Electronic Supplementary Information (ESI) for

Synthesis of Nitrogen and Sulfur Co-doped Hierarchical Porous

Carbons and Metal-free Oxidative Coupling of Silanes with Alcohols

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1. Experimental section

Chemicals. Carbon nanotubes (CNTs) were purchased from Chengdu Organic Chemicals Co. Ltd (China). The CNTs were washed with H_2SO_4/HNO_3 mixed aqueous solution to remove residual metal particles. Tetraethylorthosilicate (TEOS), ammonium hydroxide, thiourea, HCl, HF, methanol, ethanol, and n-butanol were obtained from Sinopharm Chemical Reagent Co (China). Silicon (IV) oxide (30% in H_2O, colloidal dispersion) was provided by Alfa Aeser. 2, 5-Dihydroxy-1,4-benzo-quinone, Dimethylphenylsilane, phenylsilane, diphenylsilane, triphenyl-silane, and triethylsilane were purchased from Alfa Aeser. The silica spheres (mean size: 200 nm) employed as templates were prepared by the Stöber method [1]. The SBA-15 was synthesized based on the method reported [2, 3].

Preparation of hierarchically porous N and S co-doped carbon (HPNSC). 2, 5-Dihydroxy-1, 4-benzoquinone (706 mg, 5.0 mmol) and thiourea (761 mg, 10.0 mmol) were dissolved in H_2O-EtOH solution (H_2O: 9 mL, EtOH: 6 mL) under stirring. Then, 3.9 g silica spheres (mean size: 200 nm) and 13.1 g silica colloidal particles (~10 nm, with 30% in H_2O, colloidal dispersion) were added to the solution. After stirring vigorously for 1.0 h at room temperature, solvents were removed by rotary evaporator. The dried powders were ground into fine powder with a mortal, and gently heated to 150 °C for formation of liquid mixture under stirring. The obtained mixture was then treated under flowing N_2 at 900 °C (heating rate: 2.5 °C/min) for 1 h to carbonize the precursors. The doped carbon was obtained by dissolution of the silica templates in 5 wt.% hydrofluoric acid, isolated by filtration, washed several times with ethanol (4×20 mL), and dried under vacuum at 60 °C for 12 h. The as-prepared material was denoted as HPNSC.

Preparation of N and S co-doped porous carbon (NSPC-SBA). The procedures were similar to that discussed above. The main different was that SBA-15 was used as the template. In the experiment, 2, 5-dihydroxy-1, 4-benzoquinone (5.0 mmol) and thiourea (10.0 mmol) were dissolved in H_2O-EtOH solution (H_2O: 9 mL, EtOH: 6 mL) under stirring. Then, SBA-15 (400 mg) was added to the solution. After removing solvents with a rotary evaporator, the obtained solid underwent the above-described procedure, such as heat treatment (150 °C) to form liquid mixtures, carbonization under nitrogen atmosphere (900 °C/1 h) and HF etching process, washing with ethanol, and drying under vacuum at 60 °C for 12 h. The as-prepared material was denoted as NSPC-SBA.

Preparation of hierarchically porous N-doped carbon (HPNC). 2, 5-Dihydroxy-1, 4-benzoquinone (706 mg, 5.0 mmol) and urea (605 mg, 10.0 mmol) were dissolved in H_2O-EtOH solution (H_2O: 9 mL, EtOH: 6 mL) under stirring. Then, 3.9 g silica spheres (mean size: 200 nm) and 13.1 g silica colloidal particles (10 nm, with 30% in H_2O, colloidal dispersion) were added to the solution. After stirring vigorously for 1.0 h at room temperature, solvents were removed by rotary evaporator. The dried powders were ground into fine powder with a mortal, and gently heated to 150 °C for formation of liquid mixture under stirring. The obtained mixture was then treated under flowing N2 at 900 °C (heating rate: 2.5 °C/min) for 1 h to carbonize the precursors. The doped carbon was obtained by dissolution of the silica templates in 5 wt.% hydrofluoric acid, isolated by filtration, washed several times with ethanol (4×20 mL), and dried under vacuum at 60 °C for 12 h. The as-prepared material was denoted as HPNC.

