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#### PAPER

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

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Nitrogen and sulfur co-doped carbon nanospheres (NS-CNs) have found broad applications in a large variety of areas due to their well tailed physicochemical properties. To achieve an efficient co-doping effect, the synthesis protocols usually rely on a stepwise procedure which particularly includes a post treatment of the N-doped precursors by using a sulfurcontaining material such as H<sub>2</sub>S and thiourea, accordingly making the process time-consuming and complicate in doping control. Here, we demonstrated an effective synthesis strategy to achieve a designated co-doping effect of carbon nanospheres through a molecular design of the precursors used for the formation of carbon nanospheres. Specifically, we identified an efficient co-polymerization process of both diaminobenzenesulfonic acid and melamine with formaldehyde, which forms uniform resin nanospheres at room temperature with both N and S inherited from the two reactants. After a carbonization process, carbon nanospheres were achieved with co-doped elements favorable for their applications. For example, high performance catalyst was demonstrated from this synthesis protocol with promising potential for the catalytic ethylbenzene oxidation.

#### Introduction

Compositional doping of carbon materials by different elements, particularly nitrogen and sulfur, have drawn increasing research attention. The existence of doping elements were able to endow the carbon materials interesting benefits such as good electrical conductivity, favorable chemical inertness, and high catalytic activity, thereby showing promising potentials in a wide range of research fields<sup>1-5</sup>. Moreover, co-doping of carbon materials by two or three elements with different electronegativities gives rise to a unique electron distribution and then results in a synergistic effects when used as catalyst<sup>6-8</sup>. Zheng et al.<sup>9</sup> indicated that the incorporation of B atoms into N-doped graphene created a synergistic coupling and significantly enhanced the activity of pyridinic N through a B–C–N bridge. Duan et al.  $^{\rm 10}$  incorporated sulfur and nitrogen atoms into graphene sheets and discovered that co-dopants (S and N) presented synergistically catalytic activity to enhance the peroxymonosulfate activation.

Although a co-doping effect has been highly apprecied by the research community, the synthesis for a successful doping effect with the capability to simultaneously introduce different elements into the carbon matrix has become a challenging issue. For an effective doping of both N and S elements, the pre-formation of a nitrogen-containing carbon precursor together with a post-treatment procedure to introduce sulfur is usually adopted. Different sulfur-containing precursors including element sulfur,

Na<sub>2</sub>S, and thiourea have been used to achieve a favorable sulfur doping after the high temperature treatment<sup>11-13</sup>. In addition to such a step-wise route, other synthetic routes<sup>14</sup>, typically hydrothermal based ones, have also found to be successful to simultaneously introduce different elements into the carbon structure. Despite of the success in composition control, it is noted that the current synthesis routes usually involve complicated process which are usually time and energy consuming with the use of expensive starting reagents. From the synthesis point of view, it is highly favorable that simple and economic methods be developed for the co-doping process with the use of environmental benign materials. It is equally important that the synthesis be efficient for compositional control with the potential for scale up production.

Here, we demonstrated that an effective synthesis strategy to achieve a designated co-doping effect of carbon nanospheres through a molecular design of the precursors used for the formation of carbon nanospheres. Specifically, 2,4-diaminobenzenesulfonic acid was used as the sulfur-containing reactant, which is a water soluble aromatic amine widely used in the production of dyes. The two imine groups formed by the condensation of 2,4-diamino-benzenesulfonic acid and formaldehyde, could crosslink with the nitrogen-containing species of melamine via the addition reaction, and later on nitrogen and sulfur containing colloidal spheres can form after the further polymerization. A following carbonization process at high temperature can produce carbon nanospheres with a uniformlydispersed both nitrogen and sulfur. Our preliminary test showed that the co-doped carbon nanospheres are highly active for the catalytic oxidation of ethylbenzene, which is a crucial process for converting ethylbenzene to acetophenone.

