

Nitrogen and Sulfur Co-Doped Carbon Nanospheres for Highly Efficient Oxidation of Ethylbenzene

Minghui Liu, Yingcen Liu, Zhanming Gao, Cui Wang, Wanyue Ye, Rongwen Lu,
Shufen Zhang*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian
116024, People's Republic of China.

Corresponding Author: * Rongwen Lu

E-mail: lurw@dlut.edu.cn

Figure S1 a–c shows the TEM images of the solution with time after reaction initiation, showing the formation process of colloidal nanospheres: (a) formation of small clusters, (b) aggregation of small clusters, and (c) growth of the colloidal nanospheres to nearly monodisperse colloidal nanospheres.

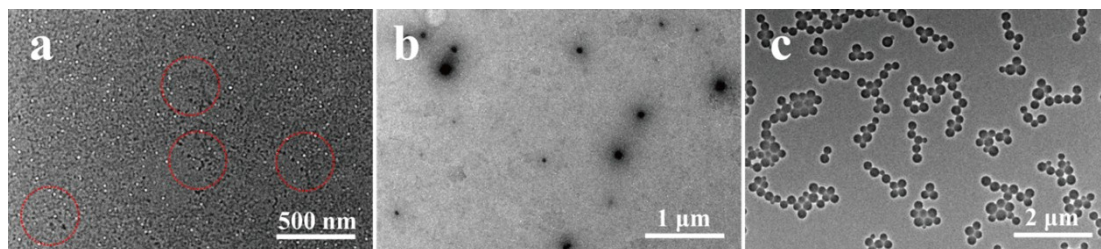


Figure S1. TEM images of the solutions (a–c) with time after the addition of formaldehyde (a, 13 min; b, 21 min; c, 90 min). The reaction was conducted in 50 mL water with the addition of melamine (0.063 g, 0.5 mmol), 2,4-diaminobenzenesulfonic acid (0.019 g, 0.01 mmol), ammonium hydroxide (0.034 mL), and formaldehyde solution (0.4 mL, 5 mmol).

Figures S2 a-c show the photographs of the solutions with time after the addition of formaldehyde. The solutions were left for 1 min at room temperature, during which they turned to turbid and the turbidity of the solution increased quickly within 1 hour.

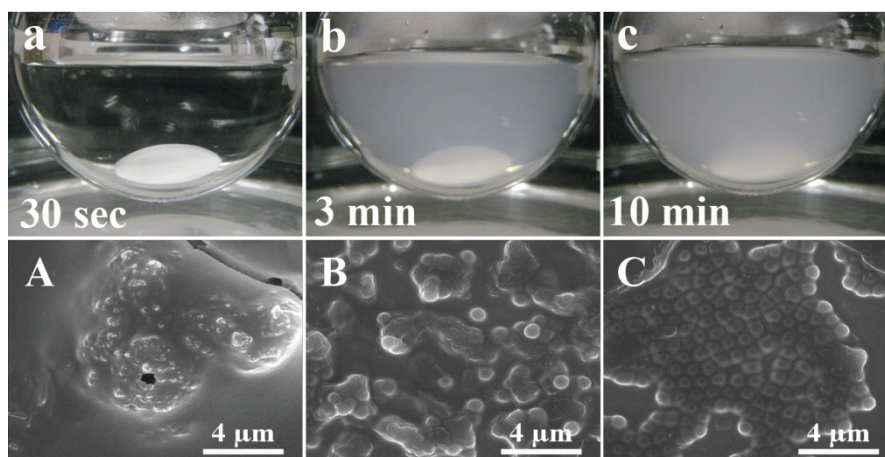


Figure S2. Photographs of the solutions (a–c) with time after the addition of formaldehyde (a, 30 sec; b, 3 min; c, 10 min) and the corresponding FESEM images (A–C). The reaction was conducted in 50 mL water with the addition of melamine (0.19 g, 1.5 mmol), 2,4-diaminobenzenesulfonic acid (0.057 g, 0.03 mmol), and ammonium hydroxide (0.1 mL), and formaldehyde solution (1.2 mL, 15 mmol).

