

Formation of Nitrogen-Doped Mesoporous Graphitic Carbon with the Help of Melamine

Ruimin Li,[†] Anmin Cao,[†] Yanjun Zhang,[†] Gen Li,[†] Feng Jiang,[†] Shumu Li,[†] Daiqin Chen,[†] Chunru Wang,[†] Jiechao Ge,^{*,‡} and Chunying Shu^{*,†}

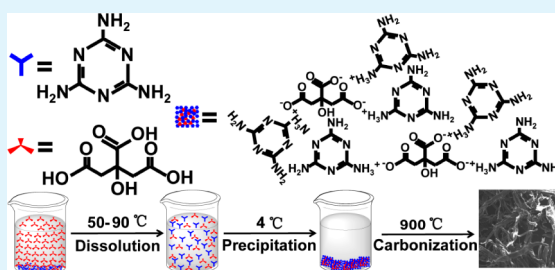
[†]Beijing National Laboratory for Molecular Sciences, Key Laboratory of Molecular Nanostructures and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[‡]Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

Supporting Information

ABSTRACT: An efficient and facile synthesis method of nitrogen-doped mesoporous graphitic carbon (NMGC) was reported with melamine as a nitrogen source and citric acid as a carbon source. By taking advantage of the functional groups on melamine and citric acid, a uniform mixture of these two components was obtained via a self-assembly process. Accordingly, the nitrogen-doped mesoporous graphitic carbon (NMGC) can be obtained by means of the high temperature treatment. This as-prepared NMGC showed a promising potential as an anode material in lithium-ion batteries.

KEYWORDS: melamine, mesoporous, self-assembly, graphitic carbon



The carbon materials with mesoporous structures have a lot of specific features including large surface area, thermal and chemical stability, hydrophobic surface properties, and mesoporous network.^{1,2} Mesoporous carbons have attracted great attention owing to their potential applications, such as molecular adsorbents, catalyst supports, electrode materials for supercapacitors, fuel cells, Li-ion batteries, etc.^{3–5} To date, the synthesis of mesoporous carbon materials has been widely studied, which promotes the development of modern science and technology.

Various synthetic routes have been proposed to produce carbon framework with mesostructure.^{6–8} A typical approach for the synthesis of mesoporous carbon is the hard-templating approach (i.e., nanocasting strategy), including the first synthesis of the carbon precursor/hard template complex materials, subsequent carbonized procedure, and finally dislodging of the template.^{9,10} For example, Wang et al. synthesized N-doped mesoporous carbon materials through the thermal decomposition of lysine and melamine under nitrogen atmosphere, using SiO₂ nanoparticles as hard templates and ferric chloride as a dopant.¹¹ However, the procedure involves multistep routines, time-consuming and high-cost production, which cannot meet the applications in a large scale. To overcome this disadvantage, researchers have recently used a soft-templating route as a universal route for the preparation of mesoporous carbon via self-assembly of some amphiphilic block copolymers and phenolic resins.^{12–14} For instance, Wu et al. used the template molecule EO106-PO70-EO106 to react with the resin building block. An ordered body-centered cubic mesostructure was obtained during the self-assembly process.

After carbonization, the carbon materials with mesostructure were obtained.¹⁵ Although this soft-templating approach provides an alternative route to prepare mesoporous carbon via direct self-assembly, the scale-up production of graphitic carbon with uniform mesostructure, in any case, still remains a challenge.

Herein, we design a simple fabrication of mesoporous graphitic carbon materials with narrow size distribution. Melamine is an ordinary and inexpensive raw material in the chemical industry with rich nitrogen content. As a nitrogen-enriched organic molecule, melamine has been commonly used as a nitrogen-source molecule for the N-doped carbon synthesis.¹⁶ In this work, melamine in hot water could self-assembly with citric acid to obtain a high-content nitrogen precursor in cold environment.^{17,18} By carbonization of the precursor, N-doping mesoporous graphitic carbon (NMGC) materials with high special surface area, uniform size and high N content were obtained. More importantly, in the system, all reagents are commercially available and inexpensive, and a mild and facile reaction condition is enough for the synthesis of high nitrogen-containing precursors in a large scale.