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, People's Republic of China. E-mail: lurw@dlut.edu.cn Electronic Supplementary Information (ESI) available:

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#### **Experimental details**

**Materials.** 2,4-diaminobenzenesulfonic acid ( $\geq$ 98.0%) was purchased from Aldrich. Tert-butyl hydroperoxide (70% aqueous solution) was acquired from J&K scientific Ltd. Melamine, formaldehyde (37 wt% - 40 wt%), ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, 25% - 28%), and ethanol were from Sinopharm Chemical Reagent Co., Ltd. All chemicals were AR-grade and used without further purification. Deionized water (18.2 M $\Omega$ ) was used in all experimental processes as needed.

## Preparation of the Nitrogen and Sulfur Co-Doped Colloidal Spheres.

The nitrogen and sulfur co-doped colloidal spheres were synthesized through a one-pot method. Typically, melamine (0.19 g, 1.5 mmol), 2,4-diaminobenzenesulfonic acid (0.057 g, 0.3 mmol), and ammonium hydroxide (0.1 mL) were added into deionized water (50 mL) in a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer and a thermometer. Then, the mixture was heated to 25 °C under stirring to obtain a transparent solution. Afterward, formaldehyde solution (1.2 mL, 15 mmol) was added to the system. After 1 h of stirring, a suspension of particles was obtained. The suspension was centrifuged at 6000 rpm for 10 min and the products were washed by ethanol (30%) three times to remove the remaining unreacted materials. After drying at 100 °C for 10 h, the light yellow product was obtained.

For comparison, resorcinol-formaldehyde spheres were prepared using resorcinol/formaldehyde as polymer precursor by using the reported method<sup>15</sup>. Melamine-formaldehyde spheres were synthesized from melamine and formaldehyde according to the method reported<sup>16</sup>.

**Carbonization.** The synthesized colloidal sphere was carbonized at 500 °C under N<sub>2</sub> flow for 2 h with a heating rate of 2.5 °C·min<sup>-1</sup>. The product was denoted as **NS-CSs**. The carbonized resorcinol/formaldehyde spheres were denoted as **CSs**, and the carbonized melamine-formaldehyde colloidal spheres were denoted as **N-CSs**.

Characterization. Field emission scanning electron microscopy (FESEM) images were recorded on a Nova Nano-SEM 450 microscope at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained using an FEI-TF30 transmission electron microscope at 300 kV. Fourier transform infrared FT-IR spectroscopy was performed on a NICOLET 6700 spectrometer, equipped with an attenuated total reflection (ATR) setup. <sup>13</sup>C and <sup>15</sup>N cross-polarization magic angle spinning (CP-MAS) NMR spectrum were obtained on an Agilent DD2-500 MHz at 125.7 MHz and 50.6 MHz, spining rate of 11 kHz and 7 kHz, respectively. <sup>13</sup>C and <sup>15</sup>N cross-polarization were performed both using a contact time of 4 s. X-ray photoelectron spectroscopy (XPS) was acquired by Thermo VG ESCALAB 250 with a Al-Ka X-ray source operating at 150 W (15 kV).The nitrogen adsorption/desorption isotherms were measured using a 3H-2000PS1, Beishide Instrument Technology Co., Ltd., China, and the surface area and pore size found using the Brunauer-Emmett-Teller (BET) method. The binding energies were calibrated using the C 1s peak at 284.6 eV, and the software XPS PEAK 4.1 was used for Curve fitting. Elemental analysis was

obtained on an Elementar Vario Macro EL Cube microanalyzer. Thermogravimetric (TG) analysis was recorded on TGR Q 500 with a heating rate of 10  $^{\circ}$ C· min<sup>-1</sup> under a nitrogen flow (100 mL· min<sup>-1</sup>) or in air.

**Catalytic Reaction.** Ethylbenzene (1.0 mmol), catalyst (0.01 g), tertbutyl hydroperoxide (413  $\mu$ L, 3.0 mmol, 70 wt% in water), and water (1 mL) were introduced into a 10 mL glass reactor sealed with Teflon lid. The reaction mixture was stirred in a preheated 80 °C oil bath for 10 h. After that, 80  $\mu$ L of anisole was added to the system as an internal standard. Then CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL) was added to extract organic compounds from the reaction system. The organic phase was filtrated with a 220  $\mu$ m size of oil film and analyzed by Agilent 6820 GC with a HP-5 capillary column (30 m×0.25 mm×0.25  $\mu$ m) and an Agilent GC-MS, with He gas as carrier gas. The temperature program was set from 120 °C (maintained for 2 min) to 280 °C by 10 °C/min for the detection of oxidation of ethylbenzene. For the recovery of catalyst, the catalyst was separated by centrifugation and washed with ethanol three times and dried under 50 °C for 10 h.

