CHEMISTRY & SUSTAINABILITY

CHEMSUSCHEM

ENERGY & MATERIALS

Accepted Article

Title: Hierarchical Hollow Covalent Organic Frameworks-derived Heteroatom-doped Carbon Spheres for Metal-free Catalysis

Authors: Liuyi Li, Lu Li, Caiyan Cui, Hongjun Fan, and Ruihu Wang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201700979

Link to VoR: http://dx.doi.org/10.1002/cssc.201700979



WILEY-VCH

www.chemsuschem.org

Hierarchical Hollow Covalent Organic Frameworks-derived Heteroatom-doped Carbon Spheres for Metal-free Catalysis

Liuyi Li,^[a] Lu Li,^[b] Caiyan Cui,^[a] Hongjun Fan*^[b] and Ruihu Wang*^[a]

Abstract: Covalent organic frameworks (COFs) with hollow structures hold great promises for developing new types of functional materials. Herein, we report a hollow spherical COF with a hierarchical shell, which serves as an effective precursor of B,N-codoped hierarchical hollow carbon spheres. Benefiting from the synergistic effect of hierarchical porosity, high surface area and B,N-codoping, the as-synthesized carbon spheres show the prospective utility as metal-free catalysts in nitroarene reduction. A mechanistic hypothesis is proposed based on theoretical and experimental studies. B atoms *meta* to pyridinic N atoms are identified to be the main catalytic active sites. The anti-aromaticity originated from the codoping of B and pyridinic N atoms, not charge distribution and deformation energy, is corroborated to play a pivotal role in the catalytic reaction.

Introduction

Covalent organic frameworks (COFs), emerging as a class of new crystalline porous materials,^[1] have shown great potential applications in gas storage,^[2] semicoductors,^[3] proton conduction^[4] and catalysis,^[5] owing to their high surface area, tunable compositions and diverse structural topologies.^[6] Besides chemical composition and inner porosity, the morphology of porous materials also plays an important role in their performances.^[7] In the context, hollow structures with spherical shape and hierarchical architecture are of great importance in catalysis because of their high surface/volume ratios and kinetically favorable open structure.^[8] The formation of such COFs may integrate crystallinity and porosity with hollow and hierarchical features, thus providing a unique opportunity to develop new types of highly tailorable materials. Although significant advances in the synthesis of functionalized COFs have been achieved, hollow COFs with hierarchical shell structures have been rarely reported.^[9]

Recently, porous carbon materials have captured considerable attention in metal-free catalysis due to their wide

[a]	Dr L. L, Li, ^[+] Dr C. Y. Cui, Prof R. H. Wang		
	State Key Laboratory of Structural Chemistry		
	Fujian Institute of Research on the Structure of Matter, Chinese		
	Academy of Sciences		
	350002, Fuzhou, China		
	E-mail: ruihu@fjirsm.ac.cn		
[b]	Dr L. Li, ^[+] Prof H. J. Fan		
	State Key Laboratory of Molecular Reaction Dynamics		
	Dalian Institute of Chemical Physics, Chinese Academy of Sciences		
	116023, Dalian, China		
	E-mail: fanhj@dicp.ac.cn		
[+]	These authors contributed equally to this work.		
	Supporting information for this article is given via a link at the end of the document.		

availability, environmental acceptability, corrosion resistance and unique surface properties.^[5f, 10] The ordered porous structures, high concentrations of carbon species and tunable chemical compositions in COFs make them intrinsic precursors for self-templated synthesis of porous carbons.^[11] Importantly, benefiting from the precise integration of heteroatom-containing building blocks and flexible synthetic strategies, the heteroatoms doping into carbons can be achieved through *in situ* carbonization of COFs, which will greatly ameliorate surface electrical and chemical properties of carbon materials to realize new functions.^[12] Accordingly, the COF-derived porous carbons can not only enlighten more intriguing applications, but also provide a platform to understand the intrinsic role of dopants in metal-free catalysis.

Herein, we report the template-free synthesis of a hollow spherical COF with hierarchical structures (H-COF), and demonstrate its prospective utility as a precursor for the fabrication of nitrogen (N) and boron (B)-codoped hollow carbon spheres (BN-HCS). The as-synthesized BN-HCS exhibit excellent catalytic activity, high selectivity, superior stability and broad substrate tolerance in metal-free catalytic reduction of nitroarenes. Moreover, the theoretical investigations together with experimental results indicate that the synergistic effects between B atoms and pyridinic N atoms are beneficial for their promising catalytic properties.

