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Synthesis of Nitrogen and Sulfur Co-doped Hierarchical Porous Carbons and Metal-free Oxidative Coupling of Silanes with Alcohols

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Hierarchically porous N and S co-doped carbon was prepared using 2,5-dihydroxy-1,4-benzoquinone as the carbon source, thiourea as N and S source, and SiO_2 particles as the template. Using the material as the catalyst, oxidative coupling of silanes with alcohols was conducted for the first time at metal-free condition.

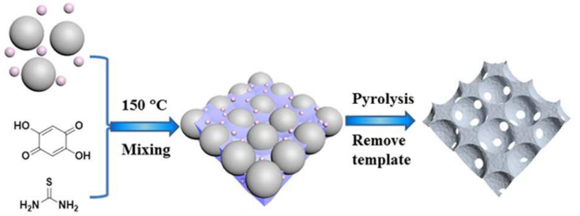
Carbon materials are promising substitutes for metal materials in some important applications due to their earth-abundant feedstocks, high specific surface area, corrosion resistance and readily tuneable properties through surface modification or heteroatom doping.[1] Heteroatom doping modifies geometric and electronic structures of carbon materials, and introduces catalytic active sites.[1a] In recent years, heteroatom doped carbon materials have attracted much attention, and many functional carbon materials, such as N-doped,[2] S-doped,[3] and P-doped carbon materials,[4] have been reported.

Multiple doping is a versatile approach for developing functional carbon materials and regulating properties of carbon by synergistic effect of dopants. Carbon materials co-doped with two or more kinds of heteroatoms have also been reported as catalytic materials. For example, S, N co-doped carbon nanotubes prepared by using CdS as template has been reported in catalytic reduction of p-nitrophenol.[5] N and S co-doped nanoporous graphene showed high catalytic activities towards hydrogen evolution reaction, which was synthesized by nanoporous Ni-based chemical vapor deposition.[6] Meng et al. showed that N, O and S-tridoped polypyrrole-derived nano-porous carbons were active for alcohol oxidation reaction.[7]

Hierarchically porous catalysts usually show excellent performance for different reactions because they integrate the advantages of the pores of different sizes in diffusion and adsorption of the species in the reaction systems.[8] Synthesis and application of this class of catalytic materials have received much attention. In this work, we developed a route to prepare hierarchically porous N and S co-doped carbon (HPNSC) using 2,5-dihydroxy-1,4-benzoquinone as the carbon source and thiourea as the source of N and S dopants, and SiO_2 particles of different sizes were used as the templates for the mesopores and macropores. The as-prepared HPNSC was very efficient catalyst for the oxidative etherification of silanes with alcohols. To the best of our knowledge, this is the first metal-free catalytic system for this kind of reactions, although many metallic catalysts have been reported.[9]

The route to prepare the HPNSC is shown schematically in Scheme 1. In the experiments, the 2, 5-dihydroxy-1, 4-benzo-quinone (carbon source) and thiourea (N and S source) were mixed and heated to 150 °C to get the liquid solution. Then SiO_2 spheres of 180-220 nm (Figure S1a) and colloidal SiO_2 nanoparticles of about 10 nm (Figure S1b) were added into the solution and were dispersed uniformly in the solution after stirring. Then the mixture underwent pyrolysis at 900 °C and acid etching process to remove template to obtain the HPNSC. Similar procedure has been adopted for synthesis hierarch-ically porous N-doped carbon (HPNC) using 2,5-dihydroxy-1,4-benzoquinone and urea as precursors. For comparison, N and S co-doped porous carbon material was synthesized by using hard template (SBA-15), which is labelled as NSPC-SBA.

The morphology and structure for the as-synthesized HPNSC are investigated by FE-SEM and TEM. As shown in Fig. 1a-c, the



Scheme 1 Schematic demonstration of the route to prepare the HPNSC.