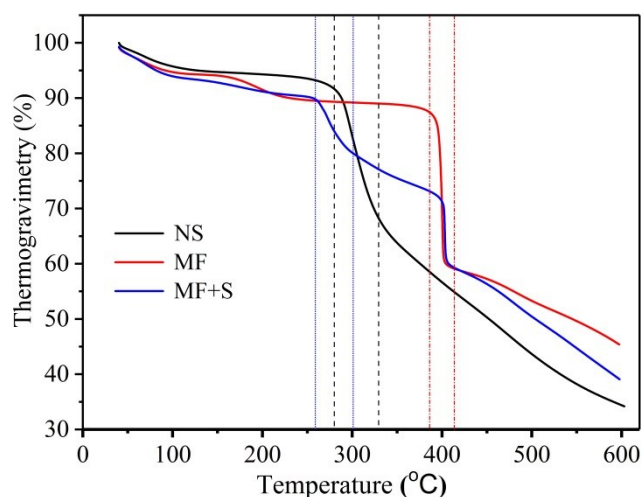


Figure S3. Thermogravimetric analysis of the synthesized colloidal spheres (NS, black line), melamine–formaldehyde spheres (MF, red line), and mixture of melamine–formaldehyde spheres and 2,4-diaminobenzenesulfonic acid (MF+S, blue line)

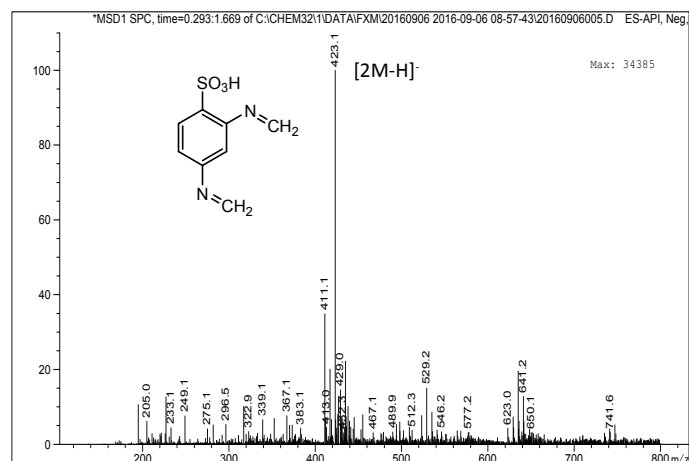


Figure S4. Negative electrospray ionization mass spectrum of mixture of 2,4-diaminobenzenesulfonic acid, formaldehyde and ammonia that stirred in water at 25 °C for 3 min.

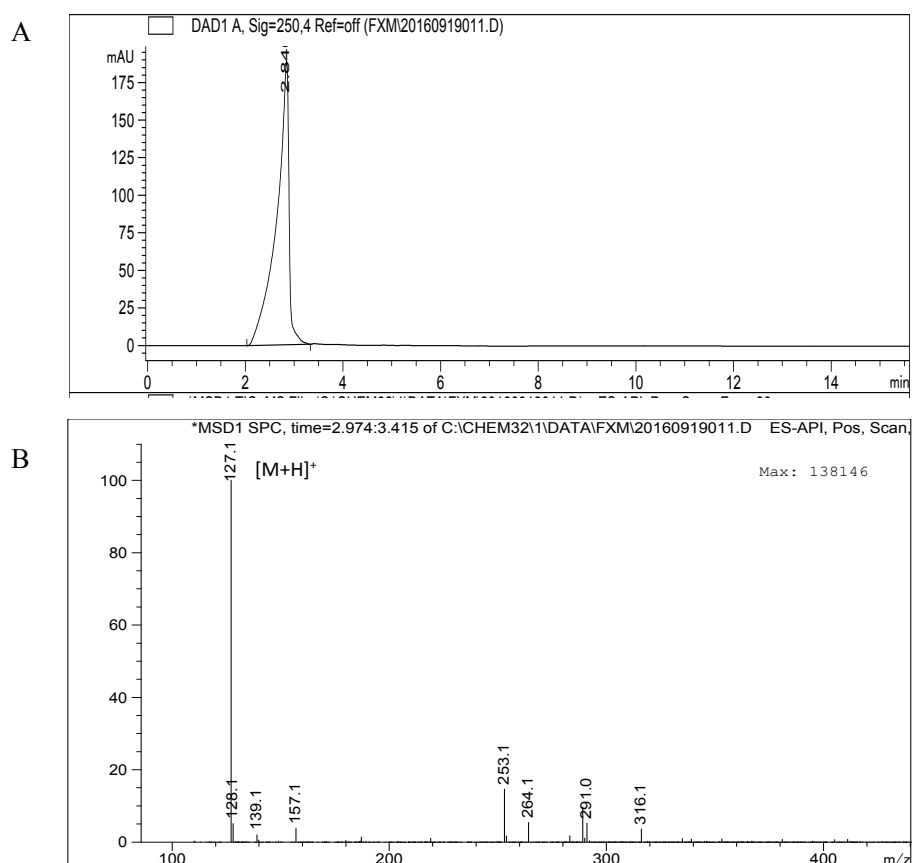


Figure S5. A) Liquid chromatogram of the mixture of melamine and formaldehyde (40 mL) that stirred in water at 25 °C for 24 h and B) corresponding positive electrospray ionization mass spectrum of component, which is consistent with the molecule weight of melamine.