#### **Results and Discussion**

The preparation of the monodisperse nitrogen and sulfur codoped carbon spheres is illustrated in Figure 1. Briefly, the formation of nanospheres is initiated with the addition of formaldehyde to the solution of 2,4-diaminobenzenesulfonic acid and melamine at room temperature. A Schiff base was formed by the reaction between 2,4-diaminobenzenesulfonic acid and formaldehyde. Then the subsequent addition of amino groups on melamine to the newly formed imine groups (-C=N-) induced the cross-linking of 2,4-diaminobenzenesulfonic acid and melamine and hence the formation of small clusters (Figure S1a). Afterwards, the small clusters self-aggregated to form colloidal nanospheres in order to minimize the total surface energy (Figure S1b)<sup>17</sup> and grew to nearly monodisperse colloidal nanospheres within a matter of a few minutes (Figure S1c). Finally, nitrogen and sulfur co-doped carbon nanospheres (denote as NS-CSs) were obtained by direct carbonization of the colloidal spheres.



**Figure 1.** Schematic representation of the preparation of nitrogen and sulfur co-doped carbon spheres from 2,4-diaminobenzenesulfonic acid, melamine, and formaldehyde.

Figure 2 shows the TEM image and corresponding elemental mapping of **NS-CSs**. Figure 2a shows the spherical morphology of the **NS-CSs**, which were obtained from the carbonize of the colloidal spheres that synthesized by stirring the reaction mixtures for only 1

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h. Figure 2b and 2c confirm the presence and homogenous distribution of N and S in **NS-CSs**. The content of N, S was 53.8% and 0.3%, respectively. Importantly, the elemental mapping images reflect the fact that the in situ incorporation of a N and S in colloidal spheres can obtain well-distributed N and S co-doped carbon spheres, which is benefit for using as a catalyst<sup>18, 19</sup>.



Figure 2. (a) BF-STEM image, (b) elemental mapping images and (c) EDS of NS-CSs.

The rapid formation of colloidal spheres in solution was evidenced by the corresponding 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). In addition, amorphous solids were observed in the image (Figure S2 A) after drying of a drop of the reaction mixtures left for 30 sec, a very clear solution (Figure S2 a) on the silicon substrate. The conversion of clear solution to amorphous solids further reflected the rapid reaction of the mixture. After 3 min reaction, a small amount of microspheres were found in the image (Figure S2 B). After 10 min reaction, microspheres can be clearly seen, showing the rapid formation of colloidal spheres (Figure S2 c).



Figure 3. FTIR spectra of 2,4-diaminobenzenesulfonic acid (a), melamine (b), and the synthesized colloidal spheres (c)

The successful incorporation of 2,4-diaminobenzenesulfonic acid in the build-up of the colloidal spheres as well as high conversion of the functional groups initially present in the starting materials was confirmed by Fourier transform infrared (FTIR) spectroscopy (Figure 3). Bands which can be attributed to the amino group of 2,4-diaminobenzenesulfonic acid at 3384 and 3322 cm<sup>-1</sup> (NH<sub>2</sub> stretching vibration), as well as to the amino group of melamine at 3469 and 3422 cm<sup>-1</sup> (NH<sub>2</sub> stretching vibration) and 1620 cm<sup>-1</sup> (NH<sub>2</sub> deformation vibration) are absent in the spectrum of the colloidal spheres. The distinct bands corresponding to asymmetric stretching vibration (1169 cm<sup>-1</sup>) of S=O, stretching vibration of C-N (1335 cm<sup>-1</sup>) and the quadrant (1552 cm<sup>-1</sup>) and semicircle stretching (1489 cm<sup>-1</sup>) vibrations of the triazine ring are present in the spectrum of the colloidal spheres<sup>20</sup>, indicating the successful incorporation of 2,4-diaminobenzenesulfonic acid and melamine into the network. While, no bands that may be attributed to imine linkages such as the C=N stretching vibration around 1600 cm<sup>-1</sup> are found in the FTIR spectrum of colloidal spheres, implying the subsequent attacking of the imine double bond, formed from reaction of 2,4-diaminobenzenesulfonic acid and formaldehyde, by the primary amine groups of melamine and the generation of an aminal.