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HPNSHC possessed hierarchical structure composed of mesopores (10 nm) templated from colloidal SiO_2 nanoparticle and macropores (180-220 nm) derived from silica spheres, which were consistent with the size of the SiO_2 templates used. The N_2 adsorption-desorption isotherm of the HPNSC exhibited a type-IV curve with a hysteresis, indicating the existence of mesopores (Fig.1d). The mesopore size distribution obtained from N_2 adsorption-desorption isotherm centred at 7.8 nm as shown in Fig 1e, which was reasonably consistent with the mesopores observed (Fig 1b). The BET surface area (S_{BET}) and total pore volume (V_p) of the material were 866 m^2g^{-1} and 1.47 cm^3g^{-1}, respectively. NSPC-SBA display type-IV isotherms with an H1 hysteresis loop (Fig. S2a), characteristic of mesoporous materials (S_{BET}: 698 m^2g^{-1}; V_p: 0.41 cm^3g^{-1}). This result is verified by TEM image (Fig. S2b) that NSPC-SBA was an inverse replica of the SBA-15 template. The presence of heteroatoms in the HPNSC was verified by high angle annular dark-field scanning TEM (HADDF-STEM) image coupled with the corresponding energy-dispersive X-ray spectroscopy (EDX) elemental mapping images, which showed the homogeneous distribution of C, N, S, and O across the selected region (Fig 1f). This may favour the (electro) catalytic performance.[10]

The composition and chemical state of the N and S co-doped carbon were elucidated by X-ray photoelectron spectroscopy (XPS) analysis (Fig. S3). According to elemental analysis, the contents of N, S, C, H in HPNSC were 6.5%, 9.9%, 65.1%, and 1.2%, respectively. The N 1s spectra (Fig. 2a) are deconvoluted into four different types of N species: pyridinic-N (N-6, 397.9 eV), pyrrolic-N (N-5, 399.8 eV), graphitic-N (N-Q, 400.8 eV), and pyridine N-oxide (N-Ox, 402.7 eV).[11] The S 2p spectra (Fig. 2b) visualize the presence of two forms of S, carbon-bonded thiophene-like sulfur (C-S-C, 163.5/164.7 eV) and oxidized sulfur species (C-SO_X-C (x=2-4), 167.4/168.6 eV).[12] As shown in Fig. 2c, the C 1s spectra can be fitted into several peaks corresponding to C-C/C=C (284.5 eV), C-O/C-N (285.6 eV), C=O (287.7 eV) and O-C=O (289.4 eV) species.[13] Therefore, the XPS analysis further confirms that the heteroatoms are successfully incorporated into the carbon framework of HPNSC.

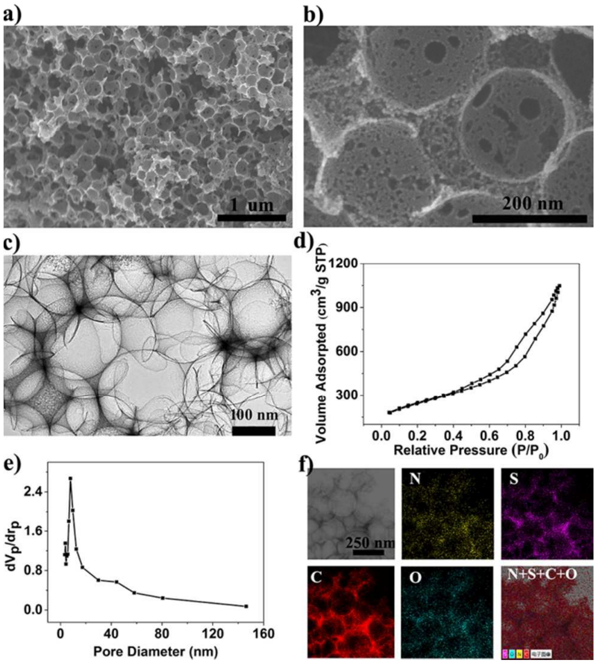

Fig. 1 a-b) SEM images and c) TEM image of the HPNSC; d) nitrogen adsorption/desorption isotherm and e) BJH pore size distribution curve; f) HADDF-STEM image and the corresponding EDX elemental mapping images of nitrogen (yellow), sulfur (purple), carbon (red), oxygen (blue) of the HPNSC.

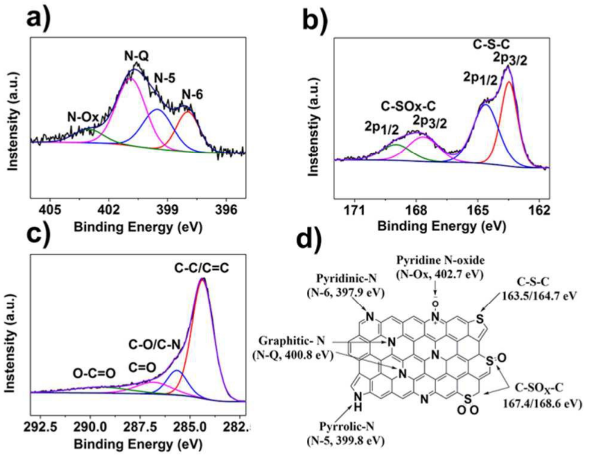

Fig. 2 High resolution XPS spectra of N 1s (a), S 2p (b) and C 1s (c) of the HPNSC material, and its schematic structure (d).