The synthetic strategy is schematically illustrated in Figure 1. In brief, melamine and citric acid were first added in Mini-Q water. Citric acid quickly dissolved, whereas melamine dissolved slowly in hot water (50–90 °C). Then a transparent aqueous solution was obtained. When the hot solution was

Received: September 9, 2014

Accepted: October 31, 2014

Published: October 31, 2014

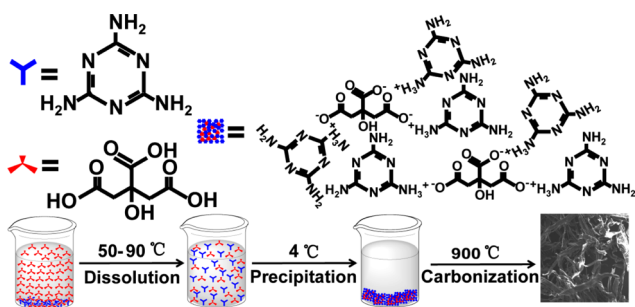


Figure 1. Schematic illustration of the synthesis process of nitrogen-enriched mesoporous graphitic carbon (NMGC) materials.

cooled down to 0–15 °C, some white flocculus precipitates appeared. To demonstrate that the as-obtained precursor was a uniform mixture of these two components via a self-assembly process, elemental mapping images of C, N, and O (see Figure S1 in the Supporting Information) were acquired. The results suggest that N and O elements are homogeneously dispersed in the banded precursors. The elemental analysis of carbon, nitrogen and hydrogen was also performed on an elemental analyzer, and the result revealed that melamine and citric acid coexisted in a molar ratio of 3:1 as listed in Table S1 in the Supporting Information. According to the references,^{17,18} we concluded that citric acid molecules were ionized in the presence of melamine molecules. As a result, amine nitrogen atom with a positive charge of melamine electrostatically interacts with carboxylic acid head with a negative charge of citric acid to precipitate together as shown in Figure 1. Upon the following carbonization procedure, striplike carbon materials were obtained.

As shown in Figure S2a in the Supporting Information, the XRD pattern of the as-obtained carbonaceous materials gives a broadened peak near 25.2°, corresponding to the (002) Bragg reflection of graphite. This result indicates that the as-prepared carbon materials are amorphous and consist of graphite crystallites and disordered areas.¹⁹ As shown in Figure S2b in the Supporting Information, the Raman spectra of carbonaceous materials demonstrate an obvious graphitic quality with the G-band (about 1590 cm⁻¹) and D-band (about 1340 cm⁻¹). The cooccurrence of the two bands suggests that the existing carbons are fractionally graphitized with some defects and disorders.²⁰

The C, H and N elemental analysis were performed for the as-obtained carbonaceous materials on an elemental analyzer. The N content in the as-obtained carbon materials is 10.02% as shown in Table S2 in the Supporting Information. In view of the surface properties, the nature of C, O, and N species at the surface of the as-obtained carbonaceous materials was investigated by XPS. The XPS spectrum of the NMGC-based carbon materials exhibits the existence of the principal C 1s, O 1s, and N 1s levels (see Figure S3a in the Supporting Information). By curve-fitting the high-resolution N 1s spectrum (see Figure S3b in the Supporting Information), three different components of nitrogen could be proposed as pyridinic N (N-1) at 397.6 eV, pyrrolic/pyridine N (N-2) at 399.7 eV, and quaternary N (N-3) at 401.2 eV. In that, the nitrogen atoms of N-1 and N-3 belong to sp² hybridization, and the nitrogen atoms of N-2 are sp³ hybridized. The improvement of the conductivity of NMGC-based materials should attribute to N-1 and N-3.^{21–25} The C 1s spectrum of the NMGC-based materials (see Figure S3c in the Supporting

Information) can be divided into the following peaks, corresponding to C in rings at 284.5 eV, C–OH at 285.4 eV, C=N at 286.2 eV, and N–C=O at 288.9 eV, respectively, further confirming the successful nitrogen-doping within the NMGC-based materials.²¹

Nitrogen adsorption–desorption isotherms of the as-obtained carbonaceous materials were performed (Figure 2).