To further confirm the successful incorporation of 2,4diaminobenzenesulfonic acid and melamine into the network, a detailed analysis of the materials chemical structure was performed by <sup>13</sup>C and <sup>15</sup>N solid-state NMR spectroscopy (Figure 4). The <sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) NMR spectrum of colloidal spheres shows eight resonances at 167, 156, 145, 130, 103, 119, 96, and 60 ppm, respectively. The signal at 167 ppm can be ascribed to the carbon atoms in the triazine ring of the melamine, whereas the signals at 156, 145, 130, 103, 119, 96 ppm originates from the CH aromatic carbons of the benzene ring of 2,4diaminobenzenesulfonic acid.



**Figure 4.** <sup>13</sup>C CP-MAS (a) and <sup>15</sup>N CP-MAS (b) NMR spectrum of the synthesized colloidal spheres. The asterisk denotes spinning side bands.

The resonance at 60 ppm can be assigned to the secondary carbon atoms formed upon addition of the primary amine groups of melamine to the newly formed imine double bond. Moreover, <sup>15</sup>N CP-MAS NMR spectrum of colloidal spheres shows two major resonances at -207 and -285 ppm, respectively. The signal at -207 ppm can be ascribed to the nitrogen atoms in the triazine ring, whereas the signal at -285 ppm can be attributed to the secondary amine present in the aminal. Importantly, no signals from unreacted primary amine groups are detected in the <sup>13</sup>C and <sup>15</sup>N CP-MAS NMR spectra of colloidal spheres, which is in accordance with the results from the FTIR analysis. In addition, no resonance at around -55 ppm corresponding to an imine nitrogen is found. Hence, the formation of the aminal in the cross-linking step mentioned above is further confirmed.

TG analysis (under nitrogen with a heating rate of 10 °C·min<sup>-1</sup>) also shows the structural difference between synthesized colloidal spheres, melamine-formaldehyde spheres, and mixture of

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melamine-formaldehyde spheres and 2,4-diaminobenzenesulfonic acid. As shown in Figure S3, the TG curve of melamineformaldehyde spheres exhibits an obvious weight loss at 400 °C and mixture of melamine-formaldehyde spheres and 2,4-diaminobenzenesulfonic acid shows a two steps weight loss in the temperature range of 255 °C to 400 °C, which can be attributed to the gradual decomposition of 2,4-diaminobenzenesulfonic acid and the decomposition of melamine-formaldehyde spheres. While, the TG curve of the synthesized colloidal spheres shows an intricate thermal decomposition process. This continuous, slow weight loss can be ascribed to the transformation of a thermally unstable polymer (containing C, H, O, and S) to a stable nitrogen and sulfur co-doped carbonaceous materials<sup>21</sup>. This further proves that 2,4diaminobenzenesulfonic acid was not simply embedded inside the synthesized colloidal spheres.

