

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

An Efficient Low-Temperature Route to Nitrogen-Doping and Activation of Mesoporous Carbon for CO₂ Capture

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Kuan Huang,^[a,b] Song-Hai Chai,^{*[a]} Richard T. Mayes,^[c] Gabriel M. Veith,^[d] Katie L. Browning,^[d] Miles A. Sakwa-Novak,^[e] Matthew E. Potter,^[e] Christopher W. Jones,^[e] You-Ting Wu,^{*[b]} and Sheng Dai^{*[a,c]}

An innovative strategy for post-synthesis nitrogen-doping of mesoporous carbons (MCs) with high yields (>90%) at low temperatures (230–380°C) by using a strong base, sodium amide (NaNH₂) was developed. The as-prepared N-doped MCs exhibit a significantly enhanced CO₂ adsorption performance in terms of capacity and selectivity when compared to their parent MCs.

The emission of CO₂ from combustion of fossil fuels has raised great challenge on global environment. It has been unlocked that CO₂ as a greenhouse gas is the major culprit for the continuously climatic warming in the past centuries. Aqueous amines are widely used in industry as liquid solvents to remove CO₂ from exhaust gas.¹ However, the inherent drawbacks, including high volatility, low thermal stability, strong corrosion and intensive energy consumption for regeneration, promote the exploration of new adsorbent materials for CO₂ capture.²

Research and development of nanostructured carbon materials for energy and sustainability applications are nowadays one of the central and thriving subjects in scientific communities.³ Doping carbon nanostructures with heteroatoms such as nitrogen, *i.e.*, chemically incorporating heteroatoms into the carbon lattice, has received tremendous interest in the past decade, due to its ability to tailor the physical and chemical properties of carbon network for specific applications including fuel cells, batteries, supercapacitors, and hydrogen storage.⁴ In particular, nitrogen-doped nanoporous carbons have shown a great potential for use as highly efficient CO₂ adsorbents.⁵ The electronegative nitrogen species (*e.g.*, pyridinic, pyrrolic,

quaternary, and oxidized nitrogen) generated during the doping process seem to have a preferred interaction with CO₂ compared to the plain carbon materials, thereby increasing the CO₂ adsorption capacity and selectivity over nonpolar N₂.⁶ Two general strategies are usually used for N-doping of nanostructured carbon materials. The first involves a post-treatment of pre-synthesized carbon nanostructures with N-containing agents (*e.g.*, gaseous NH₃) at high temperatures (>600°C),⁷ where continuous etching of carbon results in a quite low yield of the N-doped products. The low yield, plus the toxicity of NH₃, makes this process less attractive. In the second strategy, N-doped carbons are obtained by direct pyrolysis of certain N-rich organic compounds⁸ such as polypyrrole^{5c} and ionic liquids^{5l}. These precursors are not suitable for preparation of N-doped carbons in a large scale because of their limited availability and relatively high cost. Moreover, high-temperature treatment involved in both strategies requires an intensive energy input.

Herein, we present a novel post-synthesis strategy for N-doping of soft-templated mesoporous carbons (MCs) with high yields (>90%) at low temperatures (230–380°C) by using sodium amide (NaNH₂) as the nitrogen source. NaNH₂ is a readily available strong base widely used in organic synthesis.⁹ Its excellent nucleophilicity facilitates the deprotonation of functional groups with active protons (*e.g.*, alkynes, alcohols, aldehydes, esters, and ketones), leading to reactions such as elimination, addition, substitution, alkylation, condensation, and polymerization.⁹ It can also behave as a nucleophilic agent to attack the electrophilic carbon atoms in organic molecules, consequently introducing amino groups to the compounds.¹⁰ In inorganic synthesis, NaNH₂ has been reported as an efficient nitridation reagent, alternative to gaseous NH₃, for preparation of transition-metal nitrides (*e.g.*, Fe₃N, Mn₃N₂, InN) from their corresponding oxides.¹¹ The high reactivity of NaNH₂ appears to promote the breaking of metal-oxygen bonds and substitution of oxygen with nitrogen, significantly lowering the nitridation temperature (<300°C).¹¹ The ability of NaNH₂ to incorporate nitrogen species into oxygen-containing organic and inorganic compounds motivates us to explore a

