Carbon Materials

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Upper Limit of Nitrogen Content in Carbon Materials**

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Abstract: *Nitrogen-doped carbon materials (NDCs) play an important role in various fields. A great deal of effort has been devoted to obtaining carbon materials with a high nitrogen content; however, much is still unknown about the structure of the nitrogen-doped materials and the maximum nitrogen content possible for such compounds. Here, we demonstrate an interesting relationship between the N/C molar ratio and the N content of NDCs. The upper limit for the nitrogen content of NDCs that might be achieved was estimated and found to strongly depend on the carbonization temperature (14.32 wt% at 1000°C and 21.66 wt% at 900°C), irrespective of the precursor or preparation conditions. Simulations suggest that, especially in the carbon architectures obtained at high temperatures, nitrogen atoms are always located on separate hexagon moieties in a graphitic configuration, thereby yielding a critical N/C molar ratio very close to the value estimated from the experimental results.*

Nitrogen-containing carbon materials have attracted rapidly growing interest in recent years. The introduction of nitrogen into the carbon architectures greatly affects the bulk properties of the material, with effects depending on the amount of nitrogen and the type of bonding to the carbonaceous backbone. Generally, two classes of nitrogen-containing carbon materials can be distinguished: nitrogen-rich compounds and nitrogen-doped carbon.[1] Nitrogen-rich compounds (N/C $\geq$1:1), for example, cubic or graphitic carbon nitride (C_3N_4), have a high nitrogen content of up to 61 wt% and exhibit promising properties, such as superhardness or semiconductivity.[2] Carbon nitrides are generally synthesized by thermal condensation of nitrogen-rich precursors (N/C $\geq$1:1) at intermediate temperatures (ca. 550°C); at high temperatures, they become unstable and decompose completely.[3]

Nitrogen-doped carbon materials (NDCs), with nitrogen atoms doped in the large pool of sp^2-bonded carbon atoms, retain and further improve the properties of the corresponding bulk carbon material.[4] In contrast to nitrogen-rich compounds, NDCs are traditionally prepared either by in situ carbonization of nitrogen-containing precursors (N/C $<$1:1) or by post-treatment of the as-obtained carbon materials with a nitrogen-containing agent such as NH_3 or CH_3CN. Nitrogen can be viewed as an n-type carbon dopant. The conjugation between the nitrogen lone pair of electrons and the π system of the carbon lattice can result in structural irregularity of the hexagonal carbon rings, and can dramatically alter the physical and chemical properties, such as the basicity,[5] oxidative stability,[1] and catalytic activity of the carbon materials.[6] Importantly, nitrogen doping can facilitate the formation of a localized electron-donor state near the Fermi level, thereby resulting in a significant improvement in the electrical conductivity.[6d,7] NDCs thus have potential applications in diverse fields such as environmental treatment, catalysis, gas capture/storage, and energy conversion/storage.[8] In particular, NDCs have been extensively used as exciting "metal-free" electrode materials or electrocatalysts for supercapacitors, lithium-ion or lithium-sulfur batteries, and oxygen reduction and evolution reactions.[9] For example, NDCs are promising electrode materials for supercapacitors, because the introduction of nitrogen species contributes to additional pseudocapacitance beyond double-layer capacitance.[9e]

A general conclusion drawn from the reported NDCs of given porosity and graphitic structure is that the higher the nitrogen content of the carbon material, the better performance it exhibits. For example, it has recently been demonstrated that the conductivity of NDCs generally increases with increasing nitrogen content.[10] Carbons with ultrahigh nitrogen content have even exhibited conductivity superior to graphite.[1,10] Many efforts have, therefore, been devoted to developing highly nitrogen-doped carbon materials. As the nitrogen content in NDCs is variable, strongly depending on the precursor and preparation conditions,[10,11] most attempts to improve the nitrogen content have focused on the modification of doping methods, and particularly, on the development of novel N-containing precursors. For example, Antonietti and co-workers reported that the aprotic ionic liquid 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][DCA], 39.5 wt% N), with an N/C molar ratio of 0.63:1, could give rise to carbon doped with 10.4 wt% N after direct carbonization at 1000°C.[1] This value could be further improved to about 12.0 wt% through cocarbonization of [EMIm][DCA] with naturally N-rich compounds.[9c] Interestingly, protic ionic liquids based on cyanopyridinium hydrogen sulfate, despite their relatively low N/C value of 0.33:1, have been shown to produce carbon materials with nitrogen contents of up to 11.91 wt% at 1000°C.[11] In addition, some highly nitrogen-doped carbon materials (e.g. 35.1 wt% at