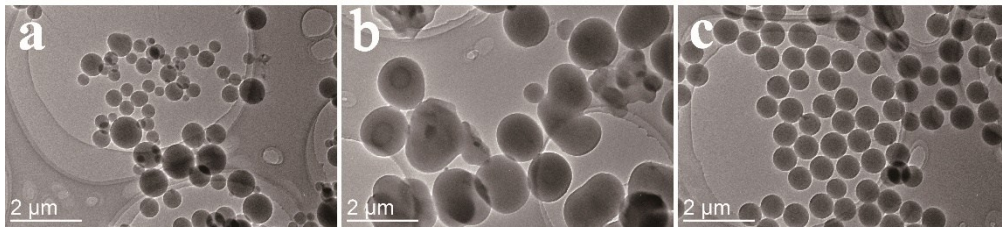


Figure S6. TEM images of the colloidal spheres obtained by using different reagents: a. benzenesulfonic acid, b. 1,3-diaminobenzene, and c. 2,4-diaminobenzenesulfonic acid.

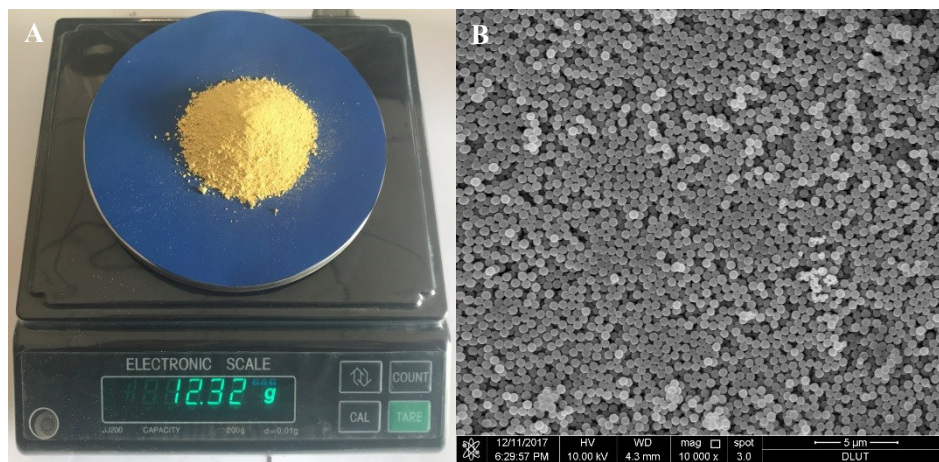


Figure S7. A) Photograph of the synthesized colloidal spheres produced in multigram scale and B) the corresponding FESEM image.

In Figure S8a, the broad peaks located around 16.5 and 33.4, indicated the amorphous structure of the obtained carbon¹. The diffraction characteristics exhibited by carbon materials may be attributed to nitrogen doping. In Figure S8b, two characteristic peaks located at 1348 cm^{-1} and 1574 cm^{-1} represented the D (disorder and defects) band and the G (graphitic) band²⁻³, respectively. The degree of ordering in the materials was evaluated by the intensity ratio between D and G bands. In a word, the XRD pattern and Raman spectrum reflected that carbon is amorphous.

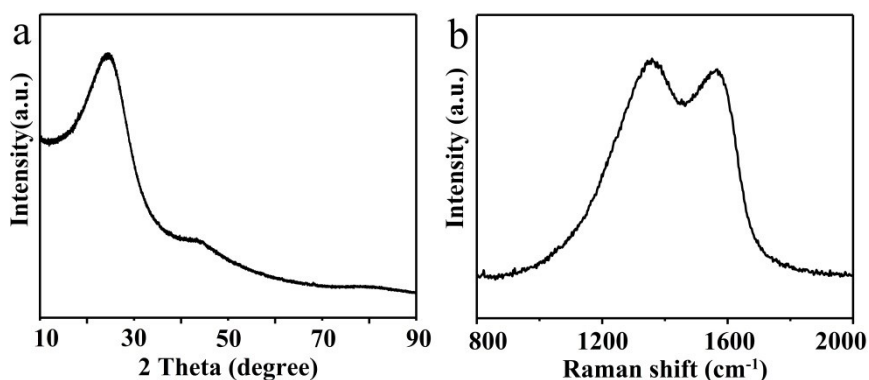


Figure S8. (a) XRD pattern and (b) FT-Raman spectrum of the NS-CNs materials.