^a Department of Chemistry, University of Tennessee, Knoxville, TN37996 (USA), E-mail: schai@utk.edu; dais@ornl.gov

^b School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093 (China), E-mail: ytwu@nju.edu.cn

^c Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 (USA)

^d Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 (USA)

^e School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, 30332 (USA)

Electronic Supplementary Information (ESI) available: experimental details and supporting figures and tables. See DOI: 10.1039/x0xx00000x

low-temperature route to the preparation of N-doped carbons by using NaNH_2 as the nitrogen source, given that most of carbon materials contain a certain amount of oxygen species that could be replaced by nitrogen. This low-temperature strategy is energy efficient and avoids the use of toxic NH_3 or costly N-rich precursors.

Table 1. Textural properties of pristine MCs and N-doped MCs

Sample	Yield (%)	$S_{\text{BET}}^{[a]}$ (m^2/g)	$S_{\text{m}}^{[b]}$ (m^2/g)	$V_{\text{t}}^{[c]}$ (cm^3/g)	$V_{\text{m}}^{[d]}$ (cm^3/g)	$w^{[e]}$ (nm)	N ^[f] (at.%)	O ^[g] (at.%)
MC400	–	304	6	0.47	0.03	11.3	0	22.4
NMC400-380-1h	78	481	360	0.37	0.15	10.0	5.5	16.3
MC600	–	479	231	0.56	0.11	9.0	0	16.4
NMC600-380-1h	90	1016	697	0.69	0.29	6.8	6.8	10.6
NMC850	–	357	93	0.52	0.04	9.3	0	7.5
NMC850-380-1h	92	588	315	0.66	0.13	9.0	2.9	4.7
NMC600-230-1h	95	584	318	0.61	0.13	9.0	6.0	11.9
NMC600-280-1h	96	737	464	0.68	0.20	9.0	6.8	9.6
NMC600-330-1h	93	907	604	0.77	0.25	8.9	6.6	9.4
NMC600-330-5h	93	953	644	0.75	0.27	8.1	6.3	10.4
NMC600-330-10h	94	959	652	0.69	0.27	7.4	6.3	9.5

[a] BET surface area. [b] Micropore surface area. [c] Total pore volume. [d] Micropore volume. [e] Mesopore diameter. [f] Nitrogen content measured by XPS. [g] Oxygen content measured by XPS.

Soft-templated MCs with a pore diameter of $\sim 10\text{nm}^{12}$ were synthesized and used as parent carbons for N-doping and activation (Experimental Details in ESI). The obtained N-doped MCs were named as $\text{NMC}_{T_1-T_2-t}$, where T_1 is the carbonization temperature of the parent carbon (400, 600, and 850 °C), T_2 is the N-doping temperature (230, 280, 330, and 380 °C), and t is the N-doping period of time (1, 5, and 10 h). The doping temperature was selected between 230–380 °C in order to keep NaNH_2 in a melting state.¹³ Table 1 lists the textural properties and nitrogen contents of all the parent MCs and N-doped MCs.

The carbonization temperature (T_1) of the parent MCs has a considerable influence on the nitrogen content and textural properties of the N-doped MCs prepared under the same doping conditions ($T_2 = 380$ °C and $t = 1$ h), although the featured mesoporous structure, as suggested by a Type VI N_2 -sorption isotherm observed for all the N-doped samples (Figure S1), is mostly retained after the N-doping. As shown in Table 1, the moderate temperature (600 °C) leads to the N-doped MC (*i.e.*, NMC600-380-1h) with higher nitrogen content (6.8 at.%) and BET surface area (1016 m^2/g) than NMC400-380-1h and NMC850-380-1h that are prepared from the parent MCs carbonized at lower and higher temperatures (400 and 850 °C). As expected, NMC850-380-1h exhibits the lowest content of nitrogen (2.9 at.%) among the three samples, because the high carbonization temperature tends to remove most of oxygen species and thus limit the nitrogen incorporation. However, lower nitrogen content of NMC400-380-1h (5.5 at.%) than NMC600-380-1h seems to be contradictory to our expectation. This could be related to the framework collapse of MC400 during the N-doping process, which is evidenced by a great decrease in its mesopore volume (from 0.44 to 0.22 cm^3/g after the doping) that can be estimated as the difference between total pore volume (V_{t}) and micropore volume (V_{m}) as shown in Table 1. The oxygen