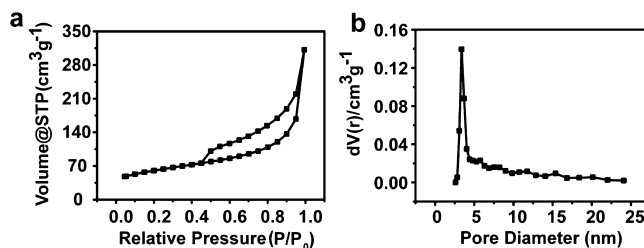


Figure 2. (a) Nitrogen adsorption–desorption isotherm and (b) pore size distribution of the NMGC-based carbon materials.

The specific Brunauer–Emmett–Teller (BET) surface area of the NMGC-based materials reaches as high as 204.8 m² g⁻¹ (Figure 2a). The pore size distribution (PSD) shown in Figure 2b suggests that the NMGC-based materials possess a single mesopore peak at 3.38 nm, demonstrating that the NMGC-based materials have uniform mesoporous. For the convenience of comparison, N-free carbon sample as a reference was also prepared by citric acid (CA) itself under the same calcination condition. The nitrogen adsorption–desorption isotherm of the CA-based carbon was tested and the corresponding result (see Figure S4 in the Supporting Information) did not show any characteristics of the mesoporous. On the basis of the above result, it is reasonable to conclude that melamine is necessary to the formation of mesoporous. The morphology and structure of the NMGC-based materials were studied by SEM and TEM (Figure 3), revealing the homogeneous properties of strip-like carbon materials (Figure 3a–c). High-

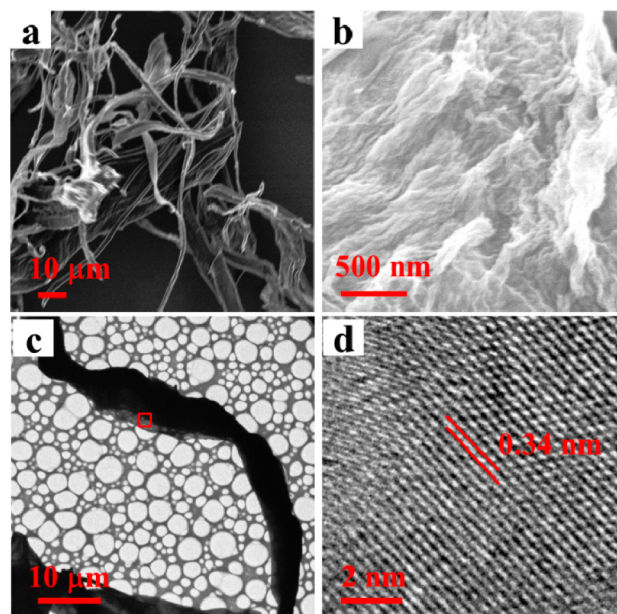


Figure 3. SEM images (a, b) and TEM images (c, d) of the NMGC-based carbon materials. Image (d) corresponds to the magnification of red square area in image (c).

resolution TEM was performed on the selected region of Figure 3c, and obvious lattice fringes with fringe spacing ca. 0.34 nm could be observed (Figure 3d), which was in good agreement with graphitic carbon. The TEM mapping images for the elements of carbon, nitrogen, and oxygen (see Figure 4)