Characterization. FE-SEM images were obtained with SU-8020 (HITACHI) field-emission scanning electron microscope. TEM images were obtained by using JEM-2100F microscope with a beam voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were recorded on an ESCALab220i-XL instrument with a monochromatized Al-Ka line source (300 W) and the peak positions were referenced internally to the C 1s peak at 284.6 eV. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku Rota flex diffractometer equipped with a rotating anode and a Cu-Kα radiation source (40 kV, 200 MA; λ=1.54056 Å). Nitrogen adsorption measurements were conducted at 77 K on a Quantachrome Quadrasorb SI-MP porosimeter. All samples were degassed at 300 °C for at least 4 h before every measurement. Specific surface areas were determined by the Brunauer-Emmet-Teller (BET) method based on the relative pressure between 0.05 and 0.30. The pore size distribution was analyzed from adsorption branch isotherms by Barrett-Joyner-Halenda (BJH) method. Raman spectra were recorded on a LabRAM HR Raman microscope equipped with 532 nm laser source and 100× objective lens. The carbon powders were sandwiched with two glass slides before the test. Elemental analysis was performed on a Varlo ELIII elemental analyzer.

Catalytic Testing. Silanes (1.0 mmol), catalyst (20.0 mg), and alcohol (3.0 mL) were added into a 25 ml grass reactor with a stirrer. Then the reaction mixture was heated to certain temperature for several hours under stirring. After cooling to room temperature, 0.05 g dodecane was added as the internal standard, and the organic phase was collected by simple filtration. The products were analyzed by a GC (Shimadzu, GC-2014) and GC-MS (Waters, GCT Premier). GC was performed by using a GC-2014 instrument (Shimadzu) with a high-temperature capillary column (MXT-1, 30 m, 0.25 mm ID) and flame ionization detector (FID). GC–MS was performed on a GCT Premier instrument (Waters) with a capillary column (DB-5MS/J&W Scientific, 30 m, 0.25 mm ID). For the test of reusability, the used catalyst was separated from the reaction mixture by centrifugation. Then it was washed with ethanol for three times and dried in a vacuum oven at 60 °C overnight. The recovered catalyst was reused in the next run.

Computation Method. All of the calculations were conducted by using Vienna ab-initio simulation package (VASP) [4-7]. The interactions between valence electrons and ion cores were treated by Blöchl's all-electron-like projector augmented wave (PAW) method[8,9]. The adopted exchange-correlation function is the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof [10]. Akinetic energy cut off of 350 eV was used with a plane-wave basis set. The integration of the Brillouin zone was conducted using a 3×3×1 Monkhorst-Pack grid [11].Geometries were optimized until the energy was converged to 1.0×10^{-6} eV/atom and the force was converged to 0.05 eV/Å.

Owing to different bond forms of nitrogen, sulfur and carbon species (XPS analysis), real model contains a large number of possible configurations. To simplify the mathematical operation, the calculation model involves graphitic N, thiophenic S and graphitic C atoms. Four kinds of pure or doped graphene, pure, N-doped, S-doped, and N, S-codoped graphene, were stablished based on the 4 × 4 graphene slab. The structures were designed according to previous reference [12]. A vacuum layer as large as 20 Å was used along direction to avoid periodic interactions.

The adsorption energies of dimethyl-phenylsilane (dps) on various graphene slabs, ΔE_{ads}, is defined as follows:

$$\Delta E_{ads} = E_{dps/slab} - E_{slab} - E_{dps}$$

Where $E_{dps/slab}$, E_{slab} and E_{dps} are the total energy of dps on the graphene slabs, free graphene slab and the isolated dps molecules, respectively. The negative ΔE_{ads} indicates exothermic chemisorption, positive value suggests endothermic chemisorption. All of the adsorption energies are corrected by taking into account the effects of basis set superposition error estimated by using the counterpoise corrections method.