Nitrogen adsorption experiments were performed to examine the pore characteristics of CSs, N-CSs, and NS-CSs (Figure S9 and Table S1). The CSs, N-CSs and NS-CSs exhibited typical I type adsorption-desorption isothermal. The Brunauer–Emmett–Teller (BET) surface areas, total pore volumes, and average pore sizes were summarized in Table S1. The data listed in Table S1 demonstrated that CSs, N-CSs and NS-CSs are mesopores. The average pore size of CSs is 3.21 nm, N-CSs is 25.14 nm and NS-CSs is 7.18 nm. Actually, it is the textural void space between the nanospheres since no pores of this scale were observed in TEM images. As shown in Table S1, N-CSs and NS-CSs possessed the specific surface area of 69.3 m²/g and 172.7 m²/g, respectively. It is obvious that the NS-CSs possessed a higher surface area, which is mainly due to different formation mechanisms of colloidal spheres.

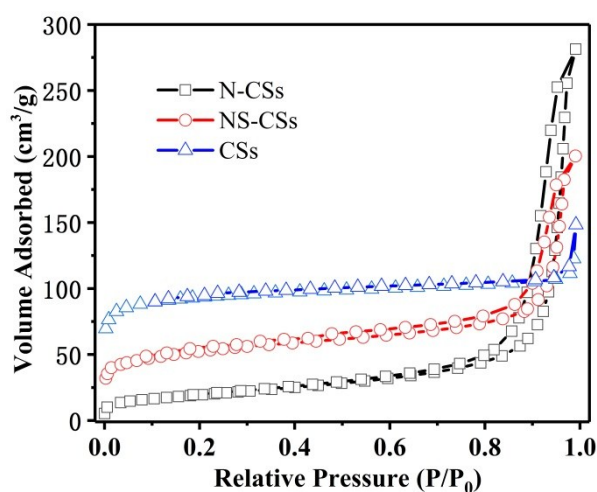
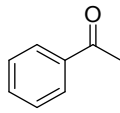
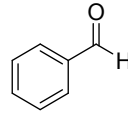
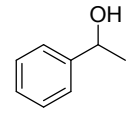
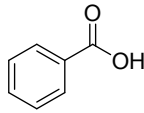


Figure S9. Nitrogen adsorption–desorption isotherms of CSs, N-CSs, and NS-CSs.

Table S1. Surface area and porosity of the prepared catalysts.

Catalyst	Surface area (m ² g ⁻¹)	Pore volume (m ³ g ⁻¹)	Average pore size (nm)
CSs	285.9	0.23	3.21
N-CSs	69.3	0.43	25.14
NS-CSs	172.7	0.31	7.18

Table S2. Catalytic activity of different carbon materials for the oxidation of ethylbenzene in the aqueous phase.

Catalyst	Conv.(%)	Yield(%)			
					
No catalyst	15.7	87.1	11.4	0.3	1.2
CSs	16.1	85.0	13.7	0.5	0.8
N-CSs	72.2	90.3	8.5	0.1	1.1
NS-CSs	93.9	94.2	4.7	0.4	0.7

Reaction conditions: Ethylbenzene (1.0 mmol), catalyst (0.01 g), TBHP (413 μ L, 70 wt% in water), H₂O (1.0 mL), 80 °C, 10 h.

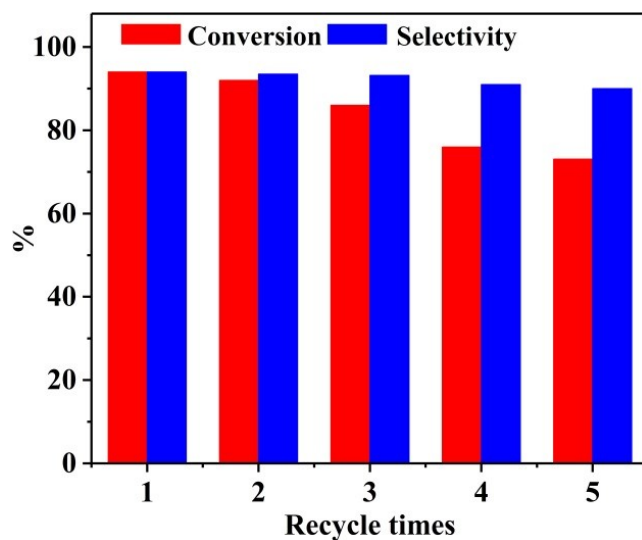


Figure S10. The recycle test of NS-CSs for catalytic oxidation of ethylbenzene.

Reference

1. C. Wang, W.-D. Wu, Y. Wang, D. Xu and F. Yan, *New J. Chem.*, 2017, **41**, 7392-7399.
2. W.-Q. Tian, X.-Y. Wu, K.-X. Wang, Y.-M. Jiang, J.-F. Wang and J.-S. Chen, *RSC Adv.*, 2013, **3**, 10823–10827.
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