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600 °C and 31 wt % at 700 °C) have also been obtained at relatively low temperatures;[1,12] the nitrogen content in carbon greatly decreases with increasing carbonization temperature.[13] Important questions remain, however: How much nitrogen can ultimately be doped into the carbon structure? What is the upper limit of the nitrogen content of carbon materials?

Herein, we report for the first time an interesting correlation between the nitrogen and the carbon compositions of NDCs from a systematic analysis of the elemental compositions of dozens of NDCs. The observed trend depends only on the carbonization temperature, and is independent of the carbonaceous precursor, preparation conditions, and carbon type (porous carbon or graphene). Based on this, the maximum nitrogen content that can be doped at a given high temperature was successfully estimated.

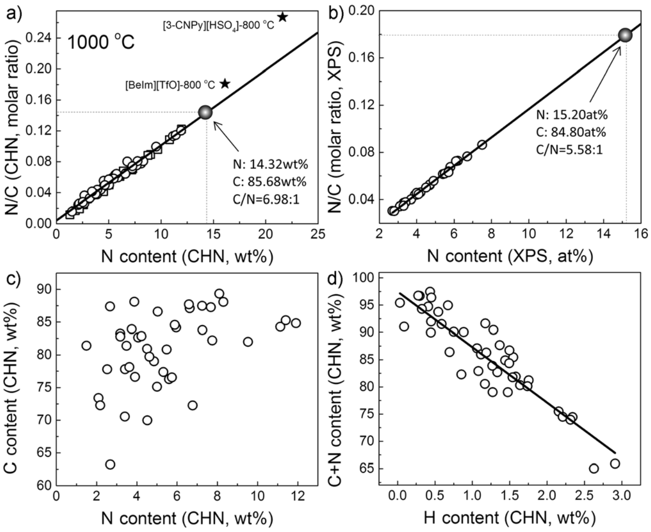

Figure 1. Correlation between the N, C, and H content of the nitrogen-doped carbon materials (NDCs) obtained at 1000 °C, as determined by CHN elemental analysis and high-resolution X-ray photoelectron spectroscopy (XPS). The line indicates the best fit result: a) for PIL/PS-based NDCs (circles): $y=0.00971x+0.00421$; $R^2=0.980$, for all NDCs, including PIL/PS-based NDCs and other reported NDCs, (squares): $y=0.00981x+0.00292$; $R^2=0.985$; b) $y=0.01202x-0.00347$; $R^2=0.989$; d) $y=-10.18000\times+97.46700$; $R^2=0.832$. The asterisks indicate the data points for [BeIm][TfO] and [3-CNPy][HSO$_4$]-based carbon obtained at 800 °C (for structures and abbreviations of the PILs/PSs, see Zhang et al.).[11] For the data of C and N content, see Tables S1 and S2 in the Supporting Information; H content data are from Zhang et al.[11] The filled circles indicate the maximum N content, which was estimated assuming that the carbon material is composed of only carbon and nitrogen.

