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ARTICLE

Mesoporous Nitrogen-Doped Carbons with High Nitrogen Content and Ultrahigh Surface Areas: Synthesis and Applications in Catalysis

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Zhishuang Ma, Hongye Zhang, Zhenzhen Yang, Guipeng Ji, Bo Yu, Xinwei Liu, Zhimin Liu*

Development of mesoporous nitrogen-doped carbons (NDCs) with high nitrogen content and high surface areas from biomass is of significance for many applications, such as oxidation reaction catalysts, electrode materials and so on. Herein we report a simple route to prepare mesoporous NDCs via calcinating the mixture of biomass feedstocks (including glucose, cellulose and lignin) and melamine using eutectic salts of KCl and $ZnCl_2$ as the porogen, and a series of mesoporous NDCs with nitrogen content up to 11.9% and BET specific surface area up to 1800 $m^2 \cdot g^{-1}$ were obtained. Served as metal-free catalyst for oxidation of hydrocarbons with *tert*-butyl hydroperoxide in aqueous phase, the mesoporous NDC with N content of 11.4% showed the highest efficiency compared to the reported N-doped carbons. Moreover, the as-prepared NDCs were indicated to be ideal support to immobilize noble nanoparticles (e.g., Pd, Rh, Ru, Pt) producing a series of NDC supported metal nanocatalysts with metal particle size around 2 nm. This work opens up a new way to prepare mesoporous N-doped carbon materials with tailored properties.

Introduction

Nitrogen-doped carbons (NDCs), especially with mesoporous structures, have received rapidly growing interest in recent years owing to their remarkable performances in various applications, such as super-capacitors[1], oxygen reduction catalyst[2], catalyst supports[3] and gas capture/storage[4], etc. The doped-nitrogen can be regarded as an n-type carbon dopant, and its lone pair of electrons can interact with the carbon π system, which causes structural irregularity of the hexagonal carbon ring and greatly alters the physical and chemical properties of the carbon materials, such as the basicity[5], catalytic activity[6-8], oxidative stability[9], and so on. The bulk properties of these kind materials mainly depend on the content as well as mode of the doped-nitrogen and the structure of the material (e.g., specific surface areas)[9-11]. Generally, two major types of the doped-nitrogen configurations can be distinguished: chemical nitrogen and structural nitrogen[8, 12]. The former appears as surface functionalities (e.g., amine or nitrosyl group), while the latter as the nitrogen directly bonded into the backbone of the carbon material (for example, pyridinic, pyrollic or quaternary-type nitrogen). As reported, NDCs with high nitrogen content, especially with high quaternary-type nitrogen content, show excellent electrocatalytic activity toward the oxygen reduction reaction (ORR)[11, 13-15]. However, it is still challenging to prepare this kind of NDCs.

NDCs can be realized either by direct synthesis using nitrogen-containing precursors such as melamine[16-18], N-heterocycles[19-21], benzylamine[22], or ionic liquids (ILs)[3, 9, 10, 12, 23, 24], or by post-treatment of carbons in the atmospheres of N-containing compounds (e.g., NH_3) at high temperatures[25-29]. As for NDCs with high contents of structural nitrogen, their preparation is usually achieved by using nitrogen-containing precursors resulting in a homogeneous incorporation of nitrogen together with controlled bulk properties. Typical examples include the use of N-containing ILs as excellent precursors to produce functional NDCs with controlled pore architectures[9, 30-33]. For example, Antonietti and coworkers[34] prepared NDCs with specific surface areas up to 1500 m^2 g^{-1} and N content around 12% via carbonization of nucleobases dissolved in an IL (i.e., 1-ethyl-3-methylimidazolium dicyanamide) using silica nanoparticles as the hard template, which showed very high catalytic activity in the oxygen reduction for fuel cells. Wang et al synthesized a kind of NDCs with N content of 12 wt% by using a nitrogen-containing IL (i.e., 3-methyl-1-butylpyridine dicyanamide) as the precursor and silica nanoparticles as hard template, which could stabilize Pd nanoparticles, and the supported Pd catalyst showed very high catalytic activity in hydrodeoxygenation of vanillin[4].

