Heterogeneous Catalysis Hot Paper

Deutsche Ausgabe: DOI: 10.1002/ange.201600455
Internationale Ausgabe: DOI: 10.1002/anie.201600455

Nitrogen, Phosphorus, and Sulfur Co-Doped Hollow Carbon Shell as Superior Metal-Free Catalyst for Selective Oxidation of Aromatic Alkanes

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Abstract: *Metal-free heteroatom-doped carbocatalysts with a high surface area are desirable for catalytic reactions. In this study, we found an efficient strategy to prepare nitrogen, phosphorus, and sulfur co-doped hollow carbon shells (denote as NPS-HCS) with a surface area of 1020 $m^2 g^{-1}$. Using a poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) (PZS) shell as carbon source and N, P, S-doping source, and the ZIF-67 core as structural template as well as extra N-doping source, NPS-HCS were obtained with a high surface area and superhydrophilicity. All these features render the prepared NPS-HCS a superior metal-free carbocatalyst for the selective oxidation of aromatic alkanes in aqueous solution. This study provides a reliable and facile route to prepare doped carbocatalysts with enhanced catalytic properties.*

Selective oxidation of C−H bonds is one of the most important reactions in organic synthesis.[1] Generally, both homogeneous and heterogeneous catalysts for this reaction need noble or transition metals.[2] Despite the high efficiency, the presence of metals is associated with high costs and contamination issues.[3] Therefore, development of metal-free catalysts is quite desirable.[4] Recently, carbon materials with or without dopant have shown promising abilities in many organic reactions as one kind of metal-free heterogeneous catalysts, including Friedel–Crafts alkylation reactions,[5] reductive hydrogen atom transfer reactions,[6] and oxidation of alcohols,[7] amines,[8] and arenes.[9] Two recent outstanding studies demonstrated that it is also feasible to catalyze oxidation of C−H bonds with carbocatalysts. Wang et al. reported boron and fluorine co-doped mesoporous carbon nitride (B, F-doped C_3N_4) as a metal-free catalyst for selective oxidation of cyclohexane to cyclohexanone with H_2O_2 as oxidant.[10] Ma and co-workers found that incorporating graphitic-type nitrogen in graphene could change the electronic structure of the adjacent carbon atoms and promoted the activity in selective oxidation of benzylic C−H bonds using *tert*-butyl hydroperoxide as oxidant.[11] However, the efficiency of this nitrogen-doped graphene was still unsatisfactory.

Apparently, the activity of carbocatalysts can be enhanced through structure design, chemical modification or heteroatoms doping (e.g., B, N, F, P or S). Fabrication of carbocatalysts with hierarchical porous structure would increase the surface area and pore volume, which are beneficial for mass adsorption and transportation. Doping heteroatoms in carbocatalysts could significantly improve the catalytic abilities in various organic reactions and electrochemical catalysis.[12] Such heteroatom doping could change the electron features of carbon for catalysis. Thus, finding a rational method to produce carbon nanostructures with controllable heteroatom doping may lead to better carbocatalysts.

In this study, we found an efficient route to produce nitrogen, phosphorus, and sulfur co-doped hollow carbon shells (denote as NPS-HCS) with a surface area of 1020 $m^2 g^{-1}$. The key of this method is to design and prepare the ZIF-67@poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) core–shell composite. The PZS shell acts as carbon source and N, P, S-doping source, and ZIF-67 core acts as structural template as well as extra N-doping source. Because nitrogen, phosphorus, and sulfur atoms are atomically dispersed in the PZS,[13] atomic-level doping with these three heteroatoms can be realized in the carbon shells. While the decomposition of the ZIF-67 core generates the hollow cavity and the released gases produce a mesoporous structure of the carbon shell, resulting in a hierarchical porous structure and high surface area of the NPS-HCS. Moreover, nitrogen atoms in the ZIF-67 are also doped into the carbon shells during thermal calcination. These extra N doping optimizes the distribution of the nitrogen species and improves the hydrophilicity of the NPS-HCS. All these features render the prepared NPS-HCS a superior metal-free carbocatalyst for selective oxidation of aromatic alkanes in aqueous solution.