Results and Discussion

H-COF was synthesized by the solvothermal reaction of 4-formylphenylboronic acid and 1,3,5-tris(4-aminophenyl)-benzene (Figure 1). Fourier-transform infrared (FTIR) spectrum of H-COF exhibits the disappearance of the hydroxyl strething band at 3210 cm⁻¹, the carbonyl stretching band at 1672 cm⁻¹, and the N-H stretching band at 3300 cm⁻¹. Meanwhile, the characteristic stretching bands of a six-membered B₃O₃ boroxine ring and an imine group at 711 and 1622 cm⁻¹ (Figure S1), respectively, emerged in the FTIR spectra. These data unambiguous indicate that H-COF are formed with dual linkages. Solid-state ¹³C NMR spectroscopy confimed the presence of the imine carbon at 158 ppm (Figure S2).^[13]

The morphology of H-COF was investigated by fieldemission scanning electron microscopy (SEM) and transmission electron microscope (TEM) analyses. The SEM images show that H-COF is composed of uniform hollow microspheres with a diameter of 2.12 \pm 0.29 µm (Figure 2b and c), and the shell thickness is approximately 500 nm (Figure S3). The hollow structure of H-COF was observed clearly from the TEM images (Figure 2d and e). Close inspection of the marked orange region demonstrates that the microspheres consist of the randomly oriented nanosheets with the thickness of 40 nm. Energy-



WILEY-VCH

dispersive spectroscopy (EDX) line-scanning analysis across the hollow microsphere reveals that C, N, B and O atoms are distributed uniformly in the shells (Figure S4). To our knowledge, such hollow configuration of COFs has not been reported heretofore. Powder X-ray diffraction (XRD) pattern of H-COF indicates highly crystalline nature of the hierarchical hollow microspheres (Figure S5), which is in good agreement with the simulated pattern of the eclipsed model.^[14] The Brunauer-Emmett-Teller (BET) surface areas of H-COF is 16 m² g⁻¹ (Figure S6), the relatively low surface area is mainly owing to the blockage of the surface pore channels by small COF nanoparticles (*vide infra* in time-dependent experiemnt of COF formation). The structure of H-COF showed high thermal stability. Thermogravimetric analysis (TGA) shows that H-COF is stable up to 450 °C (Figure S7).



Figure 1. Synthesis of H-COF (a), SEM (b, c) and TEM (d, e) images for H-COF.

The time-dependent experiments showed that the formation of hierarchical H-COF follows the Ostwald ripening process.^[9, 15] shown in Figure S8, the condensation of 4-As formylphenylboronic acid and 1,3,5-tris(4-aminophenyl)-benzene generated firstly large amount of nanoparticles, which quickly assembled into large microspheres to decrease the surface energy. In the continuous solvothermal reaction, the inner crystallites dissolve and migrate out by virtue of the reversibility of the imine bond and boroxine ring formation, thereby generating hollow cavities inside the spheres. Meanwhile, the layered stacking structure induces the growth of crystalline nanosheets outside the microspheres, producing hierarchical hollow microspheres. FTIR spectra of the isolated samples at different reaction time are identical with that of H-COF, indicating the same chemical compositions in these samples (Figure S9). Apart from reaction time, the solvents also play a decisive role in modulating the morphology of COFs. By adjusting the volume ratio of dioxane to mesitylene, nonhollow COFs microspheres (NH-COF) can be obtained (Figure S10).