To better understand the nature of 2,4-diaminobenzenesulfonic acid, electrospray ionization mass spectrometry was used for the analysis of mixture of 2,4-diaminobenzenesulfonic acid, formaldehyde and ammonia that stirred at 25 °C for 3 min. As shown in Figure S4, the spectrum of the three-component mixture contains peaks at m/z 423.1 in the m/z range from 100 to 800, which corresponds to the species [2M-H]<sup>-</sup> of the Schiff base formed from 2,4-diaminobenzenesulfonic acid and formaldehyde. We thus propose that imine groups were formed via Schiff base reaction. This is consist with the fact that the formation of Schiff base from aromatic amine and aldehyde could conduct under room temperature<sup>22</sup>. Besides, mixture of melamine, formaldehyde and ammonia was also analyzed by LC-MS and no other products were detected (Figure S5). Although melamine is also a primary amine, in fact, the reaction of -NH<sub>2</sub> groups of melamine with formaldehyde should be reliably conducted at a temperature of 50 °C<sup>16</sup>, reflecting that 2,4-diaminobenzenesulfonic acid is more active than melamine. So, it is reasonable to say that in the reaction mixtures, 2,4-diaminobenzenesulfonic acid convert to Schiff base preferentially and then melamine, a primary amine with higher concentration in the mixtures, add to the newly formed imine (-C=N-) groups and form polymeric colloidal spheres.

To further illustrate the role of 2,4-diaminobenzenesulfonic acid, supplementary experiment was carried out in the absence of 2,4-diaminobenzenesulfonic acid while keeping the other reaction conditions the same as those of this synthesized colloidal spheres. As a consequence, the reaction solution kept clear and no solid spheres obtained. This indicates that the 2,4-diaminobenzenesulfonic acid is indeed necessary to generate nanospheres. Besides 2,4diamino-benzenesulfonic acid, two other aromatic compounds. namely, an aromatic sulfonic acid without amino group (benzenesulfonic acid), and a diaminobenzene without sulfonic acid group (1,3-diaminobenzene), were employed to synthesize colloidal spheres under the same reaction conditions. Even by prolonging the reaction time to 375 min, the reaction solution kept clear when benzenesulfonic acid presented. Despite the reaction solution turned to turbid after 28 min when 1,3-diaminobenzene employed, but the obtained nanoparticles were non-spherical and were agglomerated. While, the particles are spherical and in nonagglomerated state with the presence of 2,4-diaminobenzenesulfonic acid as motioned above. These are clear indication that amino groups on benzenesulfonic acid are essential for the formation of colloidal particles and the sulfonic acid group could inhibit the aggregation of the particles. In another words, 2,4-diaminobenzenesulfonic acid

acts as a crosslinker, a stabilizer and also a source of N and S during the synthesis of colloidal spheres like cysteine did in the synthesis of phenolic resin based polymer spheres<sup>23</sup>. Thus, a molecule containing both diamino and sulfonic acid group is an indispensable factor for achieving this colloidal spheres (see Figure S6 in supporting information).

The use of other aromatic polyamines such as 2,4,6-triaminopyrimidine, 4,4',4"-triaminotriphenylamine, 1,2,4-benzenetriamine, and 1,5-diaminonaphthalene to replace melamine succeeded in generating nitrogen and sulfur containing colloidal spheres also. The corresponding FESEM images of the products are shown in Figure 5. Hence, this is a general route toward the synthesis of nitrogen and sulfur co-doped carbon spheres from 2,4-diaminobenzenesulfonic acid and aromatic polyamines.



**Figure 5.** FESEM images of the products obtained from the reaction of (a) 2,4,6-triaminopyrimidine, (b) 4,4',4''-triaminotriphenylamine, (c) 1,2,4-benzenetriamine, and (d) 1,5-diaminonaphthalene with 2,4-diaminobenzenesulfonic acid and formaldehyde, respectively.

It is worthy to note that this general method enables nitrogen and sulfur co-doped carbon spheres to be easily scaled up to multigram level with yield up to 90.3% with no special apparatus (Figure S7). X-ray photoelectron spectroscopy (XPS) analysis was employed to investigate the electric states of the surface elements of NS-CSs and the results are shown in Figure 6. The full spectrum of NS-CSs shows four typical peaks of C 1s, N 1s, O 1s and S 2p<sup>24</sup>. The C 1s peak of the NS-CSs can be split into two peaks including C-C (ca. 284.6 eV), C-O/C-N/C-S (ca. 286.3 eV, 288.5 eV) <sup>24, 25</sup>. The N 1s spectrum of the NS-CSs shows peaks centered at 398.4 eV and 399.9 eV, which can be assigned to pyrrole N and pyridinic N, respectively<sup>25, 26</sup>. Meanwhile, the S 2p spectrum of the NS-CSs shows peaks centered at 163.9 eV, 164.9 eV, and 167.8 eV, which corresponds to C–S, C=S, and C-SO<sub>x</sub> bonds<sup>18, 25</sup>. These results demonstrate that nitrogen and sulfur atoms have successfully incorporated into the NS-CSs. Besides, XRD and Raman analyses of the material were also conducted and the results indicated that carbon of the material is amorphous (see Figure S8 in supporting information).