The NPS-HCS catalyst was prepared through a three-step method (Scheme 1): 1) a highly cross-linked PZS was coated on the surface of ZIF-67 to form a core–shell composite (denote as ZIF-67@PZS); 2) the prepared ZIF-67@PZS composite was then calcined in Ar atmosphere to form the Co_2P@NPS-HCS composite; 3) Co_2P nanoparticles were removed by acid etching to form the final nitrogen, phosphorus, and sulfur co-doped hollow carbon shells (NPS-HCS). Transmission electron microscopy (TEM) images and X-ray

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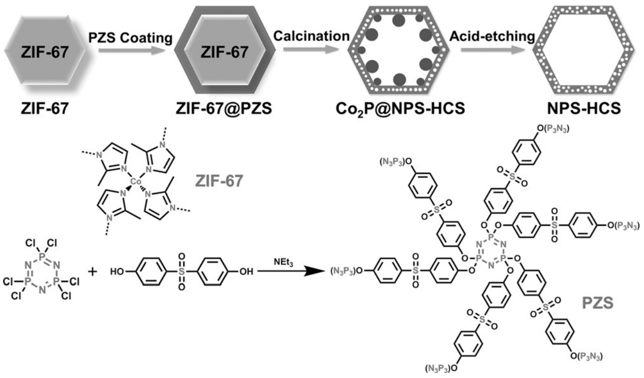
Supporting information for this article can be found under http://dx.doi.org/10.1002/anie.201600455.



Scheme 1. Preparation of NPS-HCS.

diffraction (XRD) patterns of samples obtained after each step are shown in Figure 1. The as-prepared ZIF-67 core template was polyhedral with relative uniform size (Figure 1 a and Figure S1).[14] With the assistance of triethylamine, the PZS shells were coated on the surface of ZIF-67 polyhedrons through in situ polymerization of the phosphonitrilic chloride trimer and 4,4′-sulfonyldiphenol. The thickness of the PZS shell was approximately 20 nm (Figure 1 b). After calcination at 900 °C for 2 h in Ar atmosphere, hollow carbon shells containing nanoparticles were produced (Figure 1 c). The nanoparticles in the inner carbon shells were ascribed to Co$_2$P, which were confirmed by XRD (Figure 1 f) and HRTEM (see Figure S2 in the Supporting Information). The nanoparticles were likely produced from the reaction between cobalt atoms in ZIF-67 and phosphorus atoms in PZS during thermal treatment. After etching by acid, hollow carbon shells were obtained with shell thickness of about 20 nm. The high-resolution transmission electron micrograph, X-ray diffractogram, and Raman spectrum showed that the graphitization content of the NPS-HCS was relatively low (Figure 1 e, Figure 1 f, and Figure S3, respectively).

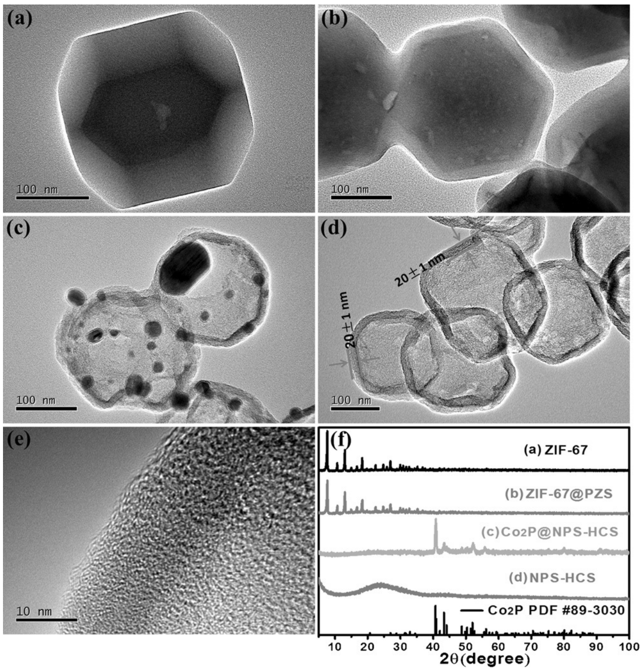


Figure 1. TEM images of a) ZIF-67 polyhedrons, b) ZIF-67@PZS, c) Co$_2$P@NPS-HCS, d,e) NPS-HCS, and f) XRD patterns of samples obtained at each step.