Considering the ordered porous structures, high concentrations of carbon species and the atomically homogeneous distribution of N and B in H-COF, the feasible utility of H-COF in the self-templated synthesis of B,N-doped porous carbons was investigated. The pyrolysis of H-COF at 700, 800 and 900 °C under N₂ flow gave rise to porous carbons, which are denoted as BN-HCS-700, BN-HCS-800 and BN-HCS-

900, respectively. Their SEM images show that the hollow spherical morphology of the precursor H-COF is well retained (Figure 2 and Figure S11), which is critical to hold the porosity, rigidity and uniform distribution of the heteroatoms. The diameters of the resultant carbon spheres and the thickness of their nanosheets become smaller and thinner, respectively, than those of the parent H-COF owing to the framework shrinkage during carbonization.^[16] By increasing pyrolysis temperature, the average outer diameters in BN-HCS-700, BN-HCS-800 and BN-HCS-900 decrease to 2.05 ± 0.31 , 1.95 ± 0.35 and 1.78 ± 0.3 µm, respectively, and the thicknesses of their nanosheets are reduced to 36.3 ± 5 , 26.5 ± 3.5 and 25 ± 3.8 nm, respectively. TEM images of BN-HCS-800 further confirm the maintenance of the hollow structure (Figure 2d). The shell of hollow spheres is composed of nanosheets with thin thickness (Figure 2e and 2f).^[17] The EDX elemental mapping images of BN-HCS-800 demonstrate uniform distribution of the B and N atoms in the hollow carbon shell (Figure 2g), which benefits from the atomically homogeneous distribution of N and B in H-COF.^[18] B and N codoping into the hollow carbon is also confirmed by FTIR and Raman spectra. In FTIR spectra of BN-HCS, the peaks around 780 and 1050 cm⁻¹ are attributed to B-N and B-C stretching bands, respectively (Figure S12).32,33 The Raman spectra of BN-HCS exhibit two characteristic peaks around 1335 and 1590 cm⁻¹ (Figure S13), corresponding to the D and G bands, respectively. The I_D/I_G ratios in BN-HCS-700, BN-HCS-800 and BN-HCS-900 gradually increase from 2.72 to 2.91 to 3.10, suggesting more defects are generated in the carbons as a result of pyrolysis at high temperatures and/or heteroatoms doping into the sp²-carbon framework. In their XRD patterns, all characteristic peaks of H-COF completely disappeared after carbonization (Figure S14 and S15). The BET surface areas of BN-HCS-700, BN-HCS-800 and BN-HCS-900 are 420, 558 and 570 m² g⁻¹ (Figure 3a), respectively. It is worth noting that the assynthesized carbon materials show a significant enhancement in their surface area compared with H-COF precursors. This is mainly ascribed to the considerable mass-loss of C, N and O in building blocks, leaving a hollow carbon network.^[19]



Figure 2. SEM images for BN-HCS-700 (a), BN-HCS-800 (b) and BN-HCS-900 (c). TEM images (d, e) high-resolution TEM (f) and EDX element mapping (g) for BN-HCS-800.

FULL PAPER

detailed chemical compositions and bonding The configurations of B and N atoms in BN-HCS were examined by X-ray photoelectron spectroscopy (XPS) analysis. The surface contents of C, N and B are consistent with the results of elemental analysis (Table S1). Their C 1s XPS spectra show four binding energy peaks at 284.4, 285.5, 286.5 and 288.6 eV, corresponding to the sp2 carbon, C-B, C-N and C-O, respectively (Figure S16a). The high-resolution B 1s XPS spectra consist of two main peaks at 190.2 and 191.1 eV, which are assigned to B-C and B-N-C, respectively (Figure 3b).^[20] The weak shoulder peak of B 1s at 192.1 eV is related to BC2O species in BN-HCS-700 and BN-HCS-800,^[21] while no obvious peak of B-O species was observed in BN-HCS-900. The deconvolution of the N 1s peak suggests the presence of pyridinic N (398.6 eV), pyrrolic N (399.7 eV), graphitic N (401.0 eV) and pyridinic N-oxide (405.3 eV) (Figure 3c). Among the BN-HCS materials, the N/C atom ratio in BN-HCS-800 is the lowest (Figure S16b), but it possesses the highest B/N ratio (Figure S16c). These clearly indicate that most of B atoms are bonded to C atoms in the form of BC₃ species in BN-HCS-800, while B atoms predominately generate N-B-C species in BN-HCS-900 (Figure 3d) owing to the ready formation of B-N bond at higher temperature.^[22] In combination with the bonding configurations and the content of N atoms on the surface of BN-HCS (Figure S16e), BN-HCS-800 and BN-HCS-900 are dominated by separated and bonded B and N,^[23] respectively. Therefore, the structural properties of the B,N-codoped carbon spheres can be reasonably tailored by changing the pyrolysis temperature of H-COF.