species contained in the collapsed mesopores may become inaccessible to NaNH_2 for nitrogen substitution. The mesopore volumes of MC600 and MC850, however, are much less affected due to their relatively rigid carbon framework, despite that a reduction of mesopore diameter from 9.0 to 6.8 nm is observed for MC600 (Figure S1). SEM images of the N-doped MCs show a highly porous surface for NMC600-380-1h, while NMC400-380-1h has a relatively smooth surface with much less pores in a similar-sized area (Figure S2). These facts suggest that high carbonization temperatures enhance the rigidity of carbon framework and thus make it resistant to the severe reaction with the strong base of NaNH_2 . The moderate carbonization temperature of MC600 endows it with balanced oxygen content and framework rigidity, resulting in a highly efficient incorporation of nitrogen species.

It is interesting that a considerable amount of micropores are created along with the nitrogen doping at such low doping temperatures. For example, the micropore surface area and volume of NMC600-380-1h are nearly three times of those of MC600 (697 vs. 231 m^2/g and 0.29 vs. 0.11 cm^3/g) as shown in Table 1. The development of the microporosity could be related to the substitution/removal of oxygen species that may open some originally closed channels and/or create new cavities in the carbon framework¹¹. Some small gaseous molecules such as NH_3 and H_2O could also be produced during the doping process and probably act as pore forming agents for the micropore generation.

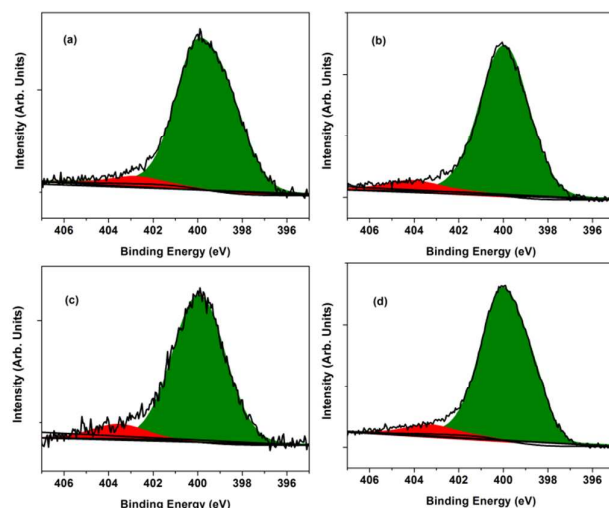


Figure 1. N1s XPS of NMC400-380-1h (a), NMC600-380-1h (b), NMC850-380-1h (c), and NMC600-330-1h (d).

EDX elemental mapping confirms the presence of nitrogen in the N-doped MC600 (Figure S3). The nature of the nitrogen species in the N-doped MCs ($\text{NMC}_{T_1-380-1h}$) was further analyzed by XPS. As shown in Figure 1, a strong and broad peak can be observed around 400.0 eV, suggesting the major nitrogen species are associated with imine/amine/amide and/or pyrrol/pyridone. A weak XPS peak found between 403 and 404 eV could be attributed to oxidized nitrogen in a minor amount (4–9 at.%). Unlike those N-doped porous carbons prepared at high temperatures^{5,7,8}, pyridinic nitrogen seems to be absent in the N-doped MCs synthesized

in the present work. Pyridinic nitrogen is usually thought more stable than imine/amine/amide and pyrrolic/pyridonic nitrogen, and consequently tends to form at high temperatures.^{5c,7c}

