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Ultrafine palladium nanoparticles were immobilized on nitrogen-riched porous carbon nanosheets (NPC), which was fabricated with $g-C_3N_4$ as nitrogen source and a self-sacrificial template. The prepared Pd@NPC delivered superior catalytic activity and chemoselectivity for the catalytic transfer hydrogenation of alkenes at mild conditions with formic acid as hydrogen donor. Moreover, the catalyst displays high structure stability, which can be reused five runs without significant decrease of its catalytic activity and obvious leaching of Pd species. This work provides a facile and feasible approach to fabricate nitrogen-riched carbon nanosheets and to construct advanced Pd supported heterogeneous catalysts for achieving high catalytic activity.

1. Introduction

Hydrogenation of double bond is a key transformation reaction in the fabrication of fine and commodity chemicals, functional materials as well as pharmaceuticals ¹. Although alkene hydrogenation with pressurized hydrogen (H₂) catalyzed by various metal catalysts is the most atom-efficient way ²⁻⁵, but the reaction is generally conducted at high pressure and high temperature. In addition, H₂ is flammable and difficult to handle.

The catalytic transfer hydrogenation (CTH) that utilizes a safe hydrogen donor other than H_2 has been considered as a prospective, multipurpose and alternative approach for the hydrogenation reaction. Different hydrogen donors, such as isopropanol, hydrazine, ammonia borane, sodium borohydride and formic acid (FA) ⁶ have been employed. Among the hydrogen sources used in transfer hydrogenation, FA has been regarded as a promising and sustainable hydrogen

source because of high energy density with a hydrogen content of 4.4 wt%, no obvious toxicity, excellent stability, and easy handling capability ⁷. Moreover, FA can be produced in large scale through the hydrogenation of CO_2 and artificial photosynthesis, which also is one of the major by-products in biomass processing.

Recently, FA has been employed as the hydrogen donor in the catalytic transfer hydrogenation of nitro-compound, preparation of γ -valerolactone from levulinic acid, reduction of alkenes, etc. For example, Basset et al. prepared fibrous silica nanospheres (KCC-1) supported palladium catalyst for the transfer hydrogenation of alkenes and carbonyl compounds at 100°C with FA as hydrogen source ⁶. Pd@CN catalyst was fabricated and used to catalyze the hydrogenation of alkene at 90°C⁸. Chen et al. reported a Mott-Schottky catalyst, Pd nanoparticles supported on g-C₃N₄, and used for the catalytic transfer hydrogenation of the C=C compounds at room temperature, however, high dosage of Pd (7.5 mol%) is required ⁹. Pd nanoparticles encapsulated in triazine functionalized porous organic polymer was prepared and used for the CTH of alkene in the presence of FA and Et₃N, the reactions were performed at 25°C for 4-15 h 10. Despite the recent progresses have been achieved, the reported catalytic systems still have one or more shortcomings, such as relative long reaction time, harsh reaction conditions and high dosage

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[†]Electronic Supplementary Information (ESI) available: Chemicals and characterization apparatus, TEM image and particle size of recycled Pd@NPC, the filtration test, comparison with reported catalysts tested for reduction of alkenes. See DOI: 10.1039/x0xx00000x

of catalyst. Therefore, exploring a highly efficient catalyst for the hydrogenation of alkene is still highly desirable.

Generally, the composition, morphology and surface physicochemical property of the support play an important role for the catalytic behavior of a heterogeneous catalyst. In recent years, the nitrogen-doped porous carbon material supported catalysts have attracted considerable interest ^{11, 12}. The nitrogen modification can not only strengthen the interaction between carbon material and reactants, but also can enhance the binding energy between the metal nanoparticle and the support, which is favorable to increase the catalytic performance and stability of the heterogeneous catalyst ¹³⁻¹⁵. In addition, nitrogen dopant can also affect the charge distribution of carbon atoms and the physical-chemical property of the support ^{16, 17}.

In this paper, a nitrogen-doped porous carbon material (micropore and mesoporous) was successfully fabricated through a facile pyrolytic approach with graphitic carbon nitride (g-C₃N₄) as sacrificial template and nitrogen source. g- C_3N_4 can be easily prepared by heating treatment of nitrogen rich precursors, such as melamine, dicyandiamide or urea 18-²¹. g- C_3N_4 with high concentration of nitrogen and quasi-twodimensional layered structure can be employed as the nitrogen source and sacrificial template for the fabrication of nitrogen-doped carbon nanosheet material²². Pd nanoparticles were assembled on the nitrogen-doped porous carbon nanosheets (Pd@NPC), which was used as a heterogeneous catalyst for the catalytic hydrogenation of alkenes with formic acid as hydrogen source for the first time. The results indicated that a series of alkenes substrates were successfully reduced to corresponding products at mild conditions. The catalyst delivered good catalytic performance and selectivity.

2. Experimental section

Basic information including chemicals, materials and the sectional TEM pictures were given in the Electronic Supporting Information (ESI).

2.1 Preparation of materials

The bulk g-C₃N₄ was prepared based on the previous work ²³. 20 g urea was heated at 550°C in a crucible with a lid for 4 h under air, then the yellow fluffy solid was obtained and ground for further use. 500 mg of bulk g-C₃N₄ was dispersed in 50 mL distilled water and sonicated for 2 h. Then 2.0 g

glucose was added to the uniform solution. The yellow milk solution was transferred to a 100 mL Teflon-sealed autoclave, heated to 180° C and maintained for 10 h. When cooled to room temperature, the brown precipitate was gained by centrifugal filtration and washed three times with ethanol and water, respectively, and dried at 60° C for 2 h, the obtained solid was named as carbonized-glucose. Then, it was heated to 800° C with the rate of 5° C/min and maintained for 2 h under nitrogen atmosphere (N₂). The obtained powder was named as NPC.

Glu was prepared by the same procedure for the NPC without the addition of $g-C_3N_4$.

 $g-C_3N_4$ -Glu was fabricated as follows: 500 mg $g-C_3N_4$ was milled with 2 g carbonized-glucose, and then it was carbonized at 800°C for 2 h under nitrogen flow.

2.2 Preparation of Pd@NPC

The catalyst preparation process was illustrated in Scheme 1. 96 mg NPC was dispersed into 5 mL water in 25 mL round bottom flask, then 4.72 mL H_2PdCl_4 solution (2 mg·mL⁻¹) was added into the mixture and stirred for 2 h. 1 mL sodium borohydride solution (2 mol mL⁻¹) was added to the solution and stirred for 2 h at room temperature. Finally, the black solid was separated by centrifugation, washed with water and dried at 80°C in vacuum overnight. The obtained solid was named as Pd@NPC.

Pd@Glu and Pd@g-C₃N₄-Glu were prepared by the same process except that 96 mg of Glu and g-C₃N₄-Glu were used, respectively.

2.3 Hydrogeation of alkenes

Hydrogenation of alkene was conducted in a 25 mL round bottom flask, which was placed in a oil bath at 50°C. Firstly, 10 mg Pd@NPC nanocatalyst and 0.25 mmoL alkene were dispersed in 5 mL ethanol. 2.5 mmoL FA and 2.5 mmoL ammonium formate (AF) were then added into the soultion and the reaction was conducted at 50°C for a certain time. The reaction was tracked by thin layered chromatography and GC. After completion of the reaction, the catalyst was recycled by filtration and washed by ethanol. The recycled catalyst was dried in a vacuum at 60°C overnight. The product was extracted with dichloromethane (3×10 mL) and dried over an anhydrous MgSO₄. The yield of the product was analyzed by GC.



Scheme 1. Schematic illustrate of the preparation process of the Pd@NPC catalyst.

3. Results and Discussion

3.1 Characterization of the catalyst

From the transmission electron microscopy (TEM) pictures of the samples (Fig. S1), we can see that the morphology of the g-C₃N₄-Glu prepared by carbonization of the mixture of the partial carbonized glucose and g-C₃N₄ was almost the same as that of the Glu because g-C₃N₄ can be completely decomposed at 800°C. With g-C₃N₄ as self-sacrificial template, carbon nanosheets with lamellar structure were obtained (Fig. 1A, and S1A). Pd nanoparticles were well dispersed on the NPC (Fig. 1B). In addition, the crystal plane spacing of Pd was measured as 0.227 nm (Fig. 1C), which can be ascribed to the lattice spacing of face centered cubic Pd. The average size of Pd nanoparticles was about 4.0 \pm 1.0 nm (Fig. 1D). And the content of Pd in the Pd@NPC sample was determined by ICP-AES and amounted to be 4.01 wt%.

The crystalline structures of the samples were characterized by X-ray diffraction (XRD) (Fig. 2 and Fig. S2B). No XRD peaks for $g-C_3N_4$ can be observed, which indicated that g- C_3N_4 was conversed completely during the pyrolysis at 800°C. For Pd@NPC and the used Pd@NPC, the reflection peaks at $2\theta = 40.1^{\circ}$ can be attributed to the Pd (111). The broad peak at $2\theta = 27.5^{\circ}$ can be attributed to the graphitic carbon face (100). The pore properties of the NPC, Pd@NPC and the reused catalyst were investigated by nitrogen adsorption desorption isotherms (Fig. 3). The specific surface area of NPC, Pd@NPC and the reused Pd@NPC were 802 m² g^{-1} , 397 m² g^{-1} and 382 m² g^{-1} , respectively. Compared with NPC, the lower surface area of Pd@NPC indicated that a certain amount of Pd successfully supported onto the NPC. Fourier transform infrared spectra of g-C₃N₄ was also provided in supplement information (Fig. S2A).



Fig 1. The TEM images of NPC (A), Pd@NPC (B and C), and Pd particle-size distribution in the Pd@NPC (D).

The elemental composition of the catalyst was determined by X-ray photoelectron spectroscopy (XPS). The XPS spectra of Pd@NPC clearly exhibited three chief peaks corresponding to C (C1s), N (N1s) and Pd (3d) elements (Fig. 4A). The results displayed the peak of C1s loated at 284.6 eV and no other peak appeared, suggesting there is no other carbon containing groups except C-C or C=C bonds in the catalyst (Fig. 4B). Beside, the carbon content was about 73.5%, the results well proved the high degree of the carbonized glucose ¹². The N 1s spectra of Pd@NPC can deconvolut into two peaks centred at 398.3 eV and 400.6 eV, which corresponding to pyridinic nitrogen and amine/amide groups, respectively ²⁴ (Fig. 4C). The two peaks of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ were observed for the Pd@NPC. The peaks at 335.9 eV, 341.2 eV are related to Pd⁰ and the peaks at 337.3 eV, 342.7 eV can be attributed to Pd²⁺ ²⁵ (Fig. 4D). The palladium in the catalyst primarily existed as Pd^{0} . The XPS image showed that a small quantity of Pd^{2+} existed because Pd supported on the suface of NPC can be oxidized in an oxygen-containing environment.



Fig. 2. The XRD patterns of NPC, Pd@NPC and the used Pd@NPC.



Fig. 3. N_2 adsorption-desorption isotherms of NPC, Pd@NPC and the used Pd@NPC.

3.2 Catalytic performance of the catalysts

To illustrate the practical application of the Pd@NPC catalyst, the catalytic hydrogenation of *trans*-stilbene was

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selected as model substrate to optimize the reaction conditions. Almost no conversion of *trans*-stilbene can be observed without catalyst, Pd nanoparticles or hydrogen source (Table 1, entries 1-3). The results testified that the Pd nanoparticles are requisite for the catalytic hydrogenation of alkene. To our delight, Pd@NPC exhibited excellent catalytic activity and selectivity for the transfer hydrogenation of *trans*-stilbene with FA and AF as hydrogen source at 50°C, achieving high conversion of 99% after 3 h (Table 1, entry 4) and 1,2-diphenylethane was the only one product in the reaction. Compared with Pd@NPC, the Pd@g-C₃N₄-Glu and commercial Pd@C catalyst exhibited much lower catalytic activity (Table 1, entries 5, 6). The results indicated that the morphology and composition of the catalysts support play a key role for the catalytic activity of the catalysts.

The effect of hydrogen donor was also investigated. The conversion of *trans*-stilbene with FA or AF as hydrogen donor was 99% and 55% after 5 h reaction (Table 1, entries 7, 8), respectively. When FA:HCOOK and FA:HCOONa were used as the hydrogen donors (Table 1, entries 9, 10), relative long reaction time was required. Only 52% conversion was achieved after 6 h with FA and Et₃N as hydrogen donor (Table 1, entry 11)

We also investigated the impact of the dosage of Pd@NPC. In order to complete the reaction, 3, 10 and 20 h were required when the dosage of Pd was 1.5, 1.0 and 0.75 mol%, respectively (Table 1, entries 4, 12-13).

The stability and reusability of the catalyst are of great importance for their practical applications in industry. For the transfer hydrogenation of *trans*-stilbene, Pd@NPC catalyst delivered superior recyclability for at least 5 times competitive catalytic cycles without significant loss of its catalytic activity (Fig. 5). The recycled Pd@NPC catalyst was analyzed by the TEM (Fig. S3), XRD (Fig. 2) and BET (Fig. 3), indicating that the XRD pattern, and crystal structure of the used Pd@NPC have not obvious change compared with the fresh catalyst. Obvious Pd leaching during the reaction was also excluded here according to the ICP result (data not shown), with the concentration of leached Pd species in the reaction solution below the detection limit of the equipment.

To demonstrate the catalytic transfer hydrogen reaction of alkenes using Pd@NPC as catalyst is a heterogeneous process, the hot leaching experiment was carried out by separating Pd@NPC catalyst after 1 h reaction (Fig. S4). No further conversion of *trans*-stilbene in the remaining liquid solution was observed even after 5 h of reaction under identical conditions, which demonstrated that the filtrate did not contain a catalytically correlative Pd species.

To prove the universal applicability of the Pd@NPC catalyst, the hydrogenation reactions of various substrates were carried out at optimal conditions. All the results are shown in Table 2. The Pd@NPC catalyst delivered high catalytic performance for the hydrogenation of differently substituted alkenes and the

desired products were afforded in quantitative yields. The unsaturated C=C bond of cyclic alkenes, such as cyclohexene, cyclooctene and norbornylene, can be completely conversed to saturated bonds after 0.5, 3 and 1.0 h reaction, respectively (Table 2, entries 1-3). For the



Fig. 4. The XPS spectra of Pd@NPC (A), high-resolution C 1s (B), N 1s (C) and Pd 3d (D) in Pd@NPC.



Fig. 5 Durability test for the transfer hydrogenation of alkenes over Pd@NPC catalyst.

electron-rich group substituted styrene, 4-methylstyrene was reduced to 4-methyl ethylbenzene within 1.5 h in an efficient way with absolute selectivity (>99%) (Table 2, entries 4, 5). Successful hydrogenation of *di*-substituted alkenes was conducted and achieved the TOF of 44 h⁻¹ (Table 2, entry 6). When 4-nitrostyrene was employed as a substrate, only the complete hydrogenation product, 4-ethylaniline, were obtained (Table 2, entry 7), which demonstrated that Pd@NPC can efficiently reduce the both functionalities. For the *p*-chlorostyrene, we can observe the dehalogenation process during the hydrogenation, which gave 99% conversion and 67% selectivity (Table 2, entry 8). Strangely, for the fluo-substituted styrene, only a slight dehalogenation process was observed, the conversion and selectivity were 99% and 89%, respectively (Table 2, entry 9). The reduction

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of stilbene (Table 2, entries 10, 11) was proceeded smoothly affording high yields of the desired products within 3 h. The chemoselectivity of the catalyst was evaluated for the hydrogenation of the substrates with reducible substituents, such as ester group and conjugated carbonyl group. The hydrogenation of ethyl cinnamate was successfully achieved with total chemoselectivity towards the hydrogenation of the double bond (Table 2, entry 12). Chalcones (α,β -unsaturated ketone) are a kind of challenging substrates for the reduction reaction. To our delight, the chemoselective hydrogenation of the chalcones to the corresponding saturated ketones were achieved with 99% selectivity (Table 2, entries 13-15). However, the transfer hydrogenation of chalcones catalyzed by the reported catalyst, Pd/KCC-1-NH₂, yielded a mixture of the products of partial and complete hydrogenation in low to moderate yields at 100 °C ²⁶. We further explored the transfer hydrogenation of 2-methylfuran and 2-furanemethanol (Table 2, entries 16, 17), which is the critical step for increasing the hydrogen/carbon ratios and thus transforming the biomass to

biofuel. The corresponding products, renewable 2methyltetrahydrofuran and 2-tetrahydrofurfuryl alcohol, were obtained in high yields. The results demonstrated that the method provided an effective way for the preparation of biomass regenerated fuel.

The Pd@NPC catalyst was compared with other reported catalysts for the CTH of alkenes in terms of turnover frequency (TOF), reaction time and temperature (Table S1). The maximum TOF value of the present catalytic system was estimated to be 132 mol mol⁻¹ Pd h⁻ ¹, surpassing most of the reported heterogeneous catalysts with FA, N_2H_4 · H_2O , or *i*-PrOH as hydrogen donor. The TOF of the reported Pd-g-C₃N₄ NS/rGO₂₀ catalyst is 9-266 mol mol⁻¹ Pd h⁻¹ for the hydrogenation of alkenes ²⁷, which is superior to the Pd@NPC catalyst. For the Pd/CN ⁹ and Pd@POP ²⁸ catalysts, the TOF is 4-53 and 4-57 h⁻¹, respectively. The results indicated that Pd@NPC was an efficient and selective catalyst for the hydrogenation of alkenes.

Table 1 Catalytic performance of the catalysts ^[a]

$\bigcirc & \frown & \bigcirc & \frown & \frown & \frown & \frown & \bigcirc & \frown & \bigcirc & \frown & \bigcirc & \bigcirc$								
Entry	Catalysts	Dosage (mol% Pd)	FA (mmol)	Formate (mmol)	Time (h)	Con. (%)	Sel. (%)	
1	-	-	2.5	2.5	12	-	-	
2	NPC	1.5	2.5	2.5	12	-	-	
3	Pd@NPC	1.5	0	0	12	-	-	
4	Pd@NPC	1.5	2.5	2.5	3	>99	>99	
5	Pd@C	1.5	2.5	2.5	5	82	>99	
6	Pd@g-C ₃ N ₄ -Glu	1.5	2.5	2.5	12	95	>99	
7	Pd@NPC	1.5	2.5	0	5	>99	>99	
8	Pd@NPC	1.5	0	2.5	5	55	>99	
9	Pd@NPC	1.5	2.5	2.5 ^[b]	8	>99	>99	
10	Pd@NPC	1.5	2.5	2.5 ^[c]	10	>99	>99	
11	Pd@NPC	1.5	2.5	2.5 ^[d]	6	52	>99	
12	Pd@NPC	1.0	2.5	2.5	10	>99	>99	
13	Pd@NPC	0.75	2.5	2.5	20	>99	>99	

[a] Reaction conditions: 0.25 mmol trans-stilbene, 5 mL EtOH, 50°C, GC analysis using n-decane as an internal standard. [b] HCOOK, [c] HCOONa. [d] Et₃N.

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Entry	Substrates	Products	Time (h)	Con. (%)	Sel. (%)	TOF (h^{-1})
1	\bigcirc	\bigcirc	0.5	99	99	132
2	\bigcirc	\bigcirc	3.0	99	99	22
3		A	1.0	99	99	66
4			1.0	98	99	66
5			1.5	99	99	44
6			1.5	99	99	44
7	0 ₂ N-	0 ₂ N-	5.0	99	99	13.2
8	ci_		6.0	99	67	7.5
9	F	F	6.0	99	89	9.9
10			3.0	99	99	22
11			2.0	99	99	33
12			6.0	90	99	10
13			6.5	99	99	10
14	Hoto	H ₆ CO	9.0	93	99	6.8
15	° N	HaN	9.5	85	99	6
16		$\langle \rangle$	2.5	99	99	26.4
17	ОН	<o⊢ OH</o⊢ 	4.5	99	99	14.7

	Fable 2	Catalytic	hydrogenation	of different	alkenes ^[a]
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[a] substrate: 0.25 mmol, catalyst: 10 mg Pd@NPC (1.5 mol %), 5 mL EtOH, 2.5 mmol HCOOH, 2.5 mmol NH₄COOH, 50°C. GC analysis using *n*-decane as an internal standard.

4. Conclusions

In summary, nitrogen-doped porous carbon nanosheets was fabricated with $g-C_3N_4$ as nitrogen source and a self-sacrificial template. Well dispersed palladium nanoparticles were supported on the NPC. The Pd@NPC exhibited high

catalytic activity and stability for the hydrogenation of alkenes with HCOOH and NH_4COOH as the hydrogen donors at mild conditions. The high catalytic activity can be ascribed to the synergistic effect between the well dispersed Pd nanoparticles and the unique nitrogen-doped carbon nanosheets structure of the NPC support, as well as the high specific surface area of the catalyst. We believe that this work

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can boost the exploring of novel two dimentional nanosheet materials via a self-sacrificial template method and highlight their broader applications in heterogeneous catalysis.

Conflicts of interest

There are no conflicts to declare.

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Nitrogen-riched porous carbon supported Pd-nanoparticles as an efficient catalyst for the transfer hydrogenation of alkenes

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Well-dispersed Pd nanoparticles supported on nitrogen-riched porous carbon was prepared and the material displayed excellent catalytic activity for the transfer hydrogenation of alkenes. The Pd@NPC exhibited high catalytic activity and stability for the hydrogenation of alkenes with HCOOH and NH₄COOH as the hydrogen donors at mild conditions.