2. Supporting figures and tables
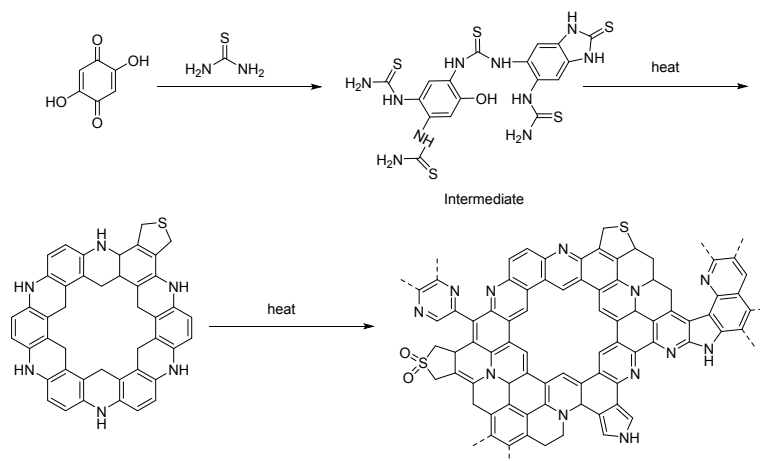
Scheme S1 The scheme of the reaction of 2, 5-dihydroxy-1, 4-benzoquinone and thiourea to prepare carbon material
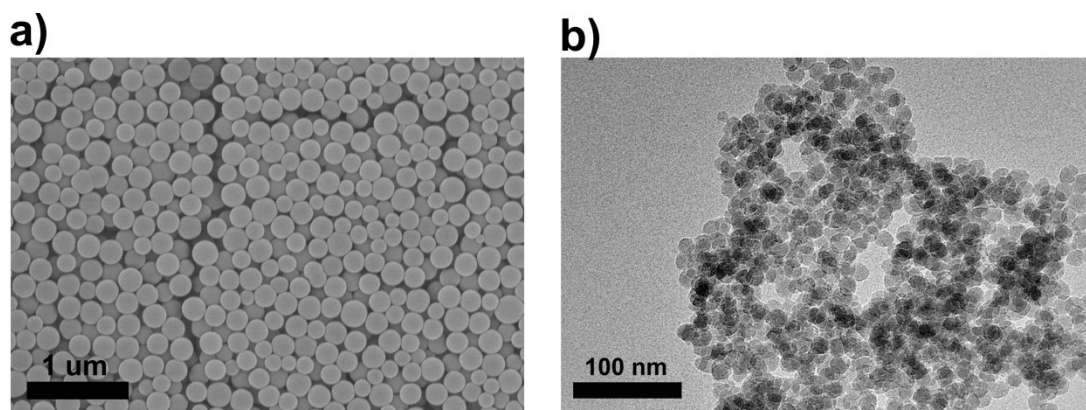
Fig. S1 SEM images of the SiO_2 spheres (a) and TEM image of commercial colloidal SiO_2 nanoparticles (b).
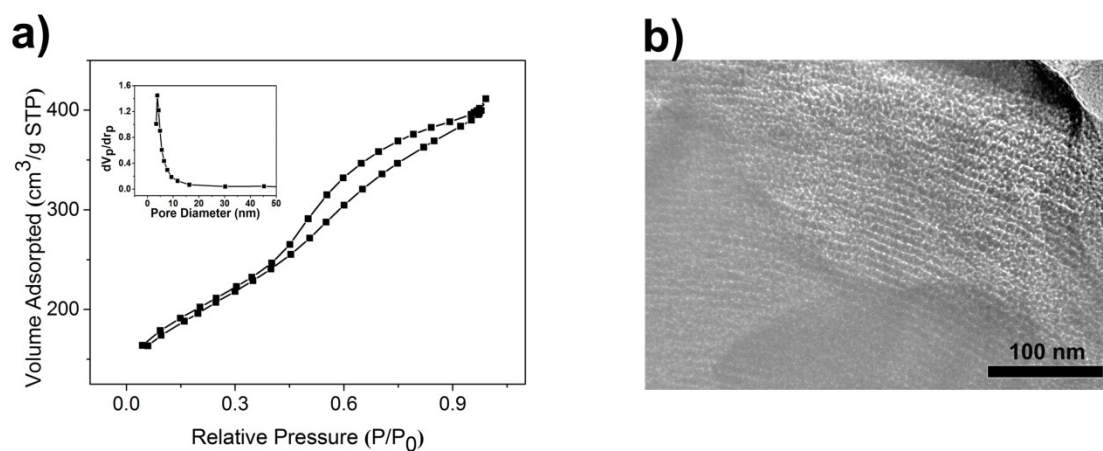