Based on the results obtained above, MC600 was selected to investigate the effect of N-doping temperature (T_2) and period of time (t). As illustrated in Table 1 and Figure S4, the doping temperature has a positive effect on the textural properties but almost no effect on the nitrogen and oxygen contents of resultant N-doped MCs. The micropore surface area and volume increase with the N-doping temperature, mainly as a result of the development of micropores. The mesopore diameter of MC600 remains almost unchanged until the doping temperature increases to 380°C, where the mesopore diameter shrinks from 9.0 nm to 6.8 nm (Figure S1d and Table 1). On the other hand, the effect of doping period of time on the textural properties and nitrogen and oxygen contents of resultant N-doped porous carbons is almost negligible (Table 1 and Figure S5). NMC600-330-5h and NMC600-330-10h have similar surface area and pore volume as NMC600-330-1h (Table 1), except for an appreciable shrinkage of mesopore diameter from 9.0 to 7.4 nm.

This low-temperature N-doping and activation process using NaNH_2 is also featured as a high product yield (>90% except for NMC400-380-1h) as shown in Table 1. This is totally different from traditional high-temperature and low-yield activation of porous carbons, in which potassium hydroxide (KOH)¹⁶ or ammonia (NH_3)⁷ is usually used as the activation agent and high surface area and pore volume are developed as a result of continuous etching of the carbons. The carbon etching appears to be greatly alleviated at low doping temperatures when using NaNH_2 , which consequently leads to high product yields.

With considerable development of microporous structure and incorporation of nitrogen species, the synthesized N-doped MCs were investigated further for CO_2 adsorption. Figure S6a shows the CO_2 adsorption isotherms of the N-doped MCs as a function of the carbonization temperature (T_1) of the parent MCs. The CO_2 adsorption capacity is significantly enhanced by two times for NMC400-380-1h and NMC600-380-1h in comparison with MC400 and MC600, respectively. However, the CO_2 capacity of NMC850-380-1h is only ~20% higher than MC850. This is mainly due to relatively underdeveloped microporosity and low nitrogen content of NMC850-380-1h, suggesting the importance of microporous structure and nitrogen species in improving CO_2 adsorption performance. NMC600-380-1h has the highest CO_2 adsorption capacity among the three N-doped MCs synthesized from different pristine MCs, which is in consistence with its most developed micropores and highest nitrogen content. This further validates the advantageous structure of MC600 for N-doping and activation with NaNH_2 . Figure S6b shows the effect of the N-doping temperature (T_2) on the CO_2 adsorption of N-doped MC600. NMC600-330-1h and NMC600-380-1h are with the best performance for CO_2 adsorption, *i.e.*, 3.97 and 4.21 mmol/g at 0 °C and 1 bar, respectively. In particular, the CO_2 capacities at low CO_2 pressure (0.1 bar) for both samples are as high as 1.66 (NMC600-330-1h) and 1.54 (NMC600-380-1h)

mmol/g, respectively, which are close to the highest values reported for N-doped porous carbons^{5,7,8}. This is important for their application in the capture of low-concentration CO_2 from flue gas. Extending the N-doping period of time, however, has no obvious contribution to enhancing the CO_2 adsorption capacity (Figure S7). Considering comparable nitrogen content of the three samples, the slightly higher CO_2 adsorption capacity of NMC600-330-5h and NMC600-330-10h can be attributed to their slightly larger BET surface areas (Table 1).

To demonstrate the superiority of the low-temperature N-doping strategy over traditional high-temperature method using gaseous NH_3 , MC600 was treated with flowing NH_3 at high temperatures ($T_3 = 600$ and 800°C) for 1 h. The resultant products, were tested for CO_2 adsorption. There is little enhancement in the surface area and CO_2 adsorption capacity when doping the MC600 at 600°C, while the treatment at 800°C increased the surface area and pore volume along with a greatly lowered product yield (Table S1 and Figure S8). Despite a similar CO_2 uptake at 0 °C and 1 bar (3.27 vs. 3.28 mmol/g), NMC600- NH_3 -800-1h has a lower CO_2 adsorption capacity at low pressure of 0.1 bar than NMC600-280-1h (1.11 vs 1.48 mmol/g) (Figure S6b and Figure S9). This comparison implies that low-temperature reaction is favorable for retaining nitrogen species because basic nitrogen species are expected to play more important role in capturing CO_2 under low pressures. As shown in Table S1, NMC600- NH_3 -800-1h has a lower nitrogen content than NMC600-280-1h (5.3 vs. 6.8 at.%).