Figure 3. N_2 adsorption-desorption isotherms (a), B 1s XPS spectra (b) and N 1s XPS spectra (c) for BN-HCS-700, BN-HCS-800 and BN-HCS-900. Atom content (at.%) of B-C and B-N on the surface of BN-HCS-700, BN-HCS-800 and BN-HCS-900 (d).

Since the replacement of high-cost precious metal catalysts with metal-free carbon materials is of great importance in catalysis,^[24] it is highly desirable to develop new types of metal-

free carbon catalysts.^[25] Hydrazine hydrate is a readily available hydrogen carrier and reductant that is commonly applied in the metal-catalyzed reduction of nitroarenes.^[26] The catalytic performances of BN-HCS-700, BN-HCS-800 and BN-HCS-900 with hydrazine as the reductant were examined by the reduction of nitroarenes to anilines, which is usually performed using metal catalysts.^[27] Kinetic profiles of nitrobenzene reduction reveal that full conversion of nitrobenzene and quantitative selectivity of aniline can be achieved in 3 h (Figure 4a), and BN-HCS-800 presents the highest catalytic activity. Notably, these BN-HCS catalysts display a remarkable enhancement in catalytic activity compared with nonhollow carbon spheres derived from NH-COF (Figure S17a), which indicates that the morphology of carbon materials is one of the important factors in the design of metalfree catalytic systems. BN-HCS-800 demonstrated competitive catalytic activity relative to reduced graphene oxide^[28], N-doped activiated carbon^[29], graphene oxide and graphite powder catalysts under identical reaction conditions (Figure S17 b).



Figure 4. (a) Kinetic profiles of nitrobenzene conversion and aniline formation for BN-HCS-700, BN-HCS-800 and BN-HCS-900; (b) recycling test of BN-HCS-800 in nitrobenzene reduction. Reaction condition: BN-HCS (10 mg), nitroarene (1 mmol), ethanol (1 mL), hydrazine hydrate (1 mL), 100 $^{\circ}$ C, 4 h.

The catalytic recyclability of BN-HCS-800 was further evaluated. The solid catalyst was readily recovered and reused for 10 runs without obvious loss of activity (Figure 4b). The chemical states and morphology of BN-HCS-800 were well retained after consecutive ten runs (Figure S18 and S19), verifying the structural stability of BN-HCS in the catalytic reactions. The generality of the catalytic system was also explored. When various nitroarenes were employed as substrates, the corresponding amine products were obtained in excellent yields regardless of their electronic and steric nature (Table 1).

Considering that the catalytic activity of BN-HCS has no direct correlation with the surface area and/or heteroatoms concentration (Figure S20), density functional theory (DFT) calculations were performed to elucidate the effects of B and N codoping on the catalytic properties. It is known that the adsorption of hydrazine onto the catalyst surface is the rate determining step in the nitrobenzene reduction reaction.^[10b, 30] The energy of hydrazine adsorption (*Ead*) on various graphene models, including pure, N-doped, B-doped and N,B-codoped

WILEY-VCH

ChemSusChem

FULL PAPER

WILEY-VCH

graphenes, were chosen as criteria to examine their catalytic activity (Figure S21-S24). The optimal *Ead* values of various graphene models are shown in Figure 5a. *Ead* values in B,N(p)-codoped graphenes are lower than those in other surveyed models, which mainly result from their highly preferred N-B adsorption patterns. Among them, the lowest *Ead* of -1.21 eV was observed in the model containing a B atom *meta* to a

Table 1. Nitroarenes reduction using BN-HCS-800 as a catalyst. ^a						
Entry	Substrate	Product	Conv.(%)	Sel.(%)		
1 ^b	NO ₂	NH ₂	100	100		
2 ^{<i>b</i>}	NO ₂	NH ₂	100	100		
3 ^b	NO ₂	NH ₂	100	100		
4	NO ₂	NH ₂	96	97		
5	NC NO2	NC NH2	100	99		
6	HO NO ₂	HO NH ₂	100	100		
7 ^c		NH ₂	100	100		
8	NO ₂	NH2 N	100	100		
9 ^d	NO ₂	NH ₂	10	100		

^a Reaction conditions: BN-HCS-800 (10 mg), nitroarene (1 mmol), ethanol (1 mL), hydrazine hydrate (1 mL), 100 °C, 4 h, the products were detected by GC. ^b 24 h; ^c 2 h. ^d without BN-HCS-800.

