 and 30 days) as catalysts for the reduction of p-NP.

suggesting that no reduction reaction takes place and pure g-C<sub>3</sub>N<sub>4</sub>-N shows no catalytic activity to reduce p-NP in the presence of NaBH<sub>4</sub>. Comparing the catalytic activities of Pd/Au bimetallic NPs with those of monometallic counterparts, it only takes 3.5 min for Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) to convert above 95% of p-NP to p-AP (Fig. 5(a)), exhibiting the superior catalytic activities. For the Pd@g-C<sub>3</sub>N<sub>4</sub>-N and Au@g-C<sub>3</sub>N<sub>4</sub>-N case, however, it takes 6.5 min and 8 min to convert 95% of p-NP, respectively (Fig. 5(b) and (c)). The results show that Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N nanohybrids have better catalytic activities than either of the constituent materials.

To further investigate the catalytic activities of  $Pd/Au@g-C_3N_4$ -N, catalysts with the different weight ratio of Pd *versus* Au were synthesized to test the catalytic performance in reduction of

p-NP to p-AP. The  $C_t/C_0$  versus reaction time in reduction of p-NP over Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N with different Pd-to-Au mass ratio (V<sub>m</sub>) is shown in Fig. 5(d). It can be observed that the conversion of p-NP reaches the maximum when the V<sub>m</sub> value is 1 compared with other catalysts. Considering that the concentration of NaBH<sub>4</sub> used in the catalytic system is highly excessive, it has no effect on the reaction rate. Thus, pseudo-first-order kinetics can be used to evaluate the reaction rate [51]. As expected, the linear relationships between  $\ln(C_t/C_0)$  and reaction time (t) are observed for the assynthesized catalysts (Fig. 5(e) and (f)), where  $C_t$  and  $C_0$  represent the residual and the initial concentrations of p-NP, respectively. Combining the results of Fig. 5(e) and (f) with Table 1, we can clearly know that all of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N catalysts exhibit a better catalytic performance compared with the corresponding Pd and Au nanohybrids, indicating the existence of the synergistic impact between Pd and Au NPs. More importantly. Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) shows the highest catalytic activity among all the asobtained catalysts in this study through the evaluation of the apparent rate constant. Meanwhile, considering the condition of low metal loading amount (1 wt%), Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) have the superior catalytic performance and exhibit the higher apparent rate constant than that of reported Pd, Au or other Pd/Au catalysts [8,41,52-55].

# 3.3. Ability of anti-oxidation and regeneration experiments of Pd/ $Au@g-C_3N_4\text{-}N$

Anti-oxidation and stability experiments of the Pd/Au@g- $C_3N_4$ -N (1:1) were investigated. Fig. 6 shows that both of the Pd/Au@g- $C_3N_4$ -N (1:1) samples exposed in air for 0 and 30 days have no significant differences for the conversion efficiency of p-NP to p-AP by NaBH<sub>4</sub>, suggesting that Pd/Au@g- $C_3N_4$ -N materials have excellent properties of anti-oxidation. According to Fig. 6,



Scheme 1. A possible schematic mechanism for the catalytic reduction of 4-nitrophenol by Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N nanohybrid.

Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) can be reused at least four times with more than 90% conversion for the fourth cycles, indicating a superior stabilities and anti-oxidation ability of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) in the reduction of p-NP.

#### 3.4. Interaction mechanism

The highly efficient catalysis process of Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N includes two main stages: (1) the adsorption and transmission of p-NP onto the catalyst surface and (2) interfacial electron transfer and desorption of p-AP from the surface [56]. In this context, the ultrathin g-C<sub>3</sub>N<sub>4</sub> nanosheets as a support and stabilizer play a key role. For one thing, the large surface area of  $g-C_3N_4-N$  are favorable for the transmission and adsorption of p-NP; for another, g-C<sub>3</sub>N<sub>4</sub>-N as a kind of semiconductor material has intrinsic advantages in electronic transmission. Scheme 1 illustrates a possible mechanism by the catalytic reduction of p-NP to p-AP in the presence of NaBH<sub>4</sub>. Firstly, the BH<sub>4</sub> and p-NP ions diffuse and get adsorbed onto the surface of Pd. Au or Pd/Au allov from aqueous solution. Then, BH<sub>4</sub> provides electrons to p-NP on the bare noble metal NPs decorated on the g-C<sub>3</sub>N<sub>4</sub>-N, resulting in the production of p-AP. On the other hand, the g-C<sub>3</sub>N<sub>4</sub>-N due to the conductive property may be favorable for the electronic transmission not only between Pd and Au NPs, but also between noble metal NPs and the  $g-C_3N_4-N$ .

## 4. Conclusion

In conclusion, we have successfully fabricated Pd/Au bimetallic NPs decorated on the ultrathin graphitic carbon nitride nanosheets (g-C<sub>3</sub>N<sub>4</sub>-N) as a heterogeneous catalyst by a one-pot deposition coreduction method. This work demonstrates that the kind of special 2D ultrathin sheet-like material is a good support and stabilizer for Pd/Au bimetallic NPs and their corresponding monometallic NPs. Also, the as-obtained Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N nanohybrids display better catalytic performance in the reduction of p-NP than either of the constituent materials, which may have resulted from strong interactions between Pd and Au. The Pd/Au@g-C<sub>3</sub>N<sub>4</sub>-N (1:1) can achieve a 100% conversion within only 4.5 min, and a large apparent rate constant k of 0.7907 min<sup>-1</sup> for the p-NP reduction. Moreover, the as-synthesized material has excellent anti-oxidation and recyclability, which greatly promotes its industrial application. This study demonstrates that the ultrathin carbon nitride material is a promising supporting material to prepare some effective metal hybrids for the catalytic reduction of organic pollutants.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.12.017.

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