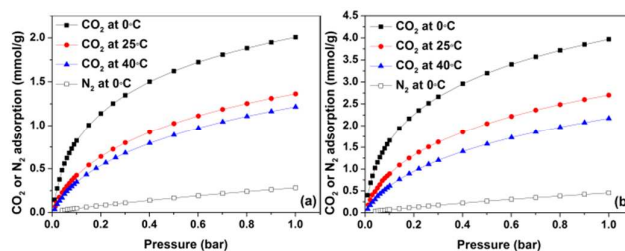


Figure 2. CO_2 and N_2 adsorption isotherms of MC600 (a) and NMC600-330-1h (b) measured at different temperatures.

N_2 adsorption on MC600 and NMC600-330-1h at 0 °C were determined to investigate the selective adsorption of CO_2 from N_2 on the N-doped MCs. As shown in Figure 2, NMC600-330-1h can only adsorb 0.45 mmol/g of N_2 at 0 °C and 1 bar, being about one ninth of CO_2 adsorption at the same conditions. The ideal adsorption selectivity of CO_2/N_2 is calculated from the ratio of initial slope of adsorption isotherms (Figures S10 and S11). The ideal CO_2/N_2 selectivity for NMC600-330-1h is calculated to be 32.1, higher than that of the parent MC600 (26.0). The high initial CO_2/N_2 selectivity is believed to arise from the strong interaction between CO_2 and basic nitrogen species. To understand the strong interaction, the CO_2 adsorption isotherms of MC600 and NMC600-330-1h measured at 0, 25, and 40°C (Figure 2) were fitted to a dual-site Langmuir-Freundlich model¹⁷ for calculation of isosteric CO_2 adsorption heat by using Clausius-Clapeyron equation. As shown in Figure S12, the initial CO_2 adsorption heat of NMC600-330-1h is about -44.7 kJ/mol,

lower than that of MC600 (−30.1 kJ/mol). The calculated adsorption heats for both samples are basically consistent with those (−42.6 kJ/mol vs. −35.3 kJ/mol) measured experimentally by calorimetric method at similar CO₂ adsorption amount (Figure S13). The enhanced adsorption heat for N-doped MCs could be responsible for its higher CO₂/N₂ selectivity.

In summary, an efficient low-temperature route to post-synthesis nitrogen-doping and activation of soft-templated mesoporous carbons has been developed in this work by using a strong base, NaNH₂, as the nitrogen source and activation agent. The strong nucleophilicity and basicity of NaNH₂ appears to facilitate the doping and carbon activation through substitution/removal of residual oxygen species in the parent MCs. Hierarchically micro-mesoporous structure of the N-doped MCs are achieved at a high yield (>90%) with significantly enhanced CO₂ adsorption performance. This strategy is believed to be easily extended to the synthesis of other N-doped carbons.

This work was supported as part of the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, at Oak Ridge National Laboratory and at Georgia Tech under DE-SC0012577. A portion of this research was supported by the Materials Sciences and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy under contract with UT-Battelle, LLC. Y.T. Wu and K. Huang were sponsored by the National Natural Science Foundation of China under Agreement 21376115 and China Scholarship Council (CSC).