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Figure 6. (a) Survey XPS spectra of NS-CSs, and high resolution spectra for the elements of (b) C, (c) N, and (d) S.

The porous properties of **CSs**, **N-CSs** and **NS-CSs** were characterized by nitrogen adsorption–desorption experiments. The **NS-CSs** exhibit typical I type adsorption desorption isothermal, indicating the porous structure of **NS-CSs** (Figure S9 and Table S1). The porous structures are beneficial for catalysis.

To test the catalytic performance of this **NS-CSs** for the selective oxidation of C-H bonds, ethylbenzene was chosen as a substrate to explore the efficiency. For comparison, control samples including the carbonized resorcinol/formaldehyde spheres (denote as **CSs**) and the carbonized melamine-formaldehyde colloidal spheres (denote as **N-CSs**), were also tested.



**Figure 7.** Catalytic activity of different carbon materials for the oxidation of ethylbenzene in aqueous phase.

We firstly examined the oxidation of ethylbenzene in aqueous phase with tert-butyl hydroperoxide (TBHP) as the oxidant without using catalyst. The conversion of ethylbenzene was only 15.7% with the selectivity 87.1% for acetophenone (Figure 7). Then we used **NS-CSs** as the catalyst for this reaction. As expected, **NS-CSs** activated ethylbenzene at 353 K to generate acetophenone in

94.2% selectivity with an ethylbenzene conversion of 93.9%. While. the conversion of ethylbenzene was only 16.1% with the selectivity 85.0% for acetophenone when CSs used, which was almost the same with control experiment. The conversion reached to 72.2% with the selectivity of 90.3% for acetophenone when N-CSs used, reflecting the enhancement of catalytic activity via N-doped. The 94.2% selectivity and 93.9% conversion, a much better than those of the test samples, catalyzed by NS-CSs proved the further improvement of catalytic activity via N and S co-doped (see Table S2 in supporting information for the detailed results of the oxidation). This result is comparable to or even better than those of nitrogen-doped graphene or nitrogen, phosphorus, and sulfur codoped carbon catalysts<sup>27, 28</sup>. Besides, the catalyst stability was tested with five cycles, during which the selectivity of the catalyst didn't change, although the conversion rate decreased gradually (see Figure S10 in supporting information).

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#### Conclusions

In summary, we developed a newly designed strategy to synthesize nitrogen and sulfur containing colloidal spheres from diaminobenzenesulfonic acid and aromatic polyamines by a facile Schiff base formation and addition of amino group to the imine group (-C=N-) of Schiff base under ambient condition, avoiding high reaction temperature, complicated time-consuming processes, or expensive starting reagents. The well-distributed N and S co-doped carbon spheres were obtained after carbonization of the formed colloidal spheres. When used as a catalyst for selective oxidation of ethylbenzene in aqueous solution, the prepared NS-CSs showed comparable activity and selectivity compared with other nitrogendoped graphene layered carbon or nitrogen, phosphorus, and sulfur co-doped hollow carbon shell catalysts, reflecting the co-doping effect achieved through the successful co-doping of both N and S in the carbon nanospheres. These findings provide a new strategy for the design and synthesis of well-distributed N and S co-doped carbon materials from large-scale industrial chemicals for a variety of fundamental studies and applications, including catalysts, sorbing materials, and high-performance electronics.

#### **Conflicts of interest**

There are no conflicts to declare

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## TOC:



A facile synthesis of well-distributed N and S co-doped carbon spheres and its enhanced activity on selective oxidation of ethylbenzene.