Fig. S2 a) Nitrogen adsorption/desorption isotherms and BJH pore-size distribution curves (insert) of NSPC-SBA derived from SBA-15 template and b) its TEM image.
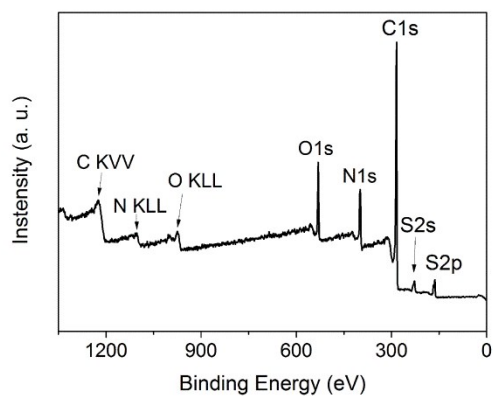
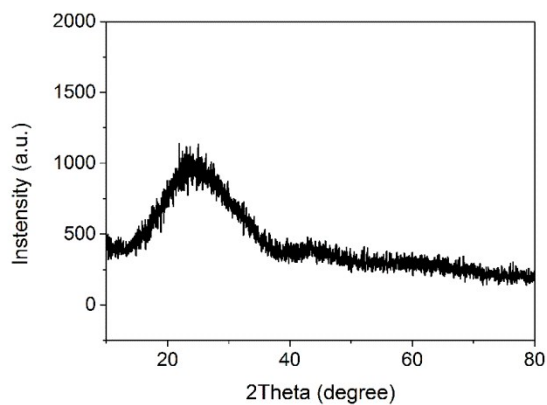Fig. S3 The XPS survey of the HPNSC material
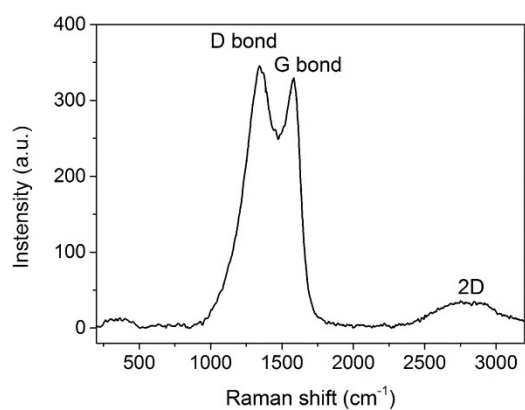

Fig. S4 XRD patterns of HPNSC material
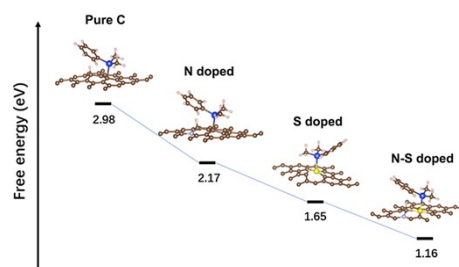

Fig. S5 Raman spectrum of the HPNSC material.

Fig. S6 The adsorption energies of dimethylphenylsilane on carbon materials doped with different heteroatoms. The white, brown, gray, blue and yellow balls stand for H, C, N, Si and S atoms, respectively.
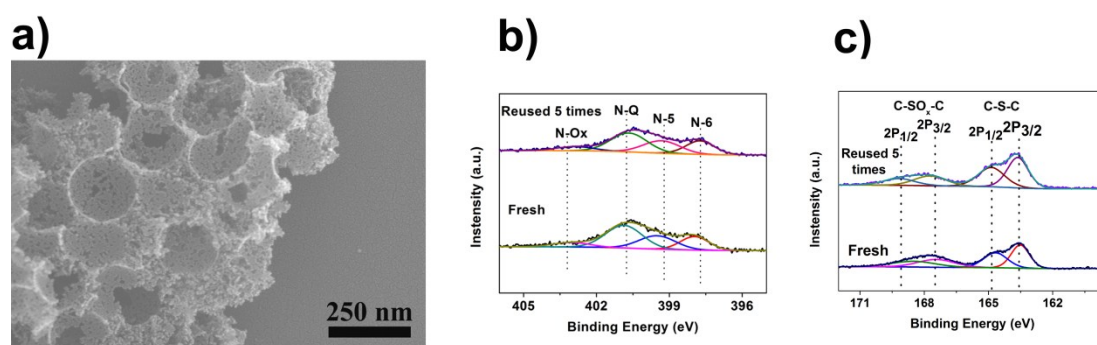

Fig. S7 a) SEM image of HPNSC catalyst after reused 5 times; b) high resolution of N 1s, and c) S 1s (d) XPS spectra for the fresh and the reused catalysts after the fifth recycling batch.

3. References

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