XRD and Raman analysis were carried out to study the carbon material. The material showed a broad peak in the range of 20-30° (Fig. S4), indicating that a carbon framework with partial graphitization was formed. Raman spectra of the HPNSC showed two typical vibration bonds of carbon materials (Fig. S5). The G bond centred at 1580 cm^{-1} is attributed to the in-plane bond stretch of sp^2-bonded carbon atoms in 2D hexagonal lattice. The D bond located at 1360 cm^{-1} is assigned to the vibration of carbon atoms of disordered graphite.[14] The relative intensity of D and G bond (I_D/I_G) is an indicator of the disorder degree in a graphite structure. The I_D/I_G ratio of HPNSC calculated was 3.7, indicating that nitrogen and sulfur co-doping led to high-density defects in the carbon framework.[15]

The selective oxidation of silanes to silanols or silyl ethers has been studied extensively using noble or transition metals catalysts.[9] In this work, we attempted to use the as-prepared HPNSC to replace the metal-based catalysts for the oxidative coupling of silanes with alcohols, and dimethylphenylsilane (1a) was used as a model substrate. The results at different conditions are given in Table 1. The conversion was very low without the catalyst (<1%, Table 1, entry 1). To our delight, the HPNSC could promote the reaction effectively. The selectivity to the desired silyl ether (1b) increased with temperature up to 120 °C, and reached 99.6% at full conversion (Table 2 entry 8). The 1b selectivity was lower at shorter reaction time.

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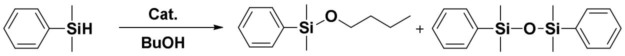
Although the surface area of the NSPC-SBA was similar to that of the HPNSC, the former gave much lower conversion at the same reaction condition than the latter probably due to lower pore volume (Table 2 entry 10). Thus, it can be deduced that the hierarchical structure of the HPNSC is beneficial to improve catalytic performance. However, conversion of dimethylphenylsilane over CNT (carbon nanotube) was only 21.8% (Table 1, entry 11). The activity of HPNC was also lower than that of HPNSC (Table 1, entry 12). These results indicate that the N and S heteroatom are all important for this reaction.

Table 1. Oxidative coupling of dimethylphenylsilane(1a) with n-butanol over the HPNSC at different conditions.[a]



1a 1b 1c

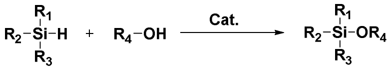
Entry	T(°C)	t(h)	Conv. (%)[b]	Sel. (%)[b]	
				1b	1c
1[c]	120	16	<1	99.9	-
2	90	16	100	73.3	15.9
3	100	16	100	78.2	11.0
4	110	16	100	83.6	2.2
5	120	16	100	99.6	0.4
6	130	16	100	98.9	0.6
7	120	8	100	83.6	10.0
8	120	12	100	92.4	3.2
10[d]	120	16	23.9	99.9	-
11[e]	120	16	21.8	99.9	-
12[f]	120	16	96.5	94.7	5.3

[a] Reaction conditions: silane (1 mmol), alcohol (3 ml), HPNSC (20 mg), 120 °C/16 h. [b] The conversion and the selectivity were obtained from GC with dodecane as internal standard. [c] No catalyst was used. [d] NSPC-SBA (20 mg). [e] CNTs (20 mg). [f] HPNC (20 mg)

It has been reported that graphitic nitrogen changed the electronic structure of the adjacent carbon atoms and promoted the carbocatalysis in the oxidation of arylalkanes and alcohols. It is generally accepted that activations of the Si-H bond in the silanes and O-H bond in the alcohol play a crucial role in the reaction.[9k-9o] We believe that the strong interaction between the lone electron pairs in the various species N and S with the Si-H bond and O-H bond also plays important role in promoting the reaction. To investigate the heteroatom-doping effect on the catalytic performance of the catalyst, the density functional theory study was conducted using the Vienna ab initio simulation package.[5] The four types of graphene structures and calculated adsorption energies (ΔE_{ads}) are shown in Fig. S6. The computational details are described in the Supporting Information. Compared with the pure, N-doped or S-doped graphenes, the N and S co-doped graphene exhibits the lowest adsorption energy. Thus, both co-existence of N and S heteroatoms and the hierarchical structure are crucial for the excellent catalytic performance of the HPNSC.