Most of the NDCs under investigation were obtained by direct carbonization of various N-containing protic ionic liquids and salts (PILs/PSs), following established procedures.[10,11] We have recently reported that PILs/PSs can be utilized as novel low-molecular weight precursors for nitrogen-doped carbon materials.[10,11] Similar to aprotic ionic liquids (ILs), PILs/PSs possess negligible volatility, but are more easily obtained and have a lower cost than conventional polymer precursors and aprotic ILs. By virtue of the wide availability and structural diversity of bases and acids, a series of nitrogen-doped carbons were obtained with variable nitrogen contents, depending on the precursor structure; this made possible an in-depth investigation of the correlation between the precursor structures and the properties of the final NDCs. At first, the composition of all NDCs obtained at 1000 °C was determined by elemental analysis (CHN) and high-resolution X-ray photoelectron spectroscopy (XPS; Figure 1 and see Table S1 in the Supporting Information). Despite the absence of systematic trends between the carbon and nitrogen contents (Figure 1 c), a linear relationship between the N/C molar ratio and nitrogen content was indeed observed (Figure 1 a). Nearly all of the data points could be fitted to a linear relationship, with a coefficient of determination (R^2) of up to 0.980. This indicates that the N/C molar ratio, and thus the carbon content, of NDCs could be feasibly calculated if one knows the nitrogen content, irrespective of the presence of other heteroatoms. Assuming that the carbon material is composed solely of carbon and nitrogen, the maximum nitrogen content that can be achieved in NDCs was further calculated (for details see the Supporting Information). The upper limit for the nitrogen content in NDCs obtained at 1000 °C was estimated to be 14.32 wt %, with a C/N molar ratio of 7:1 (Figure 1 a). To the best of our knowledge, this is the first report to predict the upper limit for the nitrogen content of NDCs. Indeed, such high nitrogen contents have never been achieved experimentally for NDCs prepared through either in situ carbonization or post-treatment. The highest value for NDCs at 1000 °C reported so far is about 12.0 wt %, obtained by cocarbonization of [EMIm][DCA] and naturally N-rich compounds.[9c] Although a N content of 13.6 wt % has been reported by Lu and co-workers,[14] this value was achieved first by carbonization at 1000 °C and then by post-functionalization of the as-prepared carbon in pure ammonia gas at 400 °C. Such a low temperature could facilitate nitrogen fixation, as is to be expected; however, the obtained NDC does not obey the relationship described above, which was obtained exclusively at 1000 °C. This finding suggests that the relationship applies only when the carbonization temperature is kept constant. As seen in Figure 1 a, carbons obtained from two PILs/PSs at 800 °C, despite their ultrahigh nitrogen content, show data points clearly deviating from the fitting line obtained at 1000 °C. In addition, as shown in Figure 1 d, the combined carbon and nitrogen content (C + N) for all the PIL/PS-based NDCs was generally found to decrease with increasing hydrogen content. Our previous studies have also demonstrated that the surface area of PIL/PS-based NDCs generally increases as the C + N content decreases (see Figure S3 in the Supporting Information).[11] Thus, for a specific PIL/PS-based NDC with a given C + N content, not only the H content but also the surface area may be estimated approximately. Carbons with a lower C + N content tend to have a higher H content, thus having a high surface area, because highly porous carbons contain a larger number of edge plane sites with dangling C−H bonds.

Interestingly, it was further found for other reported NDCs, such as porous carbon, graphene, carbon nanotubes, and carbon dots, that the corresponding data points (squares in Figure 1 a) of N/C molar ratio versus N content can also be found close to the fitting line. The calculated linear relationship and the upper limit of nitrogen content (14.39 wt %) are very close to the values derived from exclusively PIL/PS-based NDCs. This result strongly suggests that the correlation established for PIL/PS-based NDCs still holds true for all NDCs obtained at 1000 °C, irrespective of the precursor structure, presence of heteroatoms, and preparation conditions such as the heating rate or holding time. Moreover, the surface composition of all the PIL/PS-derived NDCs detected by XPS affords similar results, wherein the N/C value scales linearly with the nitrogen content (Figure 1 b). The highest nitrogen content was estimated to be 15.20 at % (17.30 wt %), only slightly higher than the value determined from elemental analysis. This is reasonable because all the carbons used for XPS analysis were obtained by direct carbonization of N-containing PIL/PS precursors. Such an in situ process ensures not only a relatively homogeneous N doping but also a similarly changing trend between N content and N/C value for both CHN analysis and XPS (see Figure S4 in the Supporting Information). In contrast, NDCs obtained by post-treatment (e.g. NH_3-activated carbons) may be unsuitable for XPS analysis because of surface enrichment by N atoms.