From the standpoint of green and sustainable chemistry[18, 35, 36], exploring simple strategy using inexpensive, abundant and renewable resources to produce NDC materials with a large specific surface area and high nitrogen content is highly desirable. In a recent work, Wang et al prepared NDCs using

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Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
E-mail: liuzm@iccas.ac.cn

Electronic Supplementary Information (ESI) available: Details of experimental procedures, carbon materials characterizations and reaction conditions optimization. See DOI: 10.1039/x0xx00000x glucose as the carbon source and a (poly(ionic liquid) as the N dopant; however, the N content (~5%) and specific surface areas (~400 m^2 g^{-1}) of the resultant NDC were relatively low[10]. Melamine as a nitrogen-enriched, inexpensive and commercially available raw material is a good nitrogen-source for the synthesis of the N-doped carbons[16, 17], though it is not a green chemical. Shu and coworkers prepared nitrogen-doped mesoporous graphitic carbon with specific surface area ~200 m^2 g^{-1} using melamine as a nitrogen source and citric acid as a carbon source without any template[17]. Cellulose, lignin and their derivatives (e.g., glucose easily obtained from cellulose hydrolysis) are abundant and economical feedstocks and have been widely applied in the preparation of carbon materials. Moreover, due to the presence of plentiful oxygen in the these biomass resources, the resultant carbons are generally rich in oxygen-containing groups, which provides the resultant carbons with specific functions[37, 38].

In this article, we report a simple route to prepare NDCs with mesoporous structures based on a “Salt Templating” synthesis procedure[38] using biomass (including glucose, cellulose, lignin) and melamine as the carbon and nitrogen sources, respectively, and the KCl/$ZnCl_2$ mixture with the molar ratio of KCl: $ZnCl_2$ at 51: 49 (denoted as PZ, melting point at 230 ℃)[24] as the porogen and solvent. The resultant NDCs were characterized by means of different techniques such as XPS, SEM, TEM, FT-IR, nitrogen sorption, and so on. It was demonstrated that the as-prepared NDCs possessed high nitrogen contents up to 11.9% with quaternary-N species of 31%, and possessed mesoporous structures with specific surface area (SSA) up to 1731 m^2 g^{-1}, which was the largest one among the reported values to the best of our knowledge. The pore volume reached 1.83 cm^3 g^{-1}, dominated with mesopore volume proportion of 77.4%. The as-prepared NDC with N content of 11.4% as a metal-free catalyst showed high efficiency for the oxidation of alkanes in aqueous phase with *tert*-butyl hydroperoxide (TBHP) as the oxidant. Moreover, as supports NDCs could immobilize noble metal nanoparticles (e.g., Pd, Pt, Ru and Rh), resulting in a series of supported metal nanocatalysts.

Results and discussion

The fabrication of NDCs was based on “Salt Templating” synthesis together with gradient heating carbonization program[38]. Typically, carbon source (e.g., glucose), melamine and PZ with a certain ratio were directly mixed via grinding at room temperature, and the mixture was subsequently heated with a gradient temperature program under nitrogen atmosphere. The mixture was first heated at 240 °C for 4 h to make carbon source and melamine dissolve in PZ uniformly, and form cross-linked compounds via the reactions between glucose and melamine catalysed by PZ. Then the temperature was increased to 800 °C with a rate of 1 °C/min, and kept at 800 °C for 6 h, aiming at getting carbon materials with mesoporous pores. The NDCs with various nitrogen contents were prepared through varying mass ratios of melamine to carbon source (e.g., glucose). As reference a carbon sample without N was prepared in the absence of melamine, denoted as G-800. The as-prepared NDC samples were termed as M-G (or C and L)-c-T in this work, where M stands for nitrogen resource melamine, G for glucose (C for cellulose and L for lignin), and c corresponds to the mass ratio of melamine to carbon source and T to the final calcination temperature.