pyridinic N atom, namely B(m)N(p)-graphene (Figure 5b). We found that the configurations of the B,N(p)-codoped graphene were changed significantly by the adsorption of hydrazine *via* the B-N bond, which suggests less aromaticity of heterocycles is probably favorable for the hydrazine adsorption. Thus, the aromaticity of the BN ring in B,N-codoped graphene models was further estimated by the nucleus-independent chemical shifts (NICSs).^[31] All BN(g) rings are aromatic, while all BN(p) rings are anti-aromaticity, suggesting that the existence of pyridinic N decreases the aromaticity (Figure 5c). Clearly, B(m)N(p)-graphene shows the strongest anti-aromaticity with the most

positive NICS, which is consistent with the *Ead* value of the B,Ncodoped graphene models. Therefore, the strong antiaromaticity facilitates the adsorption of hydrazine, and thus increases the catalytic activity in the nitrobenzene reduction.

On the basis of the experimental and theoretical investigations, a plausible mechanism for nitrobenzene reduction is proposed (Figure 5d). In the initial step, the hydrazine molecules are adsorbed at B atoms meta to pyridinic N atoms on the surface of carbon materials along with the adsorption of nitrobenezene. The oxidation of hydrazine and the reduction of nitrobenzene take place synchronously, producing N₂ and aniline product. It should be noted that the catalytic performance is not directly related to the absolute amount of B and N. The catalytic activity could not be enhanced by just increasing the B and N contents unless the B-C-N active sites are accessible to the substrates. Therefore, a homogeneous distribution of active sites on the walls of the open nanopores is highly desirable to achieve enhanced catalytic activities. In our case, the B-C-N active sites, which inherit from the atomic-level distribution of N and B atoms in H-COF, in conjunction with the hierarchical hollow structure of BN-HCS lead to the superior catalytic performance.



Figure 5. (a) *Ead* of hydrazine on N- and/or B-doped graphene models; (b) optimized configuration of hydrazine adsorbed on B(m)N(p)-graphene; Calculated NICSs (ppm) for the ring including both B and N atoms in B,N-codoped graphene models (c); Schematic mechanism for nitrobenzene reduction (d). The negative and positive NICSs values indicate aromaticity and anti-aromaticity, respectively. B(o), B(m) and B(p) stand for B atom ortho, meta, and para to N atom, respectively; N(p), N(g), N(pr) and G stand for pyridinic N, graphitic N, pyrrolic N and graphene, respectively.

Conclusions

Hierarchical hollow carbon spheres have been constructed for the first time from COFs. As effective metal-free catalysts, the

as-synthesized hollow carbon materials with the retention of hollow spherical morphology and unique hierarchical structure exhibit remarkable catalytic properties in reduction reaction of nitroarenes. Based on experimental results and DFT calculations, B atoms *meta* to pyridinic N atoms are proposed to be the predominant catalytic active sites. This work has demonstrated the synthesis of hierarchical hollow COFs spheres and their feasible utility in the preparation of heteroatom-doped porous carbons for metal-free catalysis. This offers a new inspiration for the fabrication of COFs-derived carbon materials with tunability and functionality for advanced catalytic applications.

Experimental Section

Materials and methods: Chemical reagents were commercially available and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III NMR spectrometer at 400 and 100 MHz, respectively, using tetramethylsilane (TMS) as an internal standard. Solid-state ¹³C CP/MAS NMR was performed on a Bruker SB Avance III 500 MHz spectrometer with a 4-mm double-resonance MAS probe. FTIR spectra were recorded with KBr pellets using Perkin-Elmer Instrument. Raman spectra were recorded on a Renishaw inVia system by using 633 nm laser. Thermogravimetric analysis (TGA) was carried out on NETZSCH STA 449C by heating samples from 30 to 900 °C in a dynamic nitrogen atmosphere with a heating rate of 10 °C·min⁻¹. Powder X-ray diffraction (XRD) patterns were recorded in the range of $2\theta = 3-40^{\circ}$ on a desktop X-ray diffractometer (RIGAKU-Miniflex II) with Cu Ka radiation (λ = 1.5406 Å). Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 system. The samples were degassed at 150 °C for 10 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) equation. The calculation of the pore size distribution was done using the quenched-solid density functional theory (QSDFT) equilibrium model. Field-emission scanning electron microscopy (SEM) was performed on a JEOL JSM-7500F operated at an accelerating voltage of 3.0 kV. Transmission electron microscope (TEM) was obtained with TECNAI G² F20. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer, using non-monochromatic Al Kg x-rays as the excitation source and choosing C 1s (284.8 eV) as the reference line. Elemental analyses were performed on an Elementar Vario MICRO Elemental analyzer.