The catalytic performance of HPNSC was also examined in the oxidative coupling of other silanes with alcohols. As shown in Table 2, good to medium selectivity of silyl ethers were achieved with excellent conversion. Aromatic silanes were oxidized effectively in the presence of alcohols. Both dimethylphenylsilane and diphenylsilane in butanol gave excellent yield of the corresponding ethers (99.6% and 98.4%). Owing to low boiling point of ethanol and methanol, long time was required to obtain the desired yield of silyl ethers. The selectivity of silanes generally decreases with the number of Si-H bonds. Oxidation of phenylsilane afforded trialkoxyphenylsilane in medium yield (Table 2, entry 7-9) due to the competitive formation of disiloxane or siloxane oligomers.[16] It is worth noting that sterically hindered triphenylsilane was converted into the target silyl ethers with good yield (Table 2, entry 10-12). However, Au nanoparticles supported on nanohydroxyapatite gave only 25% yield of methoxytriphenylsilane in the oxidative couple of triphenylsilane with methanol.[9k] Moreover,

Table 2. Results of the oxidative coupling of silanes with alcohols catalysed by HPNSC[a]



2a 2b

Ent.	R_1	R_2	R_3	R_4	T (°C)	t (h)	Conv. (%)[b]	Sel. (%)[b]
1	Ph	Me	Me	n-Bu	120	16	100	99.6
2	Ph	Me	Me	Et	90	24	100	94.4
3	Ph	Me	Me	Me	70	48	100	80.1
4	Ph	Ph	H	n-Bu	120	16	100	98.4
5	Ph	Ph	H	Et	90	48	100	85.1
6	Ph	Ph	H	Me	70	48	100	99.9
7	Ph	H	H	n-Bu	120	48	100	82.8
8	Ph	H	H	Et	90	48	100	63.1
9	Ph	H	H	Me	70	48	100	69.2
10	Ph	Ph	Ph	n-Bu	120	24	98.0	99.9
11	Ph	Ph	Ph	Et	90	48	85.4	99.9
12	Ph	Ph	Ph	Me	70	48	99.1	99.9
13	Et	Et	Et	n-Bu	120	16	100	82.4
14	Et	Et	Et	Et	90	24	100	99.9
15	Et	Et	Et	Me	70	48	100	99.9

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[a] Reaction conditions: silane (1 mmol), alcohol (3 ml), HPNSC (20 mg). [b] The conversion and the selectivity were obtained from GC with dodecane as the internal standard.

aliphatic silane like triethylsilane also gave excellent yield of the corresponding ethers (Table 2, entry 13-15).

The recyclability of the HPNSC was evaluated using the reaction of dimethylphenylsilane with n-butanol. The catalyst was readily recovered from the solution by centrifugation, and the activity and selectivity were not changed notably after five recycles (Fig. 3). The hierarchical structure and chemical structure did not change obviously before and after the recycling reaction (Fig. S7). These results indicate that the HPNSC displayed excellent stability in the catalytic oxidation of silanes.

In summary, the HPNSC were very active and selective metal-free catalyst for oxidative coupling of silanes with alcohols. DFT calculation and control experiment showed that both co-coping of N and S and the hierarchical structure were crucial for the excellent catalytic performance. Moreover, catalytic activity and selectivity of the HPNSC did not changed notably after reused five times. We believe more reactions can be conducted at metal-free condition using heteroatom-doped hierarchically porous carbon materials as the catalysts.

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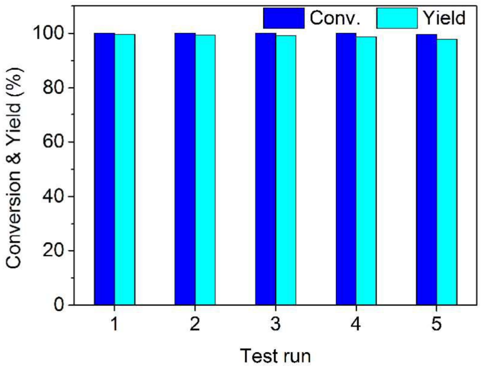

Fig. 3 Recyclability of the HPNSC catalyst in the oxidative coupling of dimethylphenylsilane with n-butanol.

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