The nitrogen content of the resulting NDCs was examined by elemental analysis, and the results are listed in Table S1. As expected, the nitrogen content of NDCs strongly depended on the ratios of melamine to carbon source in the starting materials, and increased from 1.1 wt% for G-800 to 11.9 wt% for M-G-3-800. The presence of N in G-800 may be originated from the N_2 atmosphere during the calcination process. With the melamine/glucose ratio at 1.5, the nitrogen content in the resultant NDC reached up to 11.4 wt%, comparable to the highest value reported in literature using N-containing IL as the carbon and nitrogen precursors. Further increasing the melamine amount in the starting mixture did not afford NDCs with more nitrogen contents, suggesting that the nitrogen content in the nitrogen-doped carbons cannot increase indefinitely. The solid yield of the resultant samples increased with the mass ratios of melamine to glucose increase, reaching the highest value of 27.4% at the melamine/glucose ratio of 1.5, consistent with the change tendency of nitrogen content. Further increasing the melamine/glucose ratio resulted in decrease in the sample yields. Thus, taking both of the nitrogen content and the carbon yield into account, the appropriate ratio of melamine to glucose was set at 1.5. In addition, using cellulose or lignin instead of glucose as the carbon source, samples M-C-1.5-800 and M-L-1.5-800 were prepared, respectively, both of which possessed high nitrogen contents around 9.0 wt%, as illustrated in Table S1. This suggests that the method to prepare NDCs in this work is suitable for various carbon sources with melamine as the starting materials.

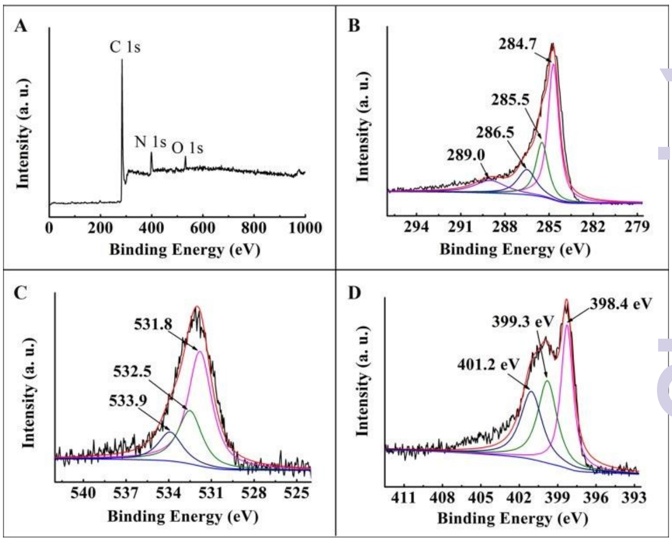


Figure 1 (A) XPS survey spectrum, (B) C1s XPS spectrum, (C) O1s XPS spectrum and (D) N1s XPS spectrum of the sample M-G-1.5-800.

The types of the structural nitrogen species in the resultant NDCs were analysed by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of sample M-G-1.5-800

(Figure 1A) showed the presence of the principal C1s, O1s, and N1s core levels. In the C1s spectrum (Figure 1B), the wide peak ranging from 282 to 290 eV can be resolved into four individual component peaks at 284.7, 285.5, 286.5 and 289.0 eV, respectively, corresponding to C-C, C-OH, C=O and C-C=O bonds. Meanwhile, the XPS spectrum of O1s (Figure 1C) (C-OH at 533.9 eV, C=O at 532.5 eV, and C(O)OH at 531.8 eV) also confirmed the existence of oxygen-containing groups. The presence of oxygen-containing groups in the resultant NDCs may afford them different properties compared to the traditional carbon materials (e.g., amphiphilicity). In the N1s XPS spectrum (Figure 1D) three peaks could be deconvoluted with binding energies (BEs) at 398.4, 399.3, 401.2 eV, assigning to pyridinic, pyrrolic and quaternary nitrogen, respectively. Based on the integration areas of the different N species in the XPS spectrum, the contents of nitrogen species in different form could be estimated, following the order for sample M-G-1.5-800: pyridinic nitrogen (36.3%), pyrrolic nitrogen (33.3%) and quaternary nitrogen (30.4%). As listed in Table S1, the quaternary nitrogen contents in the resultant NDCs increased with the ratios of melamine to glucose, and reached a maximum as the ratio increased to 1.5. However, further increasing the melamine/glucose ratio to 3, the quaternary N in M-G-3-800 decreased to 25.2%. It was reported that the quaternary N was the most active specie for catalysing selective oxidation of alkanes and alcohols[39]. The high content of quaternary N in the resultant NDCs may result in high performance if the samples serve as the catalyst for the oxidation of alkanes. In this work, the ratio of melamine to glucose set at 1.5 was appreciate for getting high quaternary nitrogen content in NDCs.