Energy-dispersive spectroscopy (EDS) mapping revealed that N, P, S were uniformly doped into the hollow carbon shells (Figure 2). The uniform doping was due to the PZS shell, which contains carbon, nitrogen, phosphorus, and sulfur atoms, thereby atomic-level doping with these three heteroatoms was possible in the carbon shell during thermal calcination. Besides the high dispersion state of the doping atoms, there are three doped atoms, while most of the reported doped-carbon materials were limited to two doped heteroatoms.[15]

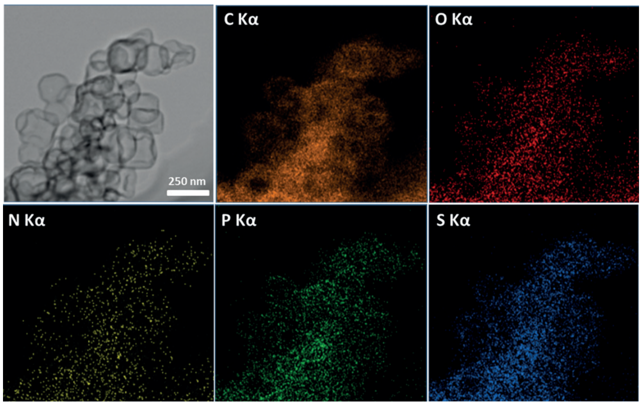


Figure 2. Compositional EDS mapping of the NPS-HCS using scanning transmission electron microscopy.

The states of the N, P, and S atoms in the NPS-HCS were then analyzed by X-ray photoelectron spectroscopy (XPS). The full spectrum of NPS-HCS (Figure 3 a) confirmed the existence of the N, P, and S atoms. As shown in Figure 3 b, the

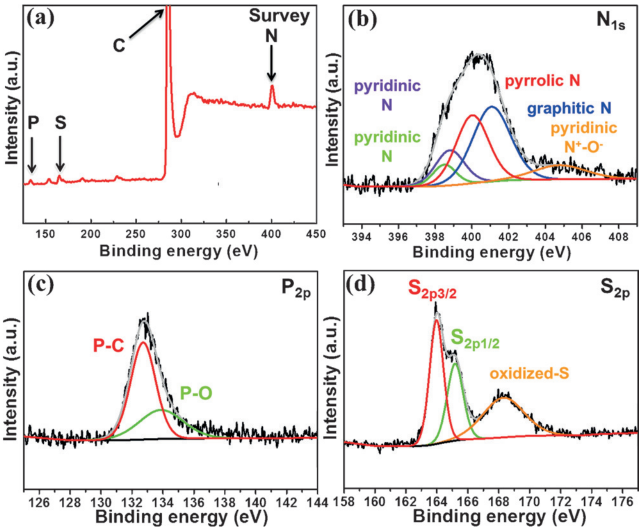


Figure 3. a) Full spectrum and high-resolution XPS spectra of b) N1s, c) P2p, and d) S2p of NPS-HCS.

high-resolution N1s spectrum of NPS-HCS can be fit well with four kinds of N species. Peaks at about 398.8, 400.0, 401.0, and 404.9 eV were corresponding to pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and pyridinic N^{+}-O^{-}, respectively.[16] Besides above four peaks, another peak at 398.6 eV can also be seen, which may be ascribed to the pyridinic nitrogen or P=N/P−N bonds.[17] A similar peak was also found in the pure PZS (Figure S4). The P2p spectrum showed two peaks at 132.7 and 133.9 eV, corresponding to P-C and P-O, respectively (Figure 3c).[18] The S2p spectrum displayed three peaks at 164.0, 165.2, and 168.3 eV, which were ascribed to $2p^{3/2}$, $2p^{1/2}$ splitting of the S2p spin orbital (-C-S-C-) and oxidized S, respectively (Figure 3d).[19] These data adequately confirmed that N, P and S atoms have been successfully incorporated into the hollow carbon shells.