The correlation between the N/C molar ratio and the N content for NDCs obtained at 90 °C is still highly linear (Figure 2 a). Analogously, the estimated highest nitrogen content is 21.66 wt %, clearly higher than the estimated maximum at 1000 °C. This value is also higher than the highest experimental result reported for NDCs at 900 °C, about 19 wt %, obtained by direct carbonization of [EMIm][DCA].[1] In contrast, for NDCs obtained at 800 °C and below, instead of the aforementioned linear relationship, the N/C molar ratio was found to increase polynomially with the N content (Figure 2). The highest values for the nitrogen content at 800 and 700 °C are estimated to be 55.75 wt % and 64.65 wt %, respectively. The very high N content and N/C ratio could not be ascribed to the architecture of the NDCs, but are very close to that of carbon nitride (Figure 2 d).[12] Although carbon nitride is generally thermally unstable above 750 °C (see Figure S5 in the Supporting Information),[3] the existence of carbon nitride above this temperature has been confirmed experimentally; graphitic carbon nitride (g-C_3N_4) has been synthesized through a two-step pyrolysis of melamine even at 800 °C under vacuum conditions.[15] This temperature-dependent result demonstrates two points. First, when a nitrogen content is detected, the comparison between different NDCs should be conducted at the same carbonization temperature for the values to be comparable. Second, nitrogen-rich compounds such as carbon nitride are thermally unstable above 800 °C.

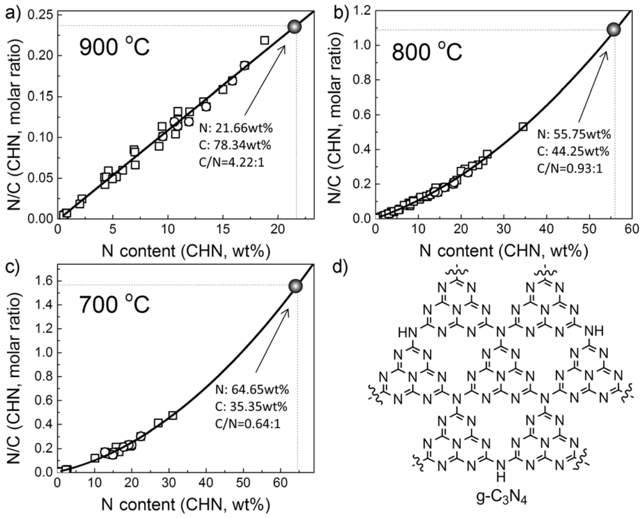

Figure 2. Correlation between the N/C molar ratio and N content determined by CHN elemental analysis in nitrogen-doped carbon materials (NDCs) obtained at a) 900 °C, b) 800 °C, and c) 700 °C. The line indicates the best fit: 900 °C, $y = 0.01100x - 0.00126$, $R^2 = 0.967$; 800 °C, $y = 0.00019x^2 + 0.00862x + 0.00168$; $R^2 = 0.997$; 700 °C, $y = 0.0002x^2 + 0.00701x + 0.00544$; $R^2 = 0.961$. Circles and squares indicate the data obtained in this work (protic ionic liquid and salt-based carbons) and that previously reported, respectively. The filled circles indicate the maximum N content, estimated assuming that the carbon material is composed of only carbon and nitrogen. For the data, see Tables S3–S5 in the Supporting Information. d) Tri-s-triazine-based planar extended structures of graphitic carbon nitride.

Having uncovered interesting correlations between the C and N compositions in NDCs, we next attempted to find the mechanism behind these relationships. To shed light on the estimated upper limit for the N content of NDCs, we used a series of nitrogen-containing planar conjugated compounds as model structures (Figure 4). Several assumptions relating to the doping structure were proposed prior to calculation: 1) All the nitrogen atoms in the "real" NDCs (obtained at high temperatures) are assumed to be doped as graphitic N for reasons laid out below (for details see the Supporting Information). It is well known that the nitrogen configuration in NDCs can be broadly categorized into pyridinic, graphitic (or quaternary), pyrrolic, and oxidized species, the first two classes being the most important.[16] A close inspection of PIL/PS-based NDCs and most reported NDCs revealed that an increasing heating temperature led to not only a decrease in the total N content of the NDCs but also a decrease in the percentage of pyridinic N atoms, while that of graphitic N atoms increased.[13a,16] This is because of the continuous release of thermally unstable pyridinic N atoms and condensation from pyridinic N atoms to valley or central graphitic N atoms during heating,[13a] a result of graphitic N atoms being much more stable than pyridinic N atoms at high temperatures. The nitrogen environment in the [3-CNPy][HSO_4]-based NDCs was examined by XPS; a typical example is shown in Figure 3. The graphitic/pyridinic ratio clearly increased on increasing the carbonization temperature from 800 to 1000 °C. 2) For each hexagon unit in the NDC structure, only one nitrogen atom is allowed to be replaced. This assumption was guided by the theoretical calculation of several isomers of coronene doped with two-nitrogen atoms (2a–g in Figure 4); the relative energies of these isomers were calculated at the MP2/6-311G**//B3LYP/6-31G* level by Gaussian 03 (see the Supporting Information). The results revealed that isomers with separated nitrogen species (2d–f) have much lower energies, and are therefore more stable than those containing two nitrogen atoms in the same hexagon unit (2a–c). Moreover, the reduction of energy from 2d to 2g suggested that carbons with a longer distance between the