The morphology and structure of the samples were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and Figure 2A and 2B show the typical SEM and TEM images of M-G-1.5-800. The SEM image (Figure 2A) revealed that M-G-1.5-800 appeared to be composed of uniform rough carbon nanoparticles, which aggregated to give a porous structure. The TEM image (Figure 2B) showed that M-G-1.5-800 had an obvious interconnected mesoporous network with well-dispersed spherules. The EDS profile (Figure 2B inset) obtained during the TEM observation indicated the existence of N element together with trace amount of $ZnCl_2$, consistent with the elemental analysis results, and also suggesting that most of the porogen salts could be removed by washing. In addition, the XRD pattern (Figure 2C) of M-G-1.5-800 had two diffraction peaks at $2\theta \approx 23°$ and 44° with large width and low intensity, which may be ascribed to the graphitic carbon, albeit with disorder. The above analyses indicate that nitrogen-doped material with mesoporous structures was successfully synthesized.

N_2 sorption analysis was performed to determine the pore textural properties of the as-prepared NDCs. Typically, M-G-1.5-800 exhibited type IV sorption isotherm (Figure 2D), typical feature of mesoporous materials, whose pore diameter was centred at 3.8 nm according to the DFT model (Figure 2D, inset). Based on the sorption isotherms, the BET specific surface area (SSA), pore volume and size distribution of the resultant NDC samples were obtained, and summarized in Table 1. To our delight, all the samples prepared in this work showed high SSAs in the range from 1273 to 1834 $m^2\ g^{-1}$, with large mesopore volumes from 1.00 to 3.00 $cm^3\ g^{-1}$. For example, M-G-1.5-800 showed a BET SSA of 1731 $m^2\ g^{-1}$ and a pore volume of 1.83 $cm^3\ g^{-1}$ dominated with mesopore volume proportion of 77.4%. These values rank the as-prepared NDCs among the nitrogen-doped porous carbons with the high SSA together with high pore volumes.

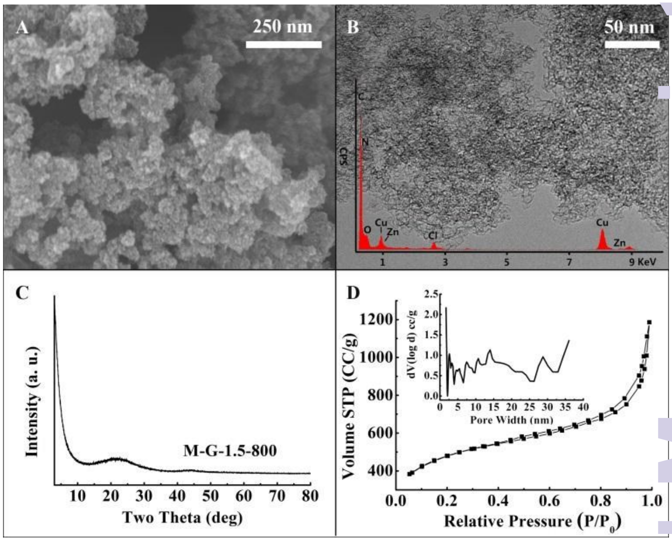


Figure 2 (A) SEM image, (B) TEM image and EDS profile (inset), (C) XRD pattern and (D) N_2 sorption isotherm and DFT pore size distribution of the M-G-1.5-800 sample (inset).

Table 1 Pore textural properties of the mesoporous nitrogen-doped carbon materials. [a]

Sample name	S_{total} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)			V_{meso}/V_{total} (%)
		V_{total}	V_{micro}	V_{meso}	
G-800	1424	1.64	0.19	1.45	88.3
M-G-0.33-800	1273	1.65	0.25	1.40	85.1
M-G-0.67-800	1671	1.44	0.44	1.00	69.3
M-G-1-800	1834	1.45	0.45	1.00	69.0
M-G-1.5-800	1731	1.83	0.41	1.42	77.4
M-G-3-800	1500	3.08	0.08	3.00	97.5
M-C-1.5-800	1787	1.47	0.45	1.02	69.2
M-L-1.5-800	1578	1.41	0.34	1.08	76.2

[a] S_{total}: total BET specific surface area; V_{total}: total pore volume; V_{micro}: micropore volume; V_{meso}/V_{total}: mesopore volume proportion.