Computational Method: All calculations were carried out with Gaussian 09 program. The M06-2X/cc-pVDZ method was utilized for geometry optimizations and vibrational frequency calculations. The energy of hydrazine adsorption (E_{ad}) on various graphene models, which is the rate-determining step of the nitroarenes reduction reaction, was used as the criteria to estimate catalytic activity of each catalyst. For pure and N-doped graphene, hydrazine is adsorbed through the weak N-H···C hydrogen bond, and their *Ead* values are less than -0.5 eV. Although hydrazine may be also adsorbed by the additional N-B dative bond in B-doped and B,N-codoped graphene, this adsorption pattern is less preferred. Thus, their *Ead* values are close to those in pure and N-doped graphenes. E_{ad} is defined as:

 $E_{ad} = E_{total} - (E_{substrate} + E_{N_2H_4})$

where E_{total} is the total energy of the system with adsorbed N₂H₄, $E_{substrate}$ and E_{N2H4} are the energies of the investigated substrates (graphene or doped graphene clusters) and isolated hydrazine, respectively.

A further analysis of decomposition energy and interaction energy of two fragments in various coordination complexes was carried out. The energies of the hydrazine and B,N-codoped graphene models in the coordination complexes were evaluated through single-point calculations. These single point energies, together with the energy of the respective fragments in their optimized geometry, allow for the estimation of the deformation energies of the two fragments, $E_{def(N2H4)}$ and $E_{def(Substrate)}$. Such single-point energies of the fragments and the electronic energy of coordination complexes were used to estimate the interaction energy E_{int} between two fragments.

Synthesis of H-COF: 1,3,5-Tris(4-aminophenyl)-benzene (100 mg, 0.28 mmol) and 4-formylphenylboronic acid (130 mg, 0.87 mmol) were dissolved in solution of 1,4-dioxane/mesitylene (1/1 v/v, 10 mL) in a 100 mL thick walled pressure bottle. The bottle was tightened by the screw cap and then sonicated for 1 min. The reaction mixture was heated at 120 °C for 3 d. The precipitate was isolated by filtration and washed with anhydrous 1,4-dioxane. The resultant material was purified by Soxhlet extraction using dichloromethane, dried in vacuo at 80 °C for 12 h to afford H-COF as a yellowish powder. Yield: 105 mg (54%). Anal. calcd. for (C15H10BNO)n: C, 77.97; H, 4.36; N, 6.06; found: C, 72.59; H, 5.07; N, 5.75.

Synthesis of BN-HCS-700, BN-HCS-800 and BN-HCS-900: H-COF (100 mg) was pyrolyzed at 700, 800 and 900 $^{\circ}$ C, respectively, with a heating rate of 5 $^{\circ}$ C min⁻¹ under N₂ atmosphere in a ceramic boat for 2 h. The resultant black material was treated with water at 70 $^{\circ}$ C overnight, followed by washing with water and methanol, and dried at 80 $^{\circ}$ C in vacuo for 6 h to afford BN-HCS-700, BN-HCS-800 and BN-HCS-900, respectively.

Typical procedure for reduction of nitroarenes: Nitroarene (1 mmol), hydrazine hydrate (1 mL), BN-HCS catalyst (10 mg) and ethanol (1 mL) were placed in a Schlenk flask (20 mL), and the reaction mixture was stirred at 100 °C for a given time. After the reaction, the resultant mixture was transferred into a tube and the solid was separated by centrifugation. The organic phase was analyzed with GC to determine conversion and selectivity. The identity of products was confirmed by comparison with GC retention times of commercial materials and literature NMR spectroscopic data.