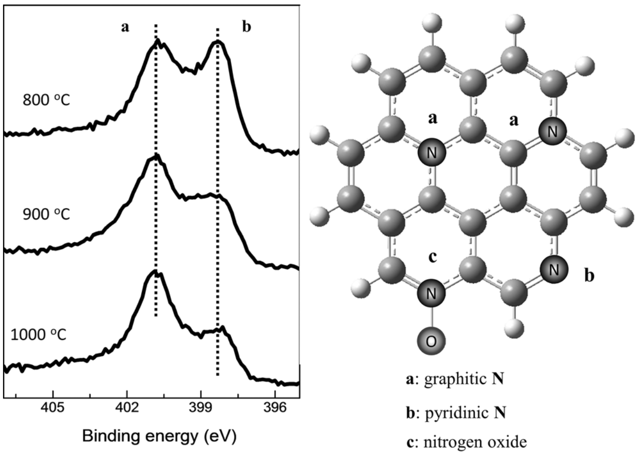

Figure 3. High-resolution N1s X-ray photoelectron spectra of [3-CNPy]-[HSO_4]-based nitrogen-doped carbon materials carbonized at different temperatures.

Table 1: The maximum nitrogen content and C/N molar ratio predicted from the model structures with increasing numbers of total atoms.

	G24	G54	G96	G150
N content (wt %)	13.72	14.40	16.27	16.43
C/N (molar ratio)	7.00	6.71	5.85	5.82

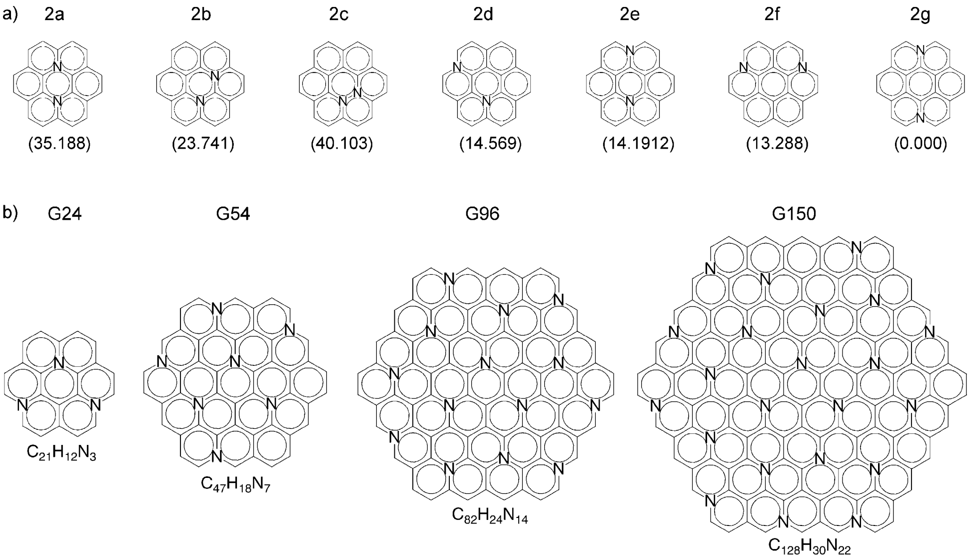

Figure 4. a) Optimized geometries of two-nitrogen-doped coronenes as model structures for carbons containing two nitrogen atoms in the same hexagon unit. Values in parentheses indicate the calculated energy in kcal mol^{-1}. b) The maximum nitrogen doping in the model structures with increasing number of total atoms based on the three assumptions.

nitrogen atoms, and thus a lower nitrogen doping density, are energetically more stable. This result may also account for the general trend that the nitrogen content in carbons greatly decreases with increasing carbonization temperature. 3) Nitrogen should be distributed as homogenously as possible in the entire structure while satisfying the above two assumptions.