In order to investigate the NDCs formation process, the samples prepared with the melamine/glucose ratio of 1.5 at different calcination temperatures were examined by XPS and FT-IR. The XPS results (Table S2) showed that only the sample obtained at 800 °C, i.e., M-G-1.5-800, had quaternary nitrogen specie, suggesting that high temperature (e.g., 800 °C) was required for the formation of quaternary N species. This implies that the carbon and nitrogen atoms of the NDCs probably underwent an arrangement or condensation reaction in the temperature range of 600-800 °C to make the pyrrolic N o pyridinic N convert to more stable quaternary N. This phenomenon was also reported by M. Watanabe[11].

The FT-IR spectrums are shown in Figure 3. Compared to that of melamine, the spectrum of each resultant sample shows declined or disappeared corresponding peaks accompanied with appearance of new bands around 1623 and 1337 cm^{-1}, assigning to C=C and C=N vibration, respectively. This indicates that in PZ molten solution the reactions occurred to form C=C and C=N containing materials. Notably, with increase in carbonization temperature the peak intensity of the band at 1337 cm^{-1} of the resultant samples increased and shifted to low wavenumbers, indicating that more C=N bonds formed in the resultant samples, originated from the reaction of glucose and melamine catalysed by PZ. In the spectrum of M-G-1.5-800, there was an obvious wavenumber shift around 1337 cm^{-1}, suggesting that from 600 to 800 °C the sample may undergo a rearrangement reaction and form quaternary N, consistent with the results of XPS analysis (Table S2). In addition, the bands in the range of 3470-3135 cm^{-1} and at 1652 cm^{-1} were assigned to the stretching vibration and bending vibration of the primary amine N-H bond of melamine, whose intensity became weaker in the spectra of the samples obtained with the increased carbonization temperature. This also suggests that the -NH$_2$ groups from melamine may react with glucose and weaken the hydrogen bond interaction.

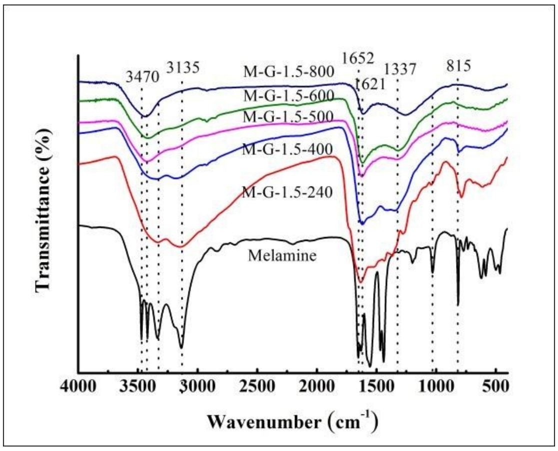


Figure 3 FT-IR spectrums of the resultant NDCs.

As reported, the N-doped carbons could catalyse the oxidation of alkanes using *tert*-butyl hydroperoxide (TBHP) as the oxidant. In this work, M-G-1.5-800 with a nitrogen content of 11.4% was used to catalyse the oxidation of aryl alkanes with TBHP in aqueous phase, and the oxidation of ethylbenzene was first investigated as a model reaction. The optimization of reaction conditions are shown in Figure S1. It was indicated that M-G-1.5-800 was very active for catalysing the ethylbenzene oxidation, and acetophenone was obtained as the main product accompanied with a trace amount of 1-phenylethanol. Figure 4 shows the dependences of the ethylbenzene conversion and product yields on the reaction time. It is demonstrated that under the experimental conditions ethylbenzene could convert to acetophenone rapidly with a conversion of 93.8% and acetophenone yield of 91.2% within 6 h. This result is comparable to those obtained over metal or organometallic complex catalysts[40, 41], and much better than those obtained over nitrogen-doped graphene materials[39] (Table 2, entry 3). The good performance of M-G-1.5-800 may be originated from its unique features with mesoporous structure, high quaternary nitrogen content, and high BET SSA. Further prolonging reaction time resulted in the complete conversion of ethylbenzene, however, with slight decline in the product yield, which may be caused by the further conversion of the product under the experimental conditions. It was reported that the quaternary-type nitrogen was the most active specie for catalyzing selective oxidation of alkanes and alcohols[14, 15, 39]. To verify this, M-G-3-800 with similar nitrogen content and less quaternary-N percentage than M-G-1.5-800 was examined, and it was demonstrated that M-G-1.5-800 was more active than M-G-3-800 (Table 2, entries 1 and 4), consistent with the reported results. In addition, the catalyst M-G-1.5-800 showed good reusability, confirmed by the fact that 88.4% yield of acetophenone was obtained after the catalyst was reused five times (Table 2, entry 5).