The porous structure of NPS-HCS was determined by the N_2 adsorption–desorption method. As shown in Figure 4a, a typical type-IV isotherms with a distinct hysteresis loop was observed, indicating a mesoporous structure of hollow carbon shells.[20] The pore size distribution calculated by the Barrett–Joyner–Halenda (BJH) method showed a peak centered at around 4.3 nm (Figure 4b). The NPS-HCS had a Brunauer–Emmett–Teller (BET) surface area of 1020 $m^2 g^{-1}$ with a total pore volume of 1.31 $cm^3 g^{-1}$. The high surface area and porous structure are very beneficial for catalysis.

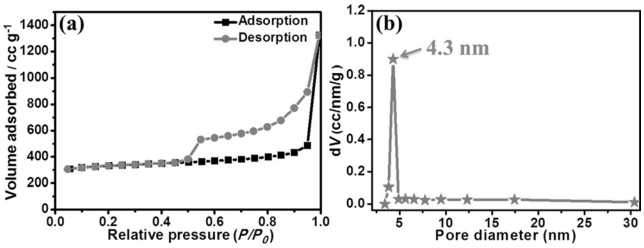
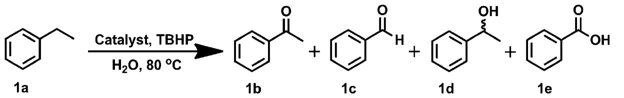


Figure 4. a) N_2 adsorption–desorption isotherms and b) mesopore size distribution curve of NPS-HCS.

The ZIF-67 core template plays a very important role in the formation of the final NPS-HCS. First, ZIF-67 was the structural template for PZS coating. ZIF-67 also helped to maintain the structural integrity of the hollow carbon shells during the calcination process. Some broken hollow carbon shells can be clearly seen in the TEM images of pure PZS hollow shells after calcination (denoted as PZS-HCS; Figure S5). Second, ZIF-67 helped to generate a mesoporous structure and to increase the surface area of NPS-HCS by the released gases after the decomposition of ZIF-67. For comparison, PZS-HCS showed no mesopores and a significantly lower surface area of 667 $m^2 g^{-1}$ (Figure S6). Third, nitrogen atoms in the ZIF-67 core were also doped into the hollow carbon shells during thermal calcination, increasing the total amount of N doping and optimizing the distribution of nitrogen species in the final NPS-HCS. According to the XPS result, the N atomic ratio increased from 1.98 % in PZS-HCS to 3.15 % in NPS-HCS (Table S1). Furthermore, the N1s spectrum of PZS-HCS (Figure S7) can be divided into three peaks of pyridinic nitrogen, graphitic nitrogen, and pyridinic N^{+}-O^{-}, while there were four nitrogen species (pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and pyridinic N^{+}-O^{-}) in NPS-HCS. Finally, the existence of a ZIF-67 core during the calcination improved the wettability of the NPS-HCS in water. Contact angle (CA) measurement (Figure S8) showed that the sample produced after calcinations of pure ZIF-67 under the same conditions displayed superhydrophilicity with a CA close to 0°, while the sample produced after calcinations of pure PZS displayed hydrophobicity with a CA of about 135°. And the NPS-HCS also showed superhydrophilicity with a CA of about 0°. A digital photo showed that NPS-HCS was well-dispersed in water (Figure S9). This is also beneficial for catalytic processes in water.

To study the performance of this NPS-HCS carbocatalyst for the selective oxidation of C−H bonds, ethylbenzene was first chosen as a substrate to explore the efficiency (Table 1).