Based on the three assumptions and the calculated stable subunits, a series of model nitrogen-doped graphene structures containing the maximum number of nitrogen substitutions that could be achieved were designed (Figure 4b). The corresponding nitrogen content in the model structure was found to decrease as the number of total atoms increased (Table 1). The maximum value of C/N was calculated to be 7:1 for G24, with a gradual decrease to 5.8:1 for G150. This result is very close to the estimated values for NDCs obtained at 1000 °C (Figure 1), thus suggesting that the NDCs obtained at high temperatures are similar to these models and that the doped nitrogen tends to exist as graphitic N atoms. It should be noted that the lateral size of the graphene layer for PIL/PS-derived carbons can be estimated by the (100) XRD peak through the Scherrer Equation, which were found to be in the range 1.4–2.0 nm.[10] This domain size fits the model sizes from G54 to G150 (see Figure S9 in the Supporting Information), thus making the proposed models reasonable. However, the predicted C/N value from model structures is clearly lower than the estimated values for NDCs obtained at 900 °C. The main reason of this difference could be the fact that only graphitic N atoms was considered in the model structure, whereas in reality pyridinic N atoms are still present in NDCs, as confirmed by the XPS results (Figure 3). The presence of pyridinic N atoms on the edge of the model structure would enhance the N content (see the Supporting Information). For example, the C/N value of G54 greatly decreases from 6.7:1 to 3.2:1 after doping with additional pyridinic N (see Figure S10 in the Supporting Information). This result also suggests that it might be possible to achieve highly nitrogen-doped carbon by enhancing the pyridinic N content. This point was indeed confirmed by our recent result of PIL/PS-derived NDCs; most NDCs with a very high N content exhibit a high pyridinic N content, while those with low N contents possess a relatively low pyridinic N content.[10]

In conclusion, we have reported for the first time a linear or polynomial relationship between the N/C molar ratio and nitrogen content of NDCs. Based on this correlation, the upper limit for the nitrogen content of NDCs could be estimated and was found to decrease with increasing carbonization temperature, as expected. The upper limits for NDCs obtained at 1000 and 900 °C are 14.32 and 21.66 wt %, respectively. However, the very high estimated maximum nitrogen content below 900 °C (ca. 60 wt %) revealed the possible existence of nitrogen-rich compounds such as carbon nitride even up to 800 °C. The estimated upper limit for NDCs obtained at 1000 °C could be readily explained by an energetically favorable N-doping architecture, in which nitrogen atoms are located on separate hexagon units as graphitic N, thereby resulting in NDCs with N contents and N/C values very close to those estimated from the experimental results. Despite the interesting relationship in NDCs, no clear correlation between the nitrogen content of the precursors and NDCs was observed (see Figure S12 in the Supporting Information), thus the precise design of precursors at the molecular level to produce desirable carbon materials is still challenging.

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[1] J. P. Paraknowitsch, J. Zhang, D. S. Su, A. Thomas, M. Antonietti, *Adv. Mater.* **2010**, *22*, 87 – 92.

[2] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76 – 80.

[3] a) A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Muller, R. Schlogl, J. M. Carlsson, *J. Mater. Chem.* **2008**, *18*, 4893 – 4908; b) Y. C. Zhao, Z. Liu, W. G. Chu, L. Song, Z. X. Zhang, D. L. Yu, Y. J. Tian, S. S. Xie, L. F. Sun, *Adv. Mater.* **2008**, *20*, 1777 – 1781.

[4] K. P. Gong, F. Du, Z. H. Xia, M. Durstock, L. M. Dai, *Science* **2009**, *323*, 760 – 764.