Notes and references

- a) N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energ. Environ. Sci.* 2010, **3**, 1645; b) G. T. Rochelle, *Science* 2009, **325**, 1652.
- a) D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Edit.* 2010, **49**, 6058; b) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.* 2012, **41**, 2308.
- a) Y. Zhai, Y. Dou, D. Zhao, P. F. Fulvio, R. T. Mayes and S. Dai, *Adv. Mater.* 2011, **23**, 4828; b) S. Dutta, A. Bhaumik, K and C. W. Wu, *Energ. Environ. Sci.* 2014, **7**, 3574; c) M. Titirici, R. J. White, N. Brun, V. L. Budarin, D. S. Su, F. Del Monte, J. H. Clark and M. J. MacLachlan, *Chem. Soc. Rev.* 2015, **44**, 250.
- a) Y. Shao, J. Sui, G. Yin and Y. Gao, *Appl. Catal. B-Environ.* 2008, **79**, 89; b) J. P. Paraknowitsch and A. Thomas, *Energ. Environ. Sci.* 2013, **6**, 2839; c) K. N. Wood, R. O'Hayre and S. Pylypenko, *Energ. Environ. Sci.* 2014, **7**, 1212; d) W. Shen and W. Fan, *J. Mater. Chem. A* 2013, **1**, 999.
- a) G. Hao, W. Li, D. Qian and A. Lu, *Adv. Mater.* 2010, **22**, 853; b) Y. Xia, R. Mokaya, G. S. Walker and Y. Zhu, *Adv. Energ. Mater.* 2011, **1**, 678; c) M. Sevilla, P. Valle-Vigón and A. B. Fuertes, *Adv. Funct. Mater.* 2011, **21**, 2781; d) S. Feng, W. Li, Q. Shi, Y. Li, J. Chen, Y. Ling, A. M. Asiri and D. Zhao, *Chem. Commun.* 2014, **50**, 329; e) B. Ashourirad, A. K. Sekizkardes, S. Altarawneh and H. M. El-Kaderi, *Chem. Mater.* 2015, **27**, 1349; f) Y. Zhao, X. Liu, K. X. Yao, L. Zhao and Y. Han, *Chem. Mater.* 2012, **24**, 4725; g) W. Xing, C. Liu, Z. Zhou, L. Zhang, J. Zhou, S. Zhuo, Z. Yan, H. Gao, G. Wang and S. Z. Qiao, *Energ. Environ. Sci.* 2012, **5**, 7323; h) J. Wei, D. Zhou, Z. Sun, Y. Deng, Y. Xia and D. Zhao, *Adv. Funct. Mater.* 2013, **23**, 2322; i) X. Zhu, P. C. Hillesheim, S. M. Mahurin, C. Wang, C. Tian, S. Brown, H. Luo, G. M. Veith, K. S. Han, E. W. Hagaman, H. Liu and S. Dai, *ChemSusChem* 2012, **5**, 1912.
- a) R. Babarao, S. Dai and D. Jiang, *J. Phys. Chem. C* 2012, **116**, 7106; b) H. M. Lee, I. S. Youn, M. Saleh, J. W. Lee and K. S. Kim, *Phys. Chem. Chem. Phys.* 2015, **17**, 10925.
- a) J. Przepiórski, M. Skrodzewicz and A. W. Morawski, *Appl. Surf. Sci.* 2004, **225**, 235; b) X. Wang, J. S. Lee, Q. Zhu, J. Liu, Y. Wang and S. Dai, *Chem. Mater.* 2010, **22**, 2178; c) X. Wang, C. Liu, D. Neff, P. F. Fulvio, R. T. Mayes, A. Zhamu, Q. Fang, G. Chen, H. M. Meyer, B. Z. Jiang and S. Dai, *J. Mater. Chem. A* 2013, **1**, 7920.
- a) M. C. Gutiérrez, D. Carriazo, C. O. Ania, J. B. Parra, M. L. Ferrer and F. Del Monte, *Energ. Environ. Sci.* 2011, **4**, 3535; b) X. Fan, L. Zhang, G. Zhang, Z. Shu and J. Shi, *Carbon* 2013, **61**, 423; c) J. Wang, I. Senkovska, M. Oschatz, M. R. Lohe, L. Borchardt, A. Heerwig, Q. Liu and S. Kaskel, *ACS Appl. Mater. Inter.* 2013, **5**, 3160; d) J. Wang, I. Senkovska, M. Oschatz, M. R. Lohe, L. Borchardt, A. Heerwig, Q. Liu and S. Kaskel, *J. Mater. Chem. A* 2013, **1**, 10951; e) J. Patiño, M. C. Gutiérrez, D. Carriazo, C. O. Ania, J. L. G. Fierro, M. L. Ferrer and F. Del Monte, *J. Mater. Chem. A* 2014, **2**, 8719.
- a) P. Caubere, *Accounts Chem. Res.* 1974, **7**, 301; b) R. Juza, *Angew. Chem. Int. Edit.* 1964, **3**, 471; c) F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.* 1933, **12**, 43; d) F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.* 1937, **20**, 413; e) R. Levine and W. C. Fernelius, *Chem. Rev.* 1954, **54**, 449.
- a) T. J. Delia, B. R. Meltsner and J. M. Schomaker, *J. Heterocyclic Chem.* 1999, **36**, 1259; b) G. Mehta and R. V. Venkateswaran, *Tetrahedron* 2000, **56**, 1399.
- a) H. Jacobs and E. Vonpinkowski, *J. Alloys Compd.* 1989, **146**, 147; b) Y. Huang, Y. Gu, M. Zheng, Z. Xu, W. Zeng and Y. Liu, *Mater. Lett.* 2007, **61**, 1056; (c) A. Miura, T. Takei and N. Kumada, *Cryst. Growth Des.* 2012, **12**, 4545; d) A. Miura, T. Takei and N. Kumada, *Inorg. Chem.* 2013, **52**, 11787.
- X. Q. Wang, J. S. Lee, C. Tsouris, D. W. DePaoli and S. Dai, *J. Mater. Chem.* 2010, **20**, 4602.
- L. Lange and W. Triebel, in *Ullmann's Encyclopedia of Industrial Chemistry*, (Eds: B. Elvers), John Wiley and Sons, Inc, German, 2003, pp. 263-272.
- a) M. J. IllanGomez, A. GarciaGarcia, C. DeLecea and A. LinaresSolano, *Energ. Fuel.* 1996, **10**, 1108; b) H. S. Teng and L. Y. Hsu, *Ind. Eng. Chem. Res.* 1999, **38**, 2947; c) D. Lozano-Castello, M. A. Lillo-Rodenas, D. Cazorla-Amoros and A. Linares-Solano, *Carbon* 2001, **39**, 741.
- a) Q. Li, J. Yang, D. Feng, Z. Wu, Q. Wu, S. S. Park, C. Ha and D. Zhao, *Nano Res.* 2010, **3**, 632; b) W. Shen, S. Zhang, Y. He, J. Li and W. Fan, *J. Mater. Chem.* 2011, **21**, 14036; c) L. Estevez, R. Dua, N. Bhandari, A. Ramanujapuram, P. Wang and E. P. Giannelis, *Energ. Environ. Sci.* 2013, **6**, 1785; d) Z. Zhang, K. Wang, J. D. Atkinson, X. Yan, X. Li, M. J. Rood and Z. Yan, *J. Hazard. Mater.* 2012, **229**, 183; e) Z. Tang, Z. Han, G. Yang, B. Zhao, S. Shen and J. Yang, *New Carbon Mater.* 2013, **28**, 55.
- a) J. Choma, K. Jedynak, W. Fahrenholz, J. Ludwinowicz and M. Jaroniec, *Appl. Surf. Sci.* 2014, **289**, 592; b) A. Silvestre-Albero, J. Silvestre-Albero, M. Martínez-Escandell and F. Rodríguez-Reinoso, *Ind. Eng. Chem. Res.* 2014, **53**, 15398; c) L. K. C. de Souza, N. P. Wickramaratne, A. S. Eflo, M. J. F. Costa, C. E. F. Da Costa and M. Jaroniec, *Carbon* 2013, **65**, 334.
- a) T. Ben, Y. Li, L. Zhu, D. Zhang, D. Cao, Z. Xiang, X. Yao and S. Qiu, *Energ. Environ. Sci.* 2012, **5**, 8370; b) Z. Xiang, X. Zhou, C. Zhou, S. Zhong, X. He, C. Qin and D. Cao, *J. Mater. Chem.* 2012, **22**, 22663.