Table 1: Optimization for the selective oxidation of ethylbenzene.[a]



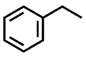
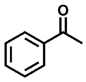
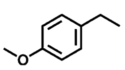
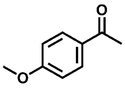
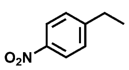
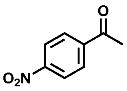
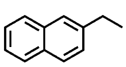
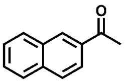
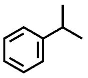
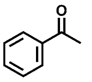
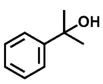
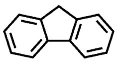
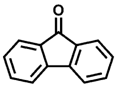
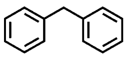
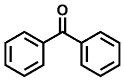
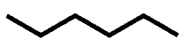
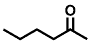
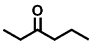
Entry	Catalyst	Time	Conversion	Selectivity			
				1b	1c	1d	1e
1	—	12 h	14%	70.6%	21.8%	7.6%	0%
2	PZS-900	6 h	12%	66.5%	19.2%	14.3%	0%
3	ZIF-67-900	6 h	76%	94.5%	2.7%	1.7%	1.1%
4	PZS-HCS	6 h	53%	74.6%	19.4%	6.0%	0%
5	NPS-HCS	6 h	91%	98.8%	0.5%	0.7%	0%
6	NPS-HCS	12 h	99%	99.5%	0.2%	0.3%	0%

[a] Reaction conditions: catalyst (0.010 g), TBHP (1.0 mL, 70 wt% in water), ethylbenzene (1.0 mmol), H_2O (2.0 mL), 80 °C.

For comparison, control samples (including pure PZS, ZIF-67, and PZS-HCS after calcination at 900 °C for 2 h in Ar atmosphere) were also tested. The NPS-HCS catalyst showed high activity and excellent selectivity during 6 h (entry 5), much better than those of the test samples (entries 2–4) and nitrogen-doped graphene reported in the literature.[11] When the reaction time was prolonged to 12 h, conversion of 99 % with a selectivity 99.5 % for acetophenone was achieved (entry 6). The NPS-HCS catalyst could be easily separated from the solution by centrifugation and was reused five times without obvious loss of activity and selectivity (Figure S10). The morphology, structure, and chemical states of the NPS-HCS after five runs were nearly the same relative to that of the fresh catalyst (Figures S11–S13). A little decrease of activity can be ascribed to the unavoidable sample loss during the recycle process and partial oxidation of carbon active sites under the oxidative conditions (Table S2).

Various benzyl aromatic hydrocarbons could also be oxidized with high yields (Table 2), indicating the superior efficiency of the NPS-HCS catalyst. The electron-donating group-substituent (MeO^{-}) showed a higher reactivity relative to those of the electron-withdrawing groups (NO_2^{-}; Table 2, entries 2–3). A high reaction activity could also be obtained for bulky and sterically hindered molecules, such as 2-ethylnaphthalene, cumene, fluorine, and diphenylmethane

Table 2: Oxidation of arylalkanes in the aqueous phase with NPS-HCS as catalyst.[a]

Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1			>99%	99%
2			>99%	99%
3			95%	99%
4			>99%	99%
5		 	90%	1.0 : 3.3
6			>99%	99%
7			>99%	99%
8		 	57%	1.0 : 1.3

[a] Reaction conditions: catalyst (5.0 mg), TBHP (500 μL, 70 wt% in water), ethylbenzene (0.5 mmol), H_2O (1.0 mL), 80 °C, 12 h.

(Table 2, entries 4–7). Besides aromatic molecules, aliphatic molecules can be oxidized. As can be seen in Table 2, entry 8, 57% conversion of *n*-hexane can be reached after 12 h at 80 °C. For aromatic hydrocarbons, usually the benzyl C−H bond adjacent to the aromatic ring is much more reactive than others, thus a high selectivity can be obtained. However, all C−H bonds of long-chain hydrocarbons show a similar selectivity. Therefore, it is difficult to gain high selectivity for the oxidation of aliphatic molecules.