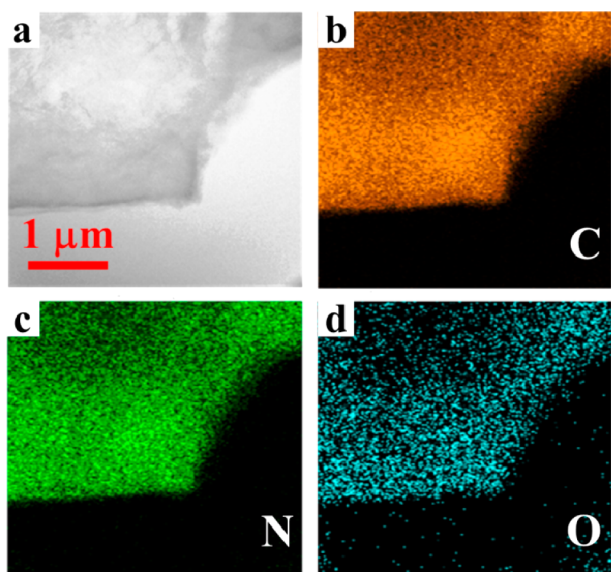


Figure 4. TEM image of (a) the NMGC-based carbon materials and the corresponding mapping images for the elements of (b) carbon, (c) nitrogen, and (d) oxygen, respectively.

overlapped well, indicating that the nitrogen and oxygen atoms are homogeneously dispersed in the carbon matrix. These analyses prove that the NMGC-based materials with both graphitic and mesoporous structures are successfully synthesized. Compared with other synthesized methods,^{9–15} our work presents a facile route to obtain nitrogen-enriched mesoporous graphitic carbonaceous materials.

Lithium-ion batteries (LIBs) presently play a preponderant role in portable electronic devices and electric or hybrid electric vehicles.^{26–28} Herein, the NMGC-based carbonaceous materials were used as anode materials for lithium ion batteries. Figure S5a in the Supporting Information shows the discharge–charge curves of the NMGC-based carbonaceous materials at a current density of 100 mA g⁻¹. The initial discharge capacity reaches 1157.6 mA h g⁻¹, whereas the matching first charge capacity is about 700.8 mA h g⁻¹. This phenomenon may be ascribed to the solid electrolyte interphase (SEI) film formed on the surface of the NMGC-

based carbon materials as well as other secondary reaction.²⁹ It still keeps a capacity of 543.9 mA h g⁻¹ after 200 cycles, whereas the citric acid (CA)-based carbon materials has a capacity of 225.7 mA h g⁻¹ after 200 cycles (see Figure S5b in the Supporting Information). Obviously, the charge and discharge voltages of the NMGC are apparently higher than those of the CA-based carbon, which may benefit from the mesoporous structures of the NMGC-based materials. During the discharge process, lithium first intercalates into graphite or graphite crystallites, and subsequently, lithium is introduced into mesoporous and forms lithium molecules. The mesoporous structures lead to vast electrode/electrolyte interface for getting in touch with the electrolyte. This in turn could increase the progress of lithium intercalation and cause the discharge voltage of the NMGC higher than that of the CA-based carbon. During the charge process, lithium is first extracted from graphite or graphite crystallites and later from mesoporous. This route is not easy for lithium to leave mesoporous, resulting in the charge voltage of the NMGC higher than that of the CA-based carbon.^{24,30} The electrochemical cycle performance is presented in Figure 5. The NMGC-based carbonaceous materials show an excellent cycle performance (Figure 5a). The coulombic efficiency of the first cycle is about 60.5%, quickly increases to 93.9% in the second cycle, and finally remains at nearly 100%. The electrode of NMGC-based carbon materials exhibits good capacity retention without distinct capacity fading. Finally, it keeps a capacity of about 544 mA h g⁻¹, whereas the electrode of CA-based carbonaceous materials gives a capacity of about 226 mA h g⁻¹ (see Figure S4 in the Supporting Information). Obviously, the NMGC-based carbonaceous materials electrode has a better cycling performance. Moreover, the NMGC-based carbonaceous materials electrode displays an initial coulombic efficiency of 60.5%, which is higher than that of the CA-based carbonaceous materials electrode (56.5%). Under the same conditions, the NMGC-based carbonaceous materials apparently exhibit better capability as anode materials in lithium ion batteries. The mesoporous of the NMGC-based carbonaceous materials should contribute a lot to the active sites for lithium storage. The NMGC-based carbonaceous materials electrode also shows good rate performance (Figure 5b). When the charge rate changes back to 100 mA g⁻¹, its reversible capacity comes back to 530 mA h g⁻¹. The capacity of the anode prepared from NMGC-based carbonaceous materials is much higher than that of the traditional graphite anode. The cycling stability and rate performance of the NMGC-based carbon materials electrode are also commendable. We speculate that such a good battery performance may benefit from the following factors: First, the