[5] J. Wei, D. Zhou, Z. Sun, Y. Deng, Y. Xia, D. Zhao, *Adv. Funct. Mater.* **2013**, *23*, 2322 – 2328.

[6] a) Y. Y. Shao, J. H. Sui, G. P. Yin, Y. Z. Gao, *Appl. Catal. B* **2008**, *79*, 89 – 99; b) C. P. Ewels, M. Glerup, *J. Nanosci. Nanotechnol.* **2005**, *5*, 1345 – 1363; c) H. B. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781 – 794; d) Q. H. Yang, W. H. Xu, A. Tomita, T. Kyotani, *Chem. Mater.* **2005**, *17*, 2940 – 2945.

[7] a) R. Czerw, M. Terrones, J. C. Charlier, X. Blase, B. Foley, R. Kamalakaran, N. Grobert, H. Terrones, D. Tekleab, P. M. Ajayan, W. Blau, M. Ruhle, D. L. Carroll, *Nano Lett.* **2001**, *1*, 457 – 460; b) A. C. M. Carvalho, M. C. dos Santos, *J. Appl. Phys.* **2006**, *100*, 084305; c) J. D. Wiggins-Camacho, K. J. Stevenson, *J. Phys. Chem. C* **2009**, *113*, 19082 – 19090.

[8] X. Xu, Y. Li, Y. T. Gong, P. F. Zhang, H. R. Li, Y. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 16987 – 16990.

[9] a) R. Ryoo, S. H. Joo, M. Kruk, M. Jaroniec, *Adv. Mater.* **2001**, *13*, 677 – 681; b) C. D. Liang, Z. J. Li, S. Dai, *Angew. Chem. Int. Ed.* **2008**, *47*, 3696 – 3717; *Angew. Chem.* **2008**, *120*, 3754 – 3776; c) W. Yang, T. P. Fellinger, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 206 – 209; d) T. P. Fellinger, F. Hasche, P. Strasser, M. Antonietti, *J. Am. Chem. Soc.* **2012**, *134*, 4072 – 4075; e) L. Zhao, L. Z. Fan, M. Q. Zhou, H. Guan, S. Y. Qiao, M. Antonietti, M. M. Titirici, *Adv. Mater.* **2010**, *22*, 5202 – 5206; f) X. G. Sun, X. Q. Wang, R. T. Mayes, S. Dai, *ChemSusChem* **2012**, *5*, 2079 – 2085; g) Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, *Nat. Commun.* **2013**, *4*, 2390.

[10] S. Zhang, M. S. Miran, A. Ikoma, K. Dokko, M. Watanabe, *J. Am. Chem. Soc.* **2014**, *136*, 1690 – 1693.

[11] S. Zhang, K. Dokko, M. Watanabe, *Chem. Mater.* **2014**, *26*, 2915 – 2926.

[12] X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu, A. Vinu, *Angew. Chem. Int. Ed.* **2009**, *48*, 7884 – 7887; *Angew. Chem.* **2009**, *121*, 8024 – 8027.

[13] a) J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon* **1995**, *33*, 1641 – 1653; b) G. Ciric-Marjanovic, I. Pasti, N. Gavrilov, A. Janosevic, S. Mentus, *Chem. Pap.* **2013**, *67*, 781 – 813.

[14] D. Hulicova-Jurcakova, M. Kodama, S. Shiraishi, H. Hatori, Z. H. Zhu, G. Q. Lu, *Adv. Funct. Mater.* **2009**, *19*, 1800 – 1809.

[15] X. F. Li, J. Zhang, L. H. Shen, Y. M. Ma, W. W. Lei, Q. L. Cui, G. T. Zou, *Appl. Phys. A* **2009**, *94*, 387 – 392.

[16] a) S. Chen, J. Y. Bi, Y. Zhao, L. J. Yang, C. Zhang, Y. W. Ma, Q. Wu, X. Z. Wang, Z. Hu, *Adv. Mater.* **2012**, *24*, 5593 – 5597; b) G. Liu, X. G. Li, J. W. Lee, B. N. Popov, *Catal. Sci. Technol.* **2011**, *1*, 207 – 217.