Recyclability tests for reduction of nitrobenzene: After the first run reaction was finished, the residual solid was recovered by centrifugation and washed with ethanol, followed by centrifugation. The processes were repeated twice, and the resultant solid was directly used for the next run with the same amount of fresh nitrobenzene, hydrazine hydrate and ethanol.

Acknowledgements

The authors appreciate the financial assistance from the National Natural Science Foundation of China (21403238, 21673224 and 21673241), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000 and XDB17010200), and Major Project of Fujian Province (2014H0053).

Keywords: Covalent organic frameworks • Porous carbon • Metal-free catalysis • DFT calculations.

- a) S. Y. Ding, W. Wang, *Chem. Soc. Rev.* 2013, *42*, 548-568; b) N.
 Huang, P. Wang, D. Jiang, *Nat. Rev. Mater.* 2016, *1*, 16068; c) P. J.
 Waller, F. Gándara, O. M. Yaghi, *Acc. Chem. Res.* 2015, *48*, 3053-3063.
- [2] Y. Zeng, R. Zou, Y. Zhao, Adv. Mater. 2016, 28, 2855-2873.
- [3] a) S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle, D. Jiang, *J. Am. Chem. Soc.* 2015, *137*, 7817-7827; b) V. S. Vyas, V. W.-h. Lau, B. V. Lotsch, *Chem. Mater.* 2016, *28*, 5191-5204.
- [4] S. Chandra, T. Kundu, S. Kandambeth, R. BabaRao, Y. Marathe, S. M. Kunjir, R. Banerjee, J. Am. Chem. Soc. 2014, 136, 6570-6573.
- [5] a) V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, *Nat. Commun.* 2015, *6*, 8508; b) S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, *J. Am. Chem. Soc.* 2011, *133*, 19816-19822; c) Z. Li, T. He, L. Liu, W. Chen, M. Zhang, G. Wu, P. Chen, *Chem. Sci.* 2017, *8*, 781-788; d) Q. Sun, B. Aguila, J. Perman, N. Nguyen, S. Ma, *J. Am. Chem. Soc.* 2016, *138*, 15790-15796; e) E. Rozhko, A. Bavykina, D. Osadchii, M. Makkee, J. Gascon, *J. Catal.* 2017, *345*, 270-280; f) K. H. Wu, Y. Liu, J. Luo, B. Wang, J. Xu, C. Pham-Huu, D. Su, *ACS Catal.* 2017, *7*, 3295-3300.
- [6] a) G. Lin, H. Ding, D. Yuan, B. Wang, C. Wang, J. Am. Chem. Soc.
 2016, 138, 3302-3305; b) N. Huang, L. Zhai, D. E. Coupry, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine, D. Jiang, Nat. Commun.
 2016, 7, 12325; c) Y. Zhao, Chem. Mater. 2016, 28, 8079-8081.
- [7] X. Wang, J. Feng, Y. Bai, Q. Zhang, Y. Yin, Chem. Rev. 2016, 116, 10983-11060.
- [8] G. Prieto, H. Tüysüz, N. Duyckaerts, J. Knossalla, G. H. Wang, F. Schüth, *Chem. Rev.* 2016, *116*, 14056-14119.
- [9] S. Kandambeth, V. Venkatesh, D. B. Shinde, S. Kumari, A. Halder, S. Verma, R. Banerjee, *Nat. Commun.* 2015, 6, 6786.
- a) Y. Xu, M. Kraft, R. Xu, *Chem. Soc. Rev.* 2016, *45*, 3039-3052; b) A.
 T. Murray, Y. Surendranath, *ACS Catal.* 2017, *7*, 3307-3312.
- [11] a) Y. B. Huang, P. Pachfule, J. K. Sun, Q. Xu, J. Mater. Chem. A 2016, 4, 4273-4279; b) L. Chen, L. Zhang, Z. Chen, H. Liu, R. Luque, Y. Li, Chem. Sci. 2016, 7, 6015-6020.
- a) S. Wang, E. Iyyamperumal, A. Roy, Y. Xue, D. Yu, L. Dai, *Angew. Chem., Int. Ed.* **2011**, *50*, 11756-11760; b) Y. Lin, S. Wu, W. Shi, B. Zhang, J. Wang, Y. A. Kim, M. Endo, D. S. Su, *Chem. Commun.* **2015**, *51*, 13086-13089.