The superior activity of the NPS-HCS catalyst can be ascribed to several features. Ma et al. suggested that the incorporated nitrogen (mostly of graphitic-type sites) in layered carbon dopant catalysts was pivotal for the C−H bond activation.[11] The nitrogen itself was not the active site, but instead changed the electronic structure of the adjacent carbon atoms and promoted the catalytic reactivity.[21] In this study, about 39 atom% of the N species on NPS-HCS was graphitic nitrogen. Besides the nitrogen dopants, the electronic structure of the carbon atoms can also be modulated by phosphorus and sulfur dopants.[17c,22] Thus, the N, P, and S dopants are an important feature of this NPS-HCS catalyst. In addition, the NPS-HCS catalyst has a high surface area, mesoporous shells, and a hollow cavity structure, which is usually beneficial for mass adsorption and transformations in catalysis. Moreover, the surface of the NPS-HCS was superhydrophilic. As a consequence, the NPS-HCS was highly dispersible in water. All these features together render the NPS-HCS a superior metal-free catalyst for selective oxidation of aromatic alkanes in aqueous solution.

In summary, we produced nitrogen, phosphorus, and sulfur co-doped hollow carbon shells with a mesoporous structure and a surface area of 1020 $m^2 g^{-1}$. When used as a metal-free carbocatalyst for selective oxidation of aromatic alkanes in aqueous solution, the prepared NPS-HCS showed excellent activity, selectivity, and good recyclability. This study provides a reliable and facile route to prepare doped carbocatalysts with enhanced catalytic properties.

Experimental Section

Synthesis of NPS-HCS: ZIF-67 polyhedrons were first prepared according to a previous report with minor modification.[14] In the second step, the above-synthesized ZIF-67 polyhedrons were dispersed into 80 mL methanol using ultrasound for five minutes. Then another solution containing 300 mg of hexachlorocyclophosphazene and 675 mg of 4,4′-sulfonyldiphenol in 20 mL of methanol was added dropwise. After stirring for five minutes, 1 mL of triethylamine was added dropwise and the solution was continued to stir for 18 h. The purple precipitates were collected and washed with methanol three times and dried in vacuum at room temperature for 12 h. In the third step, the obtained ZIF-67@PZS was calcined at 900 °C for 2 h (2 °C min^{-1}) in Ar atmosphere. Finally, Co_2P@NPS-HCS was preleached in 0.5 mol L^{-1} H_2SO_4 at 80 °C for 12 h, and washed thoroughly with deionized water/ethanol and then dried in vacuum at room temperature for 12 h.

General procedure for the catalytic test: The substrate (0.5 mmol), catalyst (5.0 mg), TBHP (*tert*-butyl hydroperoxide, 500 μL, 70 wt% in water), and water (1 mL) were introduced into a 15 mL glass reaction tube sealed with a Teflon lid. The reaction mixture was stirred in a preheated 80 °C oil bath for 12 h. After that, 77 μL anisole was added to the system as internal standard. Next, 10 mL CH_2Cl_2 was added to extract organic compounds in the reaction system. The organic phase was analyzed using a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and an Rtx-5 capillary column (0.25 mm in diameter, 30 m in length).

Acknowledgements

We thank for financial support from the National Natural Science Foundation of China (NSFC grant number 21333009, 21573244, and 21573245) and the Chinese Academy of Sciences. The XRD, SEM, TEM and XPS measurements were performed at the Center for Physicochemical Analysis and Measurements in the Institute of Chemistry, the Chinese Academy of Sciences (ICCAS). Dr. Zhijuan Zhao (XPS discussion) and Dr. Ye Tian (CA measurement) are acknowledged for their support.

Keywords: carbon · doping · heterogeneous catalysis · metal-free catalysts · selective oxidation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4016–4020
Angew. Chem. **2016**, *128*, 4084–4088

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Received: February 1, 2016