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Synthesis of Polypyrrole-based Nitrogen-containing Porous Carbon Nanotubes for CO_2 Adsorption

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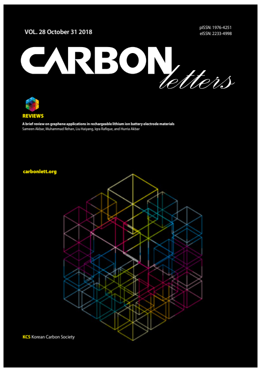

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Massive carbon dioxide (CO_2) emission has caused many environmental problems such as global warming and rising of sea levels [1,2]. It is therefore urgent to take measures to reduce CO_2 emissions. Nowadays, commercial CO_2 capture technology involves a chemical adsorption reaction between aqueous amine solution and CO_2, which has many defects such as corrosion and high cost for regeneration [3]. Thus, adsorbing CO_2 on solid adsorbents has received particular attention from scientists due to its low cost, simple operation, and clear process [4,5].

In recent years, significant progress has been made in the development of solid adsorbents, for example, metalorganic frameworks, zeolitic imidazolate frameworks, microporous coordination polymers, and carbon-based materials [6-10]. Among these materials, carbon-based adsorbents with high specific surface area, relative ease of regeneration, controllable pore structure, and low cost are considered as the most promising technologies [11,12]. Multiwalled carbon nanotubes (MWCNTs), with extremely high mechanical strength, electrical conductivity, and thermal conductivity, have been widely used in studies in many areas [13-15]. However, the defect of low surface porosity has severely limited the development of carbon nanotubes (CNTs), such as when CO_2 adsorption is involved. An effective method to address this problem is to introduce nitrogen groups into CNTs. Nitrogen doping in carbon can greatly change the surface structure, pore structure, electron transfer rate, and adsorbent interaction of the material, thus expanding the scope of application of CNTs in various fields [16-19]. There are three methods used to synthesized N-doped porous carbon, including (1) the direct carbonization of materials containing both carbon and nitrogen; (2) the introduction of N-containing materials and carbonization with a carbon source; (3) the heat-treatment of post-synthetic carbon materials with N-containing gases [20].

To date, a variety of nitrogen-containing MWCNTs (N-MWCNTs) have been reported. Fatemi et al. [17] prepared N-MWCNTs by using oxygenat-containing MWCNTs (O-MWCNTs) with ammonia. The results showed that N-MWCNTs enhanced the capacity and selectivity to adsorb CO_2. Molyanyan et al. [21] prepared amine functionalized MWCNTs (amine-MWCNTs) by functionalizing hydroxylated MWCNTs (OH-MWCNTs) and carboxylated MWCNTs (COOH-MWCNTs) in the presence of 3-[2-(2-aminoethylamino) ethylamino] propyl trimethoxysilane (TRI). It was confirmed that amine-MWCNTs exhibited high adsorption capacity of CO_2. Although there have been many studies focused on the preparation of nitrogen-containing CNTs, few studies have looked at the preparation of N-doped and high-porosity CNTs for CO_2 adsorption.

In this study, using a MWCNTs/polypyrrole (MWCNTs/PPy) mixture as the precursor and $ZnCl_2$ as the chemical activating agent, we synthesized nitrogen-containing porous carbon nanotubes (NCNTs). PPy, with high nitrogen content, is employed as both the carbon and nitrogen precursor. Enriched N and high porosity were successfully introduced onto the surface of the MWCNTs. The low activation temperature of $ZnCl_2$ ensures NCNTs that can be applied as materials with good CO_2 adsorption capacity.

The MWCNTs were treated with HNO_3/H_2SO_4 mixture solutions. Then, oxidized

MWCNTs (0.5 g) were dispersed in 100 mL 0.5 M $FeCl_3$ ($FeCl_3•6H_2O$, Sigma-Aldrich) solution under continuous stirring for 2 h. Finally, 0.0, 0.05, 0.1, 0.2, and 0.5 M PPy (Sigma-Aldrich) were added to the above mixture and reacted for 2 h. The resulting composites were then washed with distilled water and methanol, followed by drying in a vacuum oven at 80°C for 24 h. The composites were transferred to a tubular furnace for chemical activation by heating a 1:4 mixture of MWCNTs/PPy and $ZnCl_2$ (Analytical reagent, Tianjin Boda Co.) to 500°C at a heating rate of 5°C/min and maintaining isothermal conditions for 2 h under N_2 atmosphere. Then, the activated samples were washed several times with HCl (5 wt%) to remove any impurities and after that washed again with distilled water until reaching pH 7. Finally, the samples were dried in an oven at 80°C to remove the water. The chemically activated carbons containing 0.0, 0.05, 0.1, 0.2, and 0.5 M PPy were denoted as MWCNTs, CNP-0.05, CNP-0.1, CNP-0.2, and CNP-0.5, respectively.

Field-emission transmission electron microscopy (FE-TEM) was performed on a JEOL (JEM-2100F) to characterize the morphology of the NCNTs. The nitrogen absorption/desorption isotherms were obtained using a surface area analyzer (BEL, Japan) at 77 K and 1 atm. Before sorption measurements were taken, samples were degassed at 100°C for 24 h. The Brunauer-Emmett-Teller (BET) equation was used to estimate the specific surface area (S_{BET}). For a large number of microporous mediums, the Dubinin-Radushkevich (DR) equation, based on Polanyi adsorption potential theory, is a popular method of evaluating microporous structures. Therefore, we chose the DR formula to precisely estimate the micropore volume. The mesopore structures were estimated using the Barrett-Joyner-Halenda (BJH) equation. The micropore and mesopore size distributions were calculated by the Horvath-Kawazoe (HK) method and BJH method, respectively.

The CO_2 adsorption capacity of the carbon samples was measured by CO_2 isothermal adsorption at 298 K and 1 atm. In each experiment, the sample was loaded into a glass cell. Before measurements, the samples were degassed at 473 K for 24 h to obtain the residual pressure. After cooling the glass cell to room temperature, CO_2 was introduced until a pressure of 1 bar was attained. Ultra-high purity grade (99.9999%) CO_2 was used to exclude the effects of moisture and other impurities. Finally, a volumetric method was used to determine the CO_2 adsorption capacity.

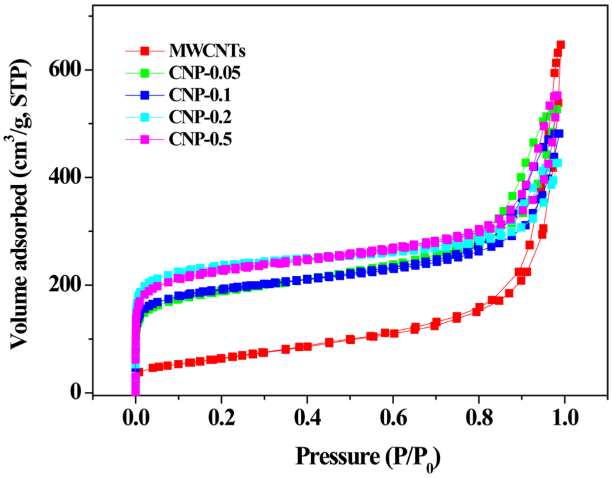

Fig. 1. N_2/77 K full isotherms of pristine MWCNTs and NCNTs.

Fig. 1 presents the N_2 adsorption isotherms (77K) of the pristine MWCNTs and synthesized NCNTs. According to the