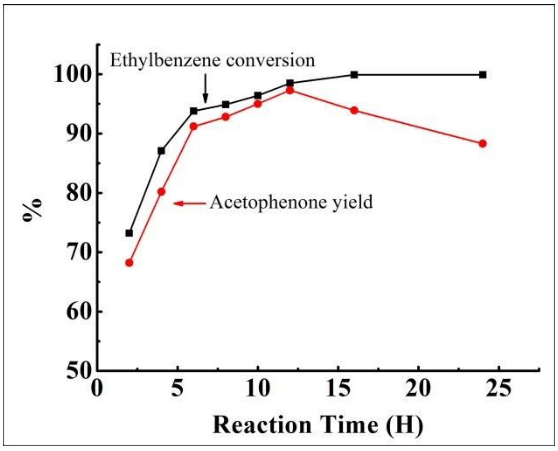
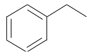
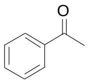
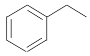
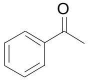
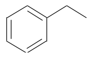
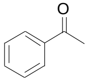
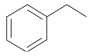
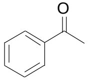
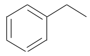
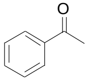
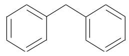
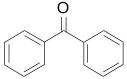
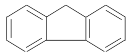
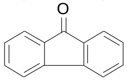
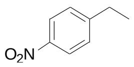
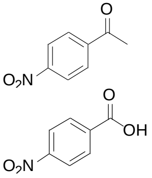
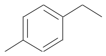
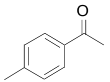
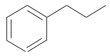
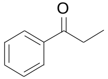
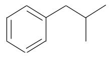
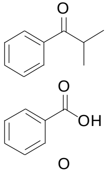
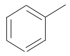
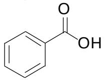
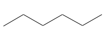
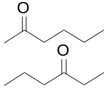
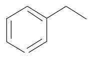
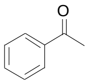
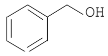
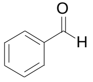


Figure 4 Reaction time optimization. Reaction conditions: substrate (1.0 mmol), solvent (H$_2$O, 3 mL), 80 °C, 3.48 mmol TBHP and 12 mg catalyst.

Based on the above results, the oxidations of other aryl alkanes with TBHP over M-G-1.5-800 were investigated under the optimized conditions, and the results are listed in Table 2. It was indicated that all the tested aryl alkanes could be oxidized to the corresponding aromatic ketones or aldehydes in high yields. Notably, even hexane could be oxidized effectively, affording a product yield of 26.3% (Table 2, entry 13), demonstrating that our NDCs catalysts were not only active for benzylic substrates but also potentially active for the linear hydrocarbons. Furthermore, this catalytic system could also realize high conversion (85%) of ethylbenzene to acetophenone (yield of 82.7%) by using O$_2$ as the oxidant with a small amount of TBHP as the initiator (Table 2, entry 14), which was superior to the reported nitrogen-doped graphene material[39]. More interestingly, benzyl alcohol could be oxidized without TBHP as the initiator under 0.1 MPa oxygen pressure, affording a benzyl alcohol conversion of 12.3% and acetophenone yield of 9.8% (Table 2, entry 15) under the experimental conditions. The above results indicate that the as-

Table 2: Oxidation of arylalkanes with M-G-1.5-800 in the aqueous phase.[a]

Entry	Substrate	Product[b]	Conv./%	Yield/%
1			93.8	91.2
2[c]			98.5	97.3
3[d]			98.6	91.3
4[e]			93.1	87.2
5[f]			90.0	88.4
6			97.6	>99
7			>99	>99
8		 5.1: 1	98.7	101.3
9			89.5	60.0
10			85.4	82.6
11			73.9	51.8
12			51.4	48.7
13		 1.3: 1	-	26.3
14[g]			85.5	82.7
15[h]			12.3	9.8