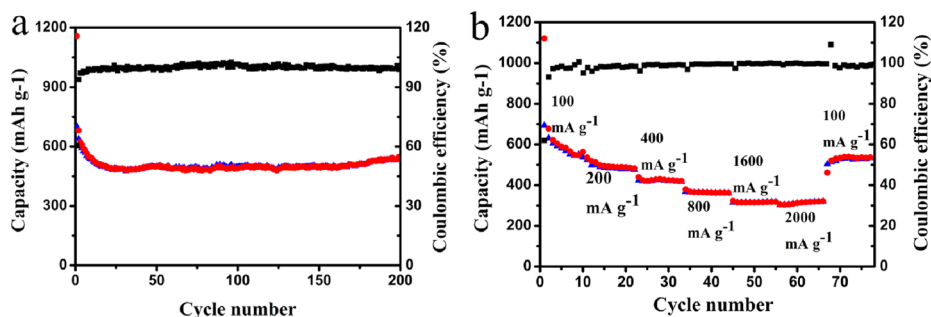


Figure 5. Cycling performances (left) and rate performances (right) for the electrodes of the NMGC-based carbonaceous materials (● = Discharge capacity, ▲ = Charge capacity, ■ = Coulombic efficiency).

mesoporous structure of the carbonaceous materials could shorten the Li ion diffusion length and present high electrode–electrolyte interface for the charge transference.^{4,5} Second, the effective doping of nitrogen leads to many defects, increases Li insertion sites, and improves the capacity of lithium storage. Third, the pyridinic (N-1) and quaternary (N-3) nitrogen atoms may be also responsible for improving the conductivity of NMGC-based materials and the increased reversible capacity.^{23–25} In a word, the good lithium diffusion and electron conductivity would facilitate the NMGC-based carbon materials to be the potential anode electrode materials for lithium-ion batteries.

In summary, the N-doped graphitic carbon with uniform mesoporous was designed using melamine as a nitrogen-source and critic acid as a carbon source. Benefiting from the relatively good solubility of melamine in hot water, self-assembly between melamine and critic acid occurs, producing the high-content nitrogen precursor in cold environment. The synthesis process neither involves hydrothermal reaction nor environment unfriendly solvents. Most importantly, critic acid and melamine used in the system are commercially available and inexpensive, which facilitate the preparation of high nitrogen-containing precursors on a large scale. After carbonization of the precursors, nitrogen-enriched mesoporous graphitic carbon materials with narrow size distribution are acquired. As anode materials in lithium-ion batteries, the as-prepared carbon materials show improved Li-storage capacity and cycling stability as compared with the N-free carbon materials without mesoporous.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, and characterization for composition and properties of NMGC-based carbonaceous materials. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jchge2010@mail.ipc.ac.cn.

*E-mail: shucy@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by 973 Program (no. 2011CB302100), National Basic Research Program (2012CB932900), the Ministry of science and technology support program (2011BAK15B04) and National Natural Science Foundation of China (51172244).