- [13] Y. Peng, W. K. Wong, Z. Hu, Y. Cheng, D. Yuan, S. A. Khan, D. Zhao, *Chem. Mater.* 2016, 28, 5095-5101.
- [14] Y. Zeng, R. Zou, Z. Luo, H. Zhang, X. Yao, X. Ma, R. Zou, Y. Zhao, J. Am. Chem. Soc. 2015, 137, 1020-1023.
- [15] J. Huo, L. Wang, E. Irran, H. Yu, J. Gao, D. Fan, B. Li, J. Wang, W. Ding, A. M. Amin, C. Li, L. Ma, *Angew. Chem., Int. Ed.* **2010**, *49*, 9237-9241.
- [16] X. Liu, L. Zhou, Y. Zhao, L. Bian, X. Feng, Q. Pu, ACS Appl. Mat. Interfaces 2013, 5, 10280-10287.
- [17] N. A. Katcho, E. Urones-Garrote, D. Ávila-Brande, A. Gómez-Herrero, S. Urbonaite, S. Csillag, E. Lomba, F. Agulló-Rueda, A. R. Landa-Cánovas, L. C. Otero-Díaz, *Chem. Mater.* **2007**, *19*, 2304-2309.
- [18] S. Yang, L. Peng, P. Huang, X. Wang, Y. Sun, C. Cao, W. Song, Angew. Chem., Int. Ed. 2016, 55, 4016-4020.
- [19] G. Srinivas, V. Krungleviciute, Z. X. Guo, T. Yildirim, *Energy Environ. Sci.* 2014, 7, 335-342.
- [20] Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec, S. Z. Qiao, Angew. Chem. 2013, 125, 3192-3198.
- [21] Y. Zhao, L. Yang, S. Chen, X. Wang, Y. Ma, Q. Wu, Y. Jiang, W. Qian, Z. Hu, J. Am. Chem. Soc. 2013, 135, 1201-1204.
- [22] L. H. Li, J. Cervenka, K. Watanabe, T. Taniguchi, Y. Chen, ACS Nano 2014, 8, 1457-1462.
- [23] T. Schiros, D. Nordlund, L. Palova, L. Zhao, M. Levendorf, C. Jaye, D. Reichman, J. Park, M. Hybertsen, A. Pasupathy, ACS Nano 2016, 10, 6574-6584.
- [24] a) P. Tang, G. Hu, M. Li, D. Ma, ACS Catal. 2016, 6, 6948-6958; b) G.
 Wen, B. Wang, C. Wang, J. Wang, Z. Tian, R. Schlögl, D. S. Su, Angew. Chem. 2017, 129, 615-619.
- [25] P. L. Bramwell, J. Gao, B. de Waal, K. P. de Jong, R. J. M. Klein Gebbink, P. E. de Jongh, *J. Catal.* **2016**, 344, 129-135.
- [26] Q. Shi, R. Lu, L. Lu, X. Fu, D. Zhao, Adv. Synth. Catal. 2007, 349, 1877-1881.
- [27] H. K. Kadam, S. G. Tilve, *RSC Adv.* **2015**, *5*, 83391-83407.
- [28] Y. Gao, D. Ma, C. Wang, J. Guan, X. Bao, Chem. Commun. 2011, 47, 2432-2434.
- [29] S.-i. Fujita, H. Watanabe, A. Katagiri, H. Yoshida, M. Arai, J. Mol. Catal. A: Chem., 2014, 393, 257-262.
- [30] J. W. Larsen, M. Freund, K. Y. Kim, M. Sidovar, J. L. Stuart, *Carbon* 2000, 38, 655-661.
- [31] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. v. E. Hommes, J. Am. Chem. Soc. 1996, 118, 6317-6318.

WILEY-VCH

Entry for the Table of Contents

FULL PAPER

Hierarchical hollow covalent organic frameworks (H-COFs) have been prepared and used as a precursor for the fabrication of heteroatom-doped porous carbons. Originated from of hierarchical porosity and crystallinity in H-COF, the as-synthesized carbons show promising performances in metal-free reduction of nitroarenes.



Liuyi Li, Lu Li, Caiyan Cui, Hongjun Fan* and Ruihu Wang*



Hierarchical Hollow Covalent Organic Frameworks-derived Heteroatomdoped Carbon Spheres for Metal-free Catalysis