[a] Reaction conditions: substrate (1.0 mmol), TBHP (3.48 mmol, 70 wt % in water), catalyst (12 mg), H_2O (3 mL), 80 °C, 6 h; the conversion and yield were determined by GC; [b] Values listed with product mixtures refer to molar ratios; [c] 12 h; [d] The result from ref. 39 with reaction time 24 h under the same other conditions to a; [e] The catalyst was M-G-3-800; [f] After the catalyst was reused five times with reaction time 6 h; [g] Reaction conditions: TBHP (3.48 mmol, 70 wt % in water) as initiator, ethylbenzene (10.0 mmol), catalyst (10 mg), H_2O (10 mL), O_2 (4.0 MPa), 100 °C, 48 h; [h] Reaction conditions: benzylalcohol (1.0 mmol), catalyst (0.10 g), C_2H_5OH (5 mL), O_2 (0.1 MPa), 120 °C, 5 h.

prepared NDCs were good catalyst for oxidation reactions, which can realize the oxidations of various alkanes or alcohol under the metal-free conditions.

Mesoporous nitrogen-doped carbons are good catalyst supports. In this work, M-G-1.5-800 as a representative was used to immobilize various metal nanoparticles including Pd, Pt, Rh, Ru via the equal volume impregnation method followed by hydrogen reduction[42], and a series of M-G-1.5-800 supported metal nanocatalysts were prepared, see Figure S2. Figure 5A shows a TEM image of M-G-1.5-800 supported Pd nanocatalyst (denoted as Pd/M-G-1.5-800). In the TEM image, the dark dots were identified as Pd nanoparticles, which were uniformly distributed on the support with average particle size around 1.4 nm. XPS analysis (Figure 5B) indicated that the Pd species in the composite were present in the form of metallic Pd^0 and Pd^{2+}. In addition, the other noble metal (e.g., Rh, Pt, Ru)/M-G-1.5-800 composites with various metal loadings showed the similar morphology to Pd/M-G-1.5-800, uniformly decorated with metal nanoparticles of size around 1.5 nm with narrow size distribution (Figure S2). These noble metal nanocatalysts are expected to have promising applications in catalysis, and the study on their catalytic performances is under way in our laboratory.

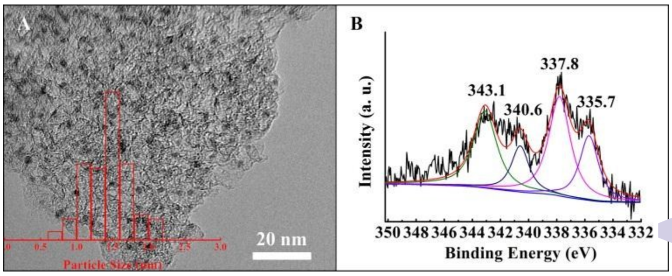


Figure 5 (A) TEM image (Scale bar, 20 nm) and the Pd particle size distribution (inset), (B) Pd 3d XPS spectrums of the 5% Pd/M-G-1.5-800 composite.

Conclusions

In summary, mesoporous nitrogen-doped carbons with nitrogen content up to 11.9% and BET specific surface area up to 1800 $m^2\ g^{-1}$ were prepared with biomass feedstocks (including glucose, cellulose and lignin) as the carbon precursor and melamine as the nitrogen resource. The as-prepared NDCs not only can serve as highly efficient catalyst for the oxidation of hydrocarbons in aqueous phase under mild conditions (e.g., 80 °C), but also can be used as ideal supports to immobilize metal nanoparticles. This study opens up a new route for the development of mesoporous heteroatom-doped carbon materials with tailored properties.

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Graphic Abstract

Mesoporous nitrogen-doped carbons with high nitrogen content and ultrahigh surface areas were prepared using biomass and melamine as the carbon and nitrogen sources, respectively, together with the eutectic salts KCl/$ZnCl_2$ (PZ) as the porogen agent and solvent through gradient heating program. As a metal-free catalyst, the as-prepared mesoporous NDCs showed the highest efficiency for the oxidation of alkanes in aqueous phase with *tert*-butyl hydroperoxide (TBHP) as the oxidant under mild conditions (80 ^{o}C). Moreover, the as-prepared NDCs were indicated to be ideal support to immobilize noble nanoparticles (e.g., Pd, Rh, Ru, Pt); producing a series of NDCs supported metal nanocatalysts with metal particle size around 2 nm.