■ REFERENCES

- (1) Chen, J. A Review of Nanostructured Lithium Ion Battery Materials via Low Temperature Synthesis. *Recent Pat Nanotechnol.* **2013**, *7*, 2–12.
- (2) Wang, L.; Zheng, Y.; Wang, X.; Chen, S.; Xu, F.; Zuo, L.; Wu, J.; Sun, L.; Li, Z.; Hou, H.; Song, Y. Nitrogen-Doped Porous Carbon/Co₃O₄ Nanocomposites as Anode Materials for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7117–7125.
- (3) Ryoo, R.; Joo, S. H.; Kruk, M.; Jaroniec, M. Ordered Mesoporous Carbons. *Adv. Mater.* **2001**, *13*, 677–681.
- (4) Walcarius, A. Mesoporous Materials and Electrochemistry. *Chem. Soc. Rev.* **2013**, *42*, 4098–4140.
- (5) Chen, L. F.; Zhang, X. D.; Liang, H. W.; Kong, M.; Guan, Q. F.; Chen, P.; Wu, Z. Y.; Yu, S. H. Synthesis of Nitrogen-doped Porous Carbon Nanofibers as An Efficient Electrode Material for Supercapacitors. *ACS Nano* **2012**, *6*, 7092–7102.
- (6) Xu, J.; Zhao, Y.; Shen, C.; Guan, L. Sulfur- and Nitrogen-Doped, Ferrocene-Derived Mesoporous Carbons with Efficient Electrochemical Reduction of Oxygen. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12594–12601.
- (7) Wang, K.; Wang, Y.; Wang, Y.; Hosono, E.; Zhou, H. Mesoporous Carbon Nanofibers for Supercapacitor Application. *J. Phys. Chem. C* **2009**, *113*, 1093–1097.
- (8) Wei, J.; Zhou, D.; Sun, Z.; Deng, Y.; Xia, Y.; Zhao, D. A Controllable Synthesis of Rich Nitrogen-Doped Ordered Mesoporous Carbon for CO₂ Capture and Supercapacitors. *Adv. Funct. Mater.* **2013**, *23*, 2322–2328.
- (9) Lee, J.; Kim, J.; Hyeon, T. Recent Progress in the Synthesis of Porous Carbon Materials. *Adv. Mater.* **2006**, *18*, 2073–2094.
- (10) Yang, C.; Weidenthaler, C.; Spliethoff, B.; Mayanna, M.; Schüth, F. Facile Template Synthesis of Ordered Mesoporous Carbon with Polypyrrole as Carbon Precursor. *Chem. Mater.* **2005**, *17*, 355–358.
- (11) Wang, R.; Zhou, T.; Li, H.; Wang, H.; Feng, H.; Goh, J.; Ji, S. Nitrogen-rich Mesoporous Carbon Derived from Melamine with High Electrocatalytic Performance for Oxygen Reduction Reaction. *J. Power Sources* **2014**, *261*, 238–244.
- (12) Górka, J.; Jaroniec, M. Tailoring Adsorption and Framework Properties of Mesoporous Polymeric Composites and Carbons by Addition of Organosilanes during Soft-Templating Synthesis. *J. Phys. Chem. C* **2010**, *114*, 6298–6303.
- (13) Kailasam, K.; Jun, Y.; Katekomol, P.; Epping, J. D.; Hong, W. H.; Thomas, A. Mesoporous Melamine Resins by Soft Templating of Block-co-Polymer Mesophases. *Chem. Mater.* **2010**, *22*, 428–434.
- (14) Gencoglu, M. F.; Spurri, A.; Franko, M.; Chen, J.; Hensley, D. K.; Heldt, C. L.; Saha, D. Biocompatibility of Soft-Templated Mesoporous Carbons. *ACS Appl. Mater. Interfaces* **2014**, *6*, 15068–15077.
- (15) Liang, Y.; Fu, R.; Wu, D. Reactive Template-induced Self-assembly to Ordered Mesoporous Polymeric and Carbonaceous Materials. *ACS Nano* **2013**, *7*, 1748–1754.
- (16) Sheng, Z. H.; Shao, L.; Chen, J. J.; Bao, W. J.; Wang, F. B.; Xia, X. H. Catalyst-free Synthesis of Nitrogen-doped Graphene via Thermal Annealing Graphite Oxide with Melamine and Its Excellent Electrocatalysis. *ACS Nano* **2011**, *5*, 4350–4358.
- (17) Fan, C.; Qiu, H.; Ruan, J.; Terasaki, O.; Yan, Y.; Wei, Z.; Che, S. Formation of Chiral Mesopores in Conducting Polymers by Chiral-Lipid-Ribbon Templating and “Seeding” Route. *Adv. Funct. Mater.* **2008**, *18*, 2699–2707.
- (18) Liu, S.; Duan, Y.; Feng, X.; Yang, J.; Che, S. Synthesis of Enantiopure Carbonaceous Nanotubes with Optical Activity. *Angew. Chem., Int. Ed.* **2013**, *52*, 6858–6862.
- (19) Wen, Z.; Ci, S.; Hou, Y.; Chen, J. Facile one-pot, one-step Synthesis of a Carbon Nanoarchitecture for an Advanced Multifunctional Electrocatalyst. *Angew. Chem., Int. Ed.* **2014**, *53*, 6496–6500.
- (20) Shao, Y.; Wang, X.; Engelhard, M.; Wang, C.; Dai, S.; Liu, J.; Yang, Z.; Lin, Y. Nitrogen-doped Mesoporous Carbon for Energy Storage in Vanadium Redox Flow Batteries. *J. Power Sources* **2010**, *195*, 4375–4379.
- (21) Li, M.; Xue, J. Integrated Synthesis of Nitrogen-Doped Mesoporous Carbon from Melamine Resins with Superior Performance in Supercapacitors. *J. Phys. Chem. C* **2014**, *118*, 2507–2517.
- (22) Bulusheva, L. G.; Okotrub, A. V.; Kurennya, A. G.; Zhang, H.; Zhang, H.; Chen, X.; Song, H. Electrochemical Properties of Nitrogen-doped Carbon Nanotube Anode in Li-ion Batteries. *Carbon* **2011**, *49*, 4013–4023.
- (23) Wu, J. J.; Zhang, D.; Wang, Y.; Hou, B. R. Electrocatalytic Activity of Nitrogen-doped Graphene Synthesized via a one-pot Hydrothermal Process towards Oxygen Reduction Reaction. *J. Power Sources* **2013**, *227*, 185–190.

(24) Mao, Y.; Duan, H.; Xu, B.; Zhang, L.; Hu, Y.; Zhao, C.; Wang, Z.; Chen, L.; Yang, Y. Lithium Storage in Nitrogen-rich Mesoporous Carbon Materials. *Energy Environ. Sci.* **2012**, *5*, 7950–7955.

(25) Xia, Y.; Mokaya, R. Generalized and Facile Synthesis Approach to N-doped Highly Graphitic Mesoporous Carbon Materials. *Chem. Mater.* **2005**, *17*, 1553–1560.

(26) Su, J.; Wu, X. L.; Lee, J. S.; Kim, J.; Guo, Y. G. A Carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Cathode Material with An Enhanced High-rate Capability and Long Lifespan for Lithium-ion Batteries. *J. Mater. Chem. A* **2013**, *1*, 2508–2514.

(27) Cao, A.; Hu, J. S.; Liang, H. P.; Wan, L. J. Self-assembled Vanadium Pentoxide (V_2O_5) Hollow Microspheres From Nanorods and Their Application in Lithium-ion Batteries. *Angew. Chem., Int. Ed.* **2005**, *44*, 4391–4395.

(28) Cao, A.; Manthiram, A. Shape-controlled Synthesis of High Tap Density Cathode Oxides for Lithium Ion Batteries. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6724–6728.

(29) Zhang, Y.; Yan, Y.; Wang, X.; Li, G.; Deng, D.; Jiang, L.; Shu, C.; Wang, C. Facile Synthesis of Porous Mn_2O_3 Nanoplates and Their Electrochemical Behavior as Anode Materials for Lithium Ion Batteries. *Chem.—Eur. J.* **2014**, *20*, 6126–6130.

(30) Wu, Y.; Wan, C.; Jiang, C.; Fang, S.; Jiang, Y. Mechanism of Lithium Storage in Low Temperature Carbon. *Carbon* **1999**, *37*, 1901–1908.