Supporting Information

Synthesis and Catalytic Activity of Heteroatoms Doped Metal-Free

Single-Wall Carbon Nanohorns

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Experimental Section

Synthesis of materials

SWCNHs was produced by using an arc-discharge method described in our previous report¹. But for the doping SWCNHs, some improvements have been made: Pure SWCNHs was produced by a DC arc-vaporization in 400 Torr pressure of CO, and N-doped SWCNHs was produced by a DC arc-vaporization in 400 Torr pressure of dried air. B-doped, P-doped, co-doped SWCNHs with different doped atom concentrations were respectively produced by a DC arc-vaporization of a B₄C-containing, PPh₃-containing, B₄C and PPh₃-containing composite carbon rod, and the doping atoms concentrations were varied between 0 and 5 atom % (At%).

In the heat treatment, the rough SWCNHs was roasted at 430° C for 1 h in the air to remove the amorphous carbon. After that, SWCNHs was oxidized by 30% H₂O₂ under 60° C in 5 hours to remove other impurities and improved its dispersibility in aqueous solution. Eventually, purified SWCNHs (CNH) and doped composites were obtained after being dried in a vacuum oven at 80° C for 9h.

Graphene in this work were produced by AC arc-discharge method in 400 Torr pressure of N₂: $H_2=1:2(v: v)$ and the current was held at 120 A, according to an improved method from Wang².

Catalytic test

The nitrobenzene reduction reaction was carried out in a sealed pressure tube at the set temperature for 3 h. For each reaction, 0.5 g nitrobenzene and 2 mL hydrazine hydrate (85%) were used as the reactants, 0.1 g dodecane and 40 mg carbon materials were used as the internal standard and the catalyst, respectively. After the reaction, 10 mL CH_2Cl_2 were added into the tube as the extraction liquid. Upon removal of the catalyst, the mixture was analyzed by AgilentGC7820A equipped with a HP-5 column and a FID detector.

Characterization

The morphologies of samples were characterized by a transmission electron microscopy at an accelerating voltage of 200 kV (TEM, JEOL-2100). The chemical states of elements and the content of dopants in the samples were investigated by X-ray photoelectron spectroscopy (XPS, Axis Ultra). Raman measurements were performed

under ambient conditions using a 633 nm laser in the back-scattering configuration on a Jobin-Yvon HR800 Spectrometer to obtain the contents of defect in the samples. Thermogravimetric analysis (TGA) was operated on a Q600 TGA thermogravimetric analyzer (Thermal Analysis Inc., USA) from room temperature to 1000°C at a rate of 10 °C /min under an air flow of 100 mL/min.

Table S1. The atomic percent of dopants in samples determined by XPS							
Sample	C (At %)	O (At %)	B (At %)	N (At %)	P (At %)		
B1-CNH	98.68	0.64	0.68	0	0		
B2-CNH	91.82	6.75	1.43	0	0		
B3-CNH	93.36	4.55	2.09	0	0		
B4-CNH	91.70	5.52	2.78	0	0		
NB-CNH	98.48	0.90	0.48	0.14	0		
NP-CNH	87.24	7.80	0	4.65	0.31		
NPB1-CNH	90.93	6.90	1.13	0.68	0.47		
NPB2-CNH	89.14	6.70	1.79	1.24	0.16		
NPB3-CNH	88.47	7.01	2.6	1.57	0.34		

Table S2. Reduction of nitrobenzene using the nanocarbon materials as catalysts at 80°C.

Entry	Catalysts	X(Nitrobenzene)/%	Y(Aniline)/%
1	B1-CNH	67.2	61.7
2	B2-CNH	80.7	76.5
3	B3-CNH	96.1	89.8
4	B4-CNH	64.3	62.4
5	N-CNH	23.4	17.3
6	P-CNH	57.0	47.9
7	NP-CNH	>99	91.1
8	NPB1-CNH	61.6	55.6
9	NPB2-CNH	>99	96.4
10	NPB3-CNH	49.9	49.4
11	NPB 4-CNH	29.4	20.1

Table S3.	Reduction	of nitrobenzen	e using the	doped S	SWCNHs as	catalysts at	70°C
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Entry	Catalysts	X(Nitrobenzene)/%	Y(Aniline)/%
1	NP-CNH	89.3	72.0
2	NPB2-CNH	90.1	76.5
3	B3-CNH	63.2	58.3



Fig. S1. TEM images of a) graphene and b) CNH. Inset shows high magnification image of protruded horns.



Fig. S2. TEM images of a) B1-CNH, b) B2-CNH, c) B3-CNH, and d) B4-CNH. Insets show high magnification image of protruded horns.



Fig. S3. TEM images of a) NPB1-CNH, b) NPB2-CNH, c) NPB3-CNH and d) NPB4-CNH. Insets show high magnification image of protruded horns.



 $Fig. \ S4. \ Raman \ spectra \ of \ D \ band \ /G \ band \ peak \ (I_D/I_G) \ of$

the samples are	e as follows:
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Sample	graphene	CNH	B1-CNH	B2-CNH	B3-CNH	B4-CNH	N-CNH	NB-CNH
I_D/I_G	0.55	1.17	0.83	0.56	0.33	0.56	0.83	0.58



Fig. S5. TGA curves of A: a) graphene and b) CNH; B: a) CNH and b) N-CNH; C: a) P-CNH and b) NP-CNH; D: a) B3-CNH, b) NP-CNH, and c) NPB2-CNH, respectively.

In TGA curves three main peaks can be classified and they respectively represent defective carbon (~514°C), tubular graphene carbon (~600°C) and graphitic carbon (~730°C)^{3, 4}. A main peak at 525°C and a concomitantly weak peak at 692°C exist in NP-CNH, corresponding to P-doped defective carbon and tubular graphene carbon. But for B3-CNH. there is a main peak at 685.4°C and a weak peak at 460.2°C, suggesting that it consists of mainly B-doped tubular graphene carbon and graphitic carbon. Most notably, NPB2-CNH shows two main peaks at 432.0°C and 672.9°C, separately, attributed to a combination of P-doped defective carbon and B-doped tubular graphene sheets, the different electron transfer reflects in the two apparent different peaks at 432.0°C and 672.9°C in DTG curve, respectively.

In order to clarify whether the graphitic impurities are essential for catalytic activity in this reaction, 40 mg pure graphite was used as catalyst to catalyze the reaction in same condition. Only 0.2 % yield of aniline was achieved. Therefore, residual graphitic impurities in CNH have no crucial function for catalytic activity.

References

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