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The preparation of amine compounds is very important for both the chemical industry and renewable feedstock processing. Nevertheless, it remains difficulties in finding a catalytic system that is sufficiently active and environmentally benign for producing amine compounds. In this work, we report that  $g-C_3N_4$  nanosheets as support materials can significantly boost the efficiency of Pd nanoparticles for the reduction of nitro compounds to primary amines. Using formic acid as hydrogen donor and water as solvent, the optimized 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst exhibited an unprecedented performance in the conversion of nitrobenzene to aniline (achieving almost full conversion with an extremely high turnover frequency of 4770 h<sup>-1</sup> at room temperature), showing the best activity ever reported for heterogeneously catalyzing nitro compounds reduction. Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst was also active for the one-pot reductive amination of carbonyl compounds with nitro compounds to obtain the corresponding secondary amines with excellent selectivity (>90%). We proposed that the protic N-H<sup>+</sup> and hydridic Pd-H<sup>-</sup> on Pd/g-C<sub>3</sub>N<sub>4</sub> are the active species for the transfer hydrogenation of nitro compounds. This work will open up a new approach for transfer hydrogenations of nitro compounds to produce primary or secondary amines in green chemistry

#### INTRODUCTION

Amine compounds, especially those of primary and secondary amines, are the significant raw materials and intermediates, and are playing remarkable roles in the syntheses of high value-added chemicals.<sup>1,2</sup> Hence, wide extensive interests from both academic and industrial researchers have been devoted to explore more efficient and environmentally benign strategies to synthesize amines. To date, numerous preparation systems of primary and secondary amines have been developed, including hydrogenation of nitro  ${\rm compounds,}^{{\rm 3},{\rm 4}} \quad {\rm reduction} \quad {\rm amination} \quad {\rm of} \quad {\rm amides,}^{\rm 5}$ direct amination of halides,<sup>6</sup> Buchwald-Hartwigand,<sup>7</sup> Ullmantypecarbon-nitrogen cross-coupling reactions,<sup>8</sup> as well as the direct N-alkylation of amines with alcohol.<sup>9</sup> Among all these methods, the synthesis of amines with nitro compounds could be the convenient and valuable reactions, because both of reactions do not require the separation and purification of

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intermediates and can solve the problem of low yield caused by the multi-step reaction. Unfortunately, traditional hydrogenation of nitro compounds to amines with molecular hydrogen as reductant is widely regarded as an environmentally unfriendly and harsh synthetic process, such as the use of toxic organic solvents and high pressure H<sub>2</sub>, which greatly limited their industrial applications.<sup>10-12</sup> Therefore, it is important to find environmentally friendly strategies to synthesize amines more efficiently and easily.

Comparing to hydrogenation reactions involving H<sub>2</sub>, catalytic transfer hydrogenation can provide a mild and safe reaction condition<sup>13</sup> using the hydrogen atoms supplied from isopropanol, <sup>14</sup> hydrazine, <sup>15</sup> ammonium borane, <sup>16</sup> carbon monoxide, <sup>17</sup> and formic acid<sup>18</sup> to replace hydrogen molecules. Among these donors, formic acid (FA), derived from the byproducts of renewable biomass, has a high energy density (4.4 wt %). Additionally, the non-toxic and stable features suggest that formic acid can be used as a safe and economical carrier of liquid hydrogen source.<sup>19,20</sup> Therefore, if choosing FA as a proton donor, the preparation of amine compounds might be realized in the mild conditions without using harsh conditions like autoclaves or high-pressure hydrogen. More importantly, in the catalytic transfer hydrogenation reaction, FA undergoes a process similar to dehydrogenation (HCOOH $\rightarrow$ H<sub>2</sub> + CO<sub>2</sub>), the two hydrogen atoms in the formic acid can participate in the

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**Journal Name** 

#### ARTICLE

hydrogenation reaction, and the decomposition only produces by-product of carbon dioxide  $\overset{21}{\ldots}$ 

Developing new catalyst is the key to achieve a high catalytic performance in transfer hydrogenation of nitro compounds with FA. Accordingly, many heterogeneous metal catalysts have been conducted.<sup>21-23</sup> Pd metal is a common active component in FA dehydrogenation.<sup>24</sup> In addition, Pdbased catalysts also show good activity in hydrogenation reaction,<sup>25</sup> which could be used in the reduction of unsaturated chemical bonds. Even so, the preparation methods for such reactions are lack of control, the catalytic activities need further improvement, and the weak CO tolerance of Pd may lead to a reduced stability of the catalyst. An alternative to these shortcomings is to modify the surface electronic structure of Pd catalyst with suitable supports, which can stabilize Pd nanoparticles (NPs), but also improve the activity of Pd NPs under transfer hydrogenation conditions due to the metal-support electronic interaction. Therefore, finding suitable and efficient supports is necessary for the transfer hydrogenations of nitro compounds. We took graphitic carbon nitride  $(g-C_3N_4)$  as a model support to study based on its unusual features: (1)  $g-C_3N_4$  is a rich-N carbon material, which could modify the surface structure of noble metal catalysts through providing an enhanced binding ability and improved basicity;<sup>26,27</sup> (2)  $g-C_3N_4$  has a typical 2D nanosheet structure, which is propitious to disperse and stabilize Pd NPs;<sup>28,29</sup> (3) the high stability of  $g-C_3N_4$  against chemical attacks from acid, base, and organic solvents enables its direct use for sustainable chemical reactions,<sup>27</sup> and what's more, and (4) different kinds of chemical environments for N atoms in g-C<sub>3</sub>N<sub>4</sub> (among of which pyridine nitrogen belongs to the Lewis base) could promote the cleavage of oxygenhvdrogen bonds.<sup>30</sup> Therefore,  $g-C_3N_4$ -engineered Pd NPs could achieve high activities in preparation of amine compounds using FA as the hydrogen donor.

In this contribution, we designed a series of  $Pd/g-C_3N_4$  catalysts (1-10 wt%  $Pd/g-C_3N_4$ ) by a wet chemical reduction method. In comparison to the existent catalysts, the engineered  $Pd/g-C_3N_4$  catalysts, especially 5 wt%  $Pd/g-C_3N_4$  showed great improvements in the transfer hydrogenation of nitro compounds to synthesize primary amine with FA as hydrogen donor at room temperature. Moreover, the catalyst was active for the one-pot reductive amination of carbonyl compounds with nitro compounds to prepare secondary amines (as summarized in Scheme 1). Moreover, the catalyst exhibited a superior recyclability and wide scope in the syntheses of various primary amine or secondary amines.

#### **RESULTS AND DISCUSSION**

#### Characterization of the prepared sample

We began our research by synthesizing  $g-C_3N_4$  nanosheets with the thermal decomposition of melamine. The obtained g- $C_3N_4$  nanosheets were then loaded with a certain content of Pd (1-10 wt% Pd/g-C<sub>3</sub>N<sub>4</sub>) by a wet chemical reduction method.



**Scheme 1.** Schematic illustration for the preparation of primary and secondary amine over  $g-C_3N_4$  supported Pd NPs.

The phase structure and composition of all samples are identified by XRD. The obtained data are shown in Fig. 1. Two diffraction peaks at two theta around 27.8° and 12.8° observed for all samples, are ascribed to the characteristic (002) and (100) peaks of  $g-C_3N_4$ ,<sup>29,31</sup> indicating that the typical graphitelike structure of C<sub>3</sub>N<sub>4</sub>-based materials was obtained during the thermal decomposition process. In addition to the characteristic peaks of g-C<sub>3</sub>N<sub>4</sub>, Pd loading samples exhibited the diffraction peaks at two theta of 39.5°, 45.6°, and 68.1° in their XRD patterns. These peaks can be assigned to the (111), (200), and (220) diffractions of Pd metal,<sup>28,32</sup> respectively (Fig.1 b-f). Moreover, the (111) diffraction of Pd gets sharper with the increase of Pd contents, demonstrating the particle size of Pd particles grew big slightly. These observations suggest that PdCl<sub>2</sub> salt had been converted to Pd metal successfully, and g- $C_3N_4$  could act as an excellent substrate to anchor Pd NPs.

FT-IR spectra of all samples were recorded to examine the chemical species, as shown in Fig. 2. In the FT-IR spectrum of  $g-C_3N_4$ , the absorption band at 1640 cm<sup>-1</sup> corresponds to the C-N



**Fig. 1** XRD patterns of the samples: (a)  $g-C_3N_4$ , and  $Pd/g-C_3N_4$  catalysts with different Pd loadings: (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 8 wt%, and (f) 10 wt%.

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**Fig. 2** FT-IR spectra of the samples: (a)  $g-C_3N_4$ , and  $Pd/g-C_3N_4$  catalysts with different of Pd loading: (b) 1 wt% Pd, (c) 3 wt% Pd, (d) 5 wt% Pd, (e) 8 wt% Pd, and (f) 10 wt% Pd.

heterocycle stretching vibration,<sup>33,34</sup> while the four at 1241, 1320, 1409, and 1567 cm<sup>-1</sup> to aromatic C-N stretching vibrations.<sup>35,36</sup> The peak at 808 cm<sup>-1</sup> is associated with the breathing mode of triazine units.<sup>37</sup> The broad band in the region of 2900-3500 cm<sup>-1</sup> can be assigned to the characteristic absorption peaks of O-H and amine groups.<sup>38</sup> FT-IR spectra of all samples did not show any observable changes before and after Pd loading, suggesting a non-covalently coupled interaction between g-C<sub>3</sub>N<sub>4</sub> and Pd NPs in the composite, as concluded elsewhere.<sup>39</sup> Moreover, BET surface areas for the



**Fig. 3** (a) SEM and (b) TEM images of pure  $g-C_3N_4$ . (c,d) TEM and (e) HTEM images of 5 wt% Pd/g-C\_3N\_4. Inset of (d) is particle size distribution of 5 wt% Pd/g-C\_3N\_4. (f) SEM-EDS elemental mapping images of 5wt% Pd/g-C\_3N\_4 and the corresponding elemental mapping images of (g) carbon, (h) nitrogen and (i) palladium.



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ARTICLE

Fig. 4 (a) XPS survey spectrum and core level spectra of C 1s (b); N 1s (c); Pd 3d (d) for 5 wt% Pd/g-C\_3N\_4.

Pd loaded samples are almost the same as that of g-C3N4 (Table.  $S1^+$ ).

Morphology and microstructure of samples are further monitored by SEM, TEM and HRTEM. As illustrated in Fig. 3, pure g-C<sub>3</sub>N<sub>4</sub> shows a wrinkled sheet structure with serious aggregation (Fig. 3a, b). TEM images for typical sample of 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> (Fig. 3c,d) reveals that Pd NPs are distinctly anchored on the g-C<sub>3</sub>N<sub>4</sub> nanosheets. The average sizes of the Pd nanoparticles are 2.48, 2.68, 3.30, 5.08, and 5.19 nm for the 1 wt%-10 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalysts, respectively (Figs. S2+-6+), indicating that the mean size of nanoparticles increased with loading, which is consistent with our XRD observation. The HRTEM image (Fig. 3e) highlights a typical metallic Pd nanoparticle with a lattice space of 0.225 nm, which is assigned to the (111) plane of metallic Pd.<sup>40</sup> In addition, SEM-EDX mapping test demonstrated an uniform distribution of C, N and Pd over 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub>, further confirming that Pd nanoparticle are well dispersed on the surface of g-C<sub>3</sub>N<sub>4</sub>.

To examine the surface chemical composition and chemical states of elements, XPS measurements are performed for 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> sample. The survey XPS spectrum in Fig. 4a show that C, N, O, Pd elements coexist in the 5 wt% Pd/g- $C_3N_4$  material, which is consistent with the EDX results (Fig.S7<sup>†</sup>). Fig. 4 (b-d) gives the XPS core level spectra of C 1s, N 1s, and Pd 3d of 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> sample. The peak at 284.6 eV in C1s is ascribed to surface adventitious carbon, whereas the other peak at 287.8 eV corresponds to the sp<sup>3</sup>bonded carbon in N-C=N of  $g-C_3N_4$  (Fig. 4b)<sup>41</sup>. For N1s, four peaks can be distinguished (Fig. 4c). The peak at 398.4 eV is assigned to the pyridinic-like nitrogen (N-C-N), and the signal at the binding energy of 399.8 eV to the tertiary nitrogen N- $(C)_{3}$ .<sup>42</sup> The peaks at 400.4 and 404.4 eV are attributed to the amino functions carrying hydrogen (C-N-H) and charging effects.<sup>43</sup> Comparing with the g-C<sub>3</sub>N<sub>4</sub> (Fig. S8<sup> $\dagger$ </sup>), the N1s signals of 5% wt Pd/g-C<sub>3</sub>N<sub>4</sub> shifts 0.4 eV towards high binding energy, indicating the presence of strong interaction between support

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#### ARTICLE

of g-C<sub>3</sub>N<sub>4</sub> and Pd NPs. The XPS spectra of Pd 3d (Fig. 4d) presents two doublet peaks, corresponding to spin-orbital splitting of Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  for two typies of Pd species. The stronger peaks at 335.2 and 340.5 eV for Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  are from metallic Pd<sup>0</sup>,<sup>44,45</sup> and that with relative low intensity at 337.2 and 342.5 eV can be assigned to Pd<sup>2+</sup>, which might be the formation of Pd-O or Pd-N bonds on the surface of catalyst.<sup>46</sup> The content of Pd<sup>0</sup> estimated by the area ratio of two doublet peaks is as high as 75% in the total Pd atoms (Table. S1<sup>†</sup>). These results demonstrate that the amine groups in the g-C<sub>3</sub>N<sub>4</sub> carrier can stabilize highly dispersed Pd<sup>0</sup> species and prevent their oxidation partly.<sup>47</sup>

#### Catalytic synthesis of primary amines

1) The selection of catalysts. Firstly, in a preliminary catalyst screening, the catalytic transfer hydrogenation nitrobenzene is selected as a model reaction to study. The experiments were carried out in deionized water at room temperature over various catalysts by using 3 mmol FA (Table. 1). Only adding pure g-C<sub>3</sub>N<sub>4</sub>, nitrobenzene did not undergo any reaction (Table. 1 entry 1). Comparatively, all the Pd/g-C<sub>3</sub>N<sub>4</sub> catalysts (Table 1 entries 2-6) exhibited excellent catalytic activity, with a conversion of nitrobenzene as high as 99% and the selectivity of anilines about 99%. Moreover, the reaction rate gradually increased with the increase of the Pd loading (Fig. S12<sup>+</sup>). However, the turnover frequency (TOF) increased significantly to a maximum of 3172  $h^{-1}$  at the Pd loading of 5%, and then slightly decreased when continuously increasing Pd loading to 8% and 10% (Fig. S13<sup>+</sup>). The 5 wt%  $Pd/g-C_3N_4$  gave the highest TOF is ascribed to its containing high Pd<sup>0</sup> (75%) comparing to the samples with light Pd loading (1 wt% and 3 wt%) and possessing small Pd particle size to the samples with high loading (8 wt% and 10 wt% ), as listed in Table. S1<sup>+</sup>. We also test the catalytic activity of other noble metals (Au, Pt, Ru and Rh) supported on g-C<sub>3</sub>N<sub>4</sub> nanosheets under the same reaction conditions (entries 7-10 in Table. 1), and found that these catalysts did not show any activity for the reduction of nitrobenzene. These results suggest that Pd NPs is the most active metal in the catalytic transfer hydrogenation for nitrobenzene in the presence of FA.

To investigate the effect of the supports on the catalytic transfer hydrogenation for nitrobenzene, a series of the Pd/ supporters composites with different supporters were examined in comparison to Pd/g-C<sub>3</sub>N<sub>4</sub> (entries 11-15). The Pd/C catalyst showed a very low activity for the reaction. This is mainly because Pd/C catalyst tends to catalyze the dehydration of formic acid, which cannot effectively break the oxygen-hydrogen bonds in FA.<sup>30</sup> Pd/g-C<sub>3</sub>N<sub>4</sub> exhibited excellent performance with higher activity and selectivity in catalytic transfer hydrogenation of nitrobenzene than other catalyst. This is mainly because g-C<sub>3</sub>N<sub>4</sub> nanosheets with electron-rich nitrogen present surface Lewis base properties and modify the electron density of the supported metals, which can promote performance in the cleavage of oxygen-hydrogen bonds in FA.<sup>30,48</sup> In addition, the formate as intermediate can be

**Table 1.** Comparisons of catalytic performance for transfer hydrogenation of nitrobenzene to aniline over various catalysts<sup>a</sup>.

Entry	Catalyst	Time [min]	Con. <sup>b</sup> [%]	Sel. <sup>b</sup> [%]	
1	g-C <sub>3</sub> N <sub>4</sub>	20	trace	trace	
2	10 wt % Pd/g- $C_3N_4$	2	99	99	
3	8 wt % Pd/g- $C_3N_4$	3	99	99	
4	5 wt% Pd/g- $C_3N_4$	3	99	99	
5	$3 wt\% Pd/g-C_3N_4$	9	99	99	
6	$1 \text{ wt\% Pd/g-}C_3N_4$	20	99	99	
7	5 wt% Au/ g- $C_3N_4$	3	trace	trace	
8	5 wt% Pt/ g- $C_3N_4$	3	trace	trace	
9	5wt% Ru/ g-C <sub>3</sub> N <sub>4</sub>	3	trace	trace	
10	5 wt% Rh/ g- $C_3N_4$	3	trace	trace	
11	5 wt% Pd/CeO <sub>2</sub>	3	29	99	
12	$5 \text{ wt\% Pd/Al}_2\text{O}_3$	3	45	99	
14	5 wt% Pd/C	3	<5	99	
15	5 wt% Pd/r-GO	3	<5	99	
16 <sup>c</sup>	5 wt %Pd/g- $C_3N_4$	20	98	99	
17 <sup>e</sup>	5 wt% Pd/g-C <sub>2</sub> N <sub>4</sub>	3	99	99	

[a] Reaction conditions: (1-6) catalyst (20 mg), water (5 mL), nitrobenzene (1 mmol), FA (3 mmol), 298 K. (7-15) catalyst (metal 1 mol%), water (5 mL), nitrobenzene (1 mmol), FA (3 mmol), 298 K. [b] Conversions [Con.] and selectivity [Sel.] were determined by GC-MS. [c] catalyst (metal 0.1 mol%), water (10 mL), nitrobenzene (20 mmol), FA (60 mmol), 298 K. [d] Reuses of the 5% wt Pd/g- $C_3N_4$  catalyst in transfer hydrogenation of nitrobenzene after 6 runs.

decomposed into carbon dioxygen and the active hydrogen is absorbed in the surface of Pd  $\rm NPs.^{49,50}$ 

In order to study whether the reaction can be used in the industrial production, a gram-scale reaction was studied (Table. 1, entry 16), and the results show that nitrobenzene was completely converted into aniline within 20 min, which suggests that the  $Pd/g-C_3N_4$  has a good prospect in industrial production of aniline. In addition, the reusability performance of catalyst is an important property for representing its stability. The catalyst was recycled at least six times without considerable change in conversion of nitrobenzene, and the

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 Table. 2
 Catalytic transfer hydrogenation of nitrobenzene to
anilines over 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> in various solvents<sup>a</sup>

Entry	Solvent	Volume [ml]	Time [min]	Con. <sup>[b]</sup> [%]	TOF h <sup>-1</sup>
1	Water	5	3	99	3172
2	Ethanol	5	5	99	1050
3	Toluene	5	5	15	154
4	Cyclohexane	5	5	21	245
5	DMF	5	5	51	592
6	THF	5	5	56	612
7	Water	1	1.5	99	4770
8	Water	3	2	99	3774
9	Water	7	5	99	2180
Ponotio	n condition: Ni	trobonzono	(1 mmol	) EA (2	mmol) 5

Reaction condition: Nitrobenzene (1 mmol), FA (3 mmol), 5 wt% Pd/g-C3N4(Pd: 1 mol%), 298K

selectivity toward aniline was always above 99% (Table. 1, entry 17 and Fig.S14<sup>+</sup>a).

2) Influence of the solvent. Solvent effects have been an important issue for liquid phase organic synthetic reactions, so we further studied the effect of different solvents on catalytic transfer hydrogenation of nitrobenzene. From Table 2, the conversion and TOF are significantly different among the solvents examined. It is noted that the catalytic activity of reaction in the protic solvents (water, ethanol) is much higher than that of the aprotic solvents (toluene, cyclohexane, THF). A possible explanation is that the hydrogenation rate is related to H-bond donor capability of the protic solvents because the strong interaction between protic solvents and substrate by hydrogen bonding lowers the activation energy barrier and leads to high hydrogenation rate. However, aprotic solvents could strongly adsorb onto the catalyst surface and block the active sites, thereby inhibiting the hydrogenation rate.<sup>51</sup> More interestingly, water has the highest TOF (3172 min<sup>-1</sup>) and gave a full conversion toward aniline, demonstrating its superiority as a green functional solvent. Compared to a number of organic solvents, water may serve as a reaction promoter for organic synthetic reactions, which is ascribable to its high hydrogen-bond-donation (HBD) capability and low hydrogenbond-acceptance (HBA) capability.<sup>52</sup> When the concentration of nitrobenzene increasing (the volume of water is 1 ml), the TOF value can reach 4770 min<sup>-1</sup>, reflecting some of the highest activity for heterogeneously catalysed nitrobenzene reduction under similar conditions (Table S2<sup>+</sup>). These results show that Pd/g-C<sub>3</sub>N<sub>4</sub> has excellent catalytic performance for the reduction of nitrobenzene using FA as the hydrogen donor in water under room temperature.

able	3.	Catalytic	transfer	hydrogenation	of	various	nitro
ompo	bun	ds to the	correspor	nding primary a	min	es over 5	5 wt%
Pd/g-	C₃N	l <sub>4</sub> a					

	R NO <sub>2 5 wt%Pd/g-</sub> HCOOH Water	<u>C3N4</u> 298 K	R NH <sub>2</sub>	
Entry	R	Time [min ]	Con. <sup>[b]</sup> [%]	Sel. <sup>[b]</sup> [%]
1		5	99	99
2		20	99	99
3		20	98	99
4		5	96	99
5	H <sub>2</sub> N-\-NO <sub>2</sub>	5	99	99
6	HO-	5	99	99
7		30	96	99
8		20	92	99
9	F	20	93	99
10		10	94	99
11		120	95	99
12		120	92	99

[a] Reaction condition: Nitro compound (1 mmol), FA (3 mmol), H<sub>2</sub>O (5 mL), 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub>(Pd: 1 mol%), 298K

[b] Conversion and selectivity were determined by GC-MS.

#### ARTICLE

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**3) Substrate scope.** To illustrate the general applicability of Pd/g-C3N4, the method was extended to a variety of other nitro compounds, and the results are presented in Table 3.

All nitro compounds have high selectivity towards the corresponding primary amines at water under room temperature over Pd/g-C<sub>3</sub>N<sub>4</sub>. However, the nitro compounds with electron-withdrawing groups showed lower activity (Table 3 entries 4-7 vs entries 8-10), possibly because the electron-withdrawing group restrain the hydrogenation.<sup>53</sup> In addition, the steric hindrance also greatly affect the activity of the substrates.<sup>54</sup> For example, the reaction rate of the ortho-isomer was slower than the para-isomers (Table 3, entries 1-3). When the ortho has two methyl groups (Table 3, entry 11 and 12), it needed a longer time to complete reaction.

#### Catalytic synthesis of secondary amines

Next, we studied the reductive amination of benzaldehyde with nitrobenzene was used as a model reaction for the preparation of secondary amines. In our study, aldehydes were excessive to nitro compounds (molar ratio=1.5) in order to promote the condensation step of the aldehyde with primary amines. Due to the transfer hydrogenation of C=N bond was much more difficult than that of C=O bond in the nitro group, the reactions were performed at higher temperatures. As shown in Fig. 5, the experimental temperatures range is set up from 60 to 110  $^{\circ}$ C. The selectivity of N-benzylaniline (2) and N-benzylideneaniline (3) were respectively 13% and 36% at 60  $^{\circ}$ C for 12 h. At the same time, there can also be a part of aniline (4) in reaction system. As the temperature increased to 100  $^{\circ}$ C, the selectivity of N-benzylaniline (2) reached as high as 95%, but the selectivity of N-benzylideneaniline (3) decreased to 1%.



Fig. 5 N-benzylaniline formation from benzaldehyde and nitrobenzene at different temperatures. Reaction conditions: benzaldehyde (1.5 mmol), nitrobenzene (1 mmol), 5 wt%Pd/g- $C_3N_4$  catalyst (2 % mol), water (5 mL), FA (4.5 mmol) and time (12 h). The conversion and the selectivity of the intermediate and the product were calculated based on nitrobenzene.

The main reason is that the transfer hydrogenation of C=N bond to synthetize secondary amines needs higher higher temperatures. However, when the temperature is much higher (above 100  $^{\circ}$ C), the by-product of benzamide (4) can be generated, resulting in a decrease in selectivity of N-benzylaniline (2).

The scope of the developed method also was explored in the preparation of secondary amines. From the Table S3<sup>+</sup>, the nitro compounds reacted smoothly with aromatic aldehyde compounds to give secondary amines with excellent selectivity. The influence of electronic effects and spatial effects was the same as the preparation of primary amines. The nitro compounds and aldehyde compounds with electronwithdrawing groups had a slower reaction rates than those with electron-donating groups. Their reaction activity markedly decreased with the increase of the steric hindrance from nitro compounds and aldehyde compounds, respectively. These obtained secondary amines are important intermediates in chemical industry. Therefore, the present catalytic system is highly promising for uses in industrial production of secondary amines.

#### **Recyclability of catalyst**

A main advantage of heterogeneous catalyst is its good stability, recyclability and ease in separation. The reusability of the 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst was investigated using the reductive amination of benzaldehyde with nitrobenzene as a model reaction. For each run, the reaction was carried out at 100 °C for 12 h. The catalyst after reaction was filtrated and washed with water, followed by drying and treatment under air at 80 °C for 12 h to remove residues. In this way, the 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst was recycled six times. No considerable change in conversion of nitrobenzene (the conversions were ranging from 99% to 97% after 12 h) was observed. Moreover, the selectivity toward N-benzylaniline was always above 92% (Fig. S14<sup>†</sup>b), suggesting this catalyst has excellent reusability. TEM images taken for the 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst after the fifth catalytic cycle did not show obvious change in morphology (Fig. S15<sup>†</sup> a). The XRD patterns and XPS spectras (Fig. S15<sup>†</sup> b and c) showed that the structure and the valence state of the 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst after six runs are almost the same, confirming the high stability and reusability of the 5 wt% Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst under reaction conditions.

A hot-filtration test was carried out to verify the heterogeneous nature of the reaction (Fig. S16<sup>†</sup>). After removal of the solid catalyst at 9 h, no reaction proceeded in the filtrate. The conversion of nitrobenzene increased with prolonging the reaction time in the presence of the catalyst. The conversion would be stable at 99% after 9 h. These results indicate that the catalytic effect in this system results from the current sample, rather than the leached metal species.

#### Mechanism analysis

In order to explore the mechanism of reaction, we studied the decomposition rate of FA with and without nitrobenzene (Fig. S17). In Fig. S17a, the decomposition rate of





**Scheme 2.** Proposed mechanism for the preparation of primary and secondary amine by transfer hydrogenation.

FA is very low in the absence of nitrobenzene. After 3 hours, only 20% of FA was decomposed. However, after the addition of nitrobenzene, the utilization of FA is significantly improved. In 3 minutes, FA can achieve 100% utilization (Fig. S17<sup>†</sup> b). It is clearly see that the reaction rate of FA catalytic transfer hydrogenation is much higher than the rate of formic acid decomposition. What's more, hydrogen was not observed in the presence of nitrobenzene, which indicates that the catalytic transfer hydrogenation reaction is preferred when nitrobenzene is involved (Fig. S18<sup>†</sup>).

According to the above discussion, the possible mechanism is proposed as follows (Scheme 2). In the first step, g-C<sub>3</sub>N<sub>4</sub> nanosheets have the electronegative nitrogen atoms, which can capture the  $H^+$  from the oxygen-hydrogen bond of FA to generate  $NH^{\dagger}$  and form the Pd-formate intermediate, which is considerable in the FA decomposition. The formate anions tended to adsorb on the surface of the Pd nanoparticles, as the formate anions can be coordinated with the empty d orbitals of Pd. In the second step, the Pd-formate intermediate can produce CO<sub>2</sub> molecule and PdH<sup>-</sup>. The third step, when the hydrogen atoms of NH<sup>+</sup> and PdH<sup>-</sup> combined, the hydrogen will be generated.<sup>55</sup> However, the combinations of hydrogen need to be sufficient energy to drive, so the hydrogen production rate is very low. When the system exists nitrobenzene, these two parts of the hydrogen in the NH <sup>+</sup> and PdH<sup>-</sup> will be preferred react with nitrobenzene nitro group and generate amino group, resulting in hydrogen does not produce and nitrobenzene reduction rate is higher in the system. The fourth step, when the system exists in the benzaldehyde, the aniline produced in the previous step will undergo a condensation reaction with benzaldehyde to form N-benzylideneaniline. In the last step, the generated N-benzylideneaniline will occurs in

the similar reaction of the reduction of nitrobenzene, reducing the nitrogen-oxygen double bond to the nitrogen-oxygen bond and generating N-benzylaniline.

#### Conclusions

In this work, we have discovered that g-C<sub>3</sub>N<sub>4</sub> supported Pd catalyst are highly active in the transfer hydrogenation of a variety of nitro compounds to generate their corresponding primary amines or secondary amines by using formic acid as hydrogen donor. Further, the catalysts showed good recyclability without significant loss of catalytic activity even up to six runs. Moreover, the contrast experiments reveal that electronegative nitrogen atoms in g-C<sub>3</sub>N<sub>4</sub> served as the base sites to generate the Pd-formate species, followed by the generation of a proton  $(H^+)$  and a hydride  $(H^-)$  to reduce the C= N bonds by Pd NPs as a metal active center. The outstanding catalytic activity, combining with the high selectivity, broad substrate scope and recyclability as well as mild reaction conditions, makes this system to be attractive alternative pathway for transfer hydrogenations of nitro compounds to produce their corresponding primary amines or secondary amines, showing potential applications in chemical industries.

#### **Experimental section**

**Synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets.** g-C<sub>3</sub>N<sub>4</sub> nanosheets were synthesized according to the procedure reported in literature.<sup>29</sup> Briefly, 10 g of melamine were first heated in a muffle furnace from room temperature to 520 °C at a heating rate of 4 °C/min. After calcination at 520 °C for 2 h, the asprepared g-C<sub>3</sub>N<sub>4</sub> was naturally cooled to room temperature, and ground to powders.

Synthesis of Pd/g-C<sub>3</sub>N<sub>4</sub>. Pd/C<sub>3</sub>N<sub>4</sub> catalysts with a Pd loading of 1-10 wt % (based on ICP bulk chemical analysis) were prepared via a facile wet chemical reduction. Briefly, 0.50 g C<sub>3</sub>N<sub>4</sub> nanosheets was introduced into 300 mL distilled H<sub>2</sub>O at 25°C under constant stirring, and an appropriate amount of PdCl<sub>2</sub> solution (6 g  $L^{-1}$ ) was added into the solution. After stirring at 25°C for 1 h, 0.1 M NaOH was slowly added into the mixed solution to adjust the pH at the constant value of 9.5. During the subsequent stirring for another 2 h, given amounts of NaBH<sub>4</sub> solution (freshly prepared, nNaBH<sub>4</sub>: nPd =15:1) was rapidly injected into the g-C<sub>3</sub>N<sub>4</sub>-PdCl<sub>2</sub> solution, while continuously stirring the resultant mixture for 3 h again at 25°C. Then, the suspension was filtered and extensively washed with distilled water till chloride species remained in the reaction solution is free. Eventually, the powers were dried in oven at 50°C for overnight to get  $Pd/g-C_3N_4$  samples.

General procedure for the preparation of primary amines. Nitro compounds (1 mmol), 5 wt % Pd/g-C<sub>3</sub>N<sub>4</sub> (20 mg), water (5 mL) were stirred for 2 min in a 10 mL glass tube at 25 °C. Next, FA (3 mmol) was added to the reaction mixture. The solution was stirred at 600 rpm at 25 °C for different periods of time. After the reaction, the conversion of nitro compounds and the

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#### ARTICLE

primary amines yields were determined by GC-MS with n-butyl alcohol as the internal standard.

General procedure for the preparation of secondary amines. Nitro compounds (1 mmol), 5 wt% Pd/g- $C_3N_4$  (20 mg), water (5 ml) was stirred for 5 min in a 25 mL flask at 25 °C, FA (4.5 mmol) was added to the reaction mixture. The solution was stirred at 600 rpm at 25 °C for 30 min. Then, aldehyde compound was added into the solution and keep it at 100 °C for 12 h. After the reaction, the conversion of nitro compounds and the secondary amines yields were determined by GC-MS with nbutyl alcohol as the internal standard.

Recycling experiments. After the reactions, catalyst was exhaustively washed with water and ethanol, respectively, and dried at 50 °C in a vacuum oven. The collected catalyst was used for the next run under the same conditions. Other cycles were repeated following the similar procedure.

Catalytic dehydrogenation of FA. 5 mL scale of 1.0 M aqueous FA and 150 mg Pd/g- $C_3N_4$  were placed in a reaction vessel (25 mL) using water bath under steady magnetic stirring (800 rpm) at room temperature. The evolved gas (CO<sub>2</sub>+H<sub>2</sub>) was then measured using a gas burette in real time at room temperature. The generated gas composition was analysed by GC.

## **Conflicts of interest**

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There are no conflicts to declare.

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**Table of Content** 

## Unprecedented catalytic performance in amines syntheses via

## Pd/g-C<sub>3</sub>N<sub>4</sub> catalyst–assisted transfer hydrogenation

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 $Pd/g-C_3N_4$  catalyst exhibited a superb performance in the transfer hydrogenation of nitro compounds to generate their corresponding primary and secondary amines with formic acid as the hydrogen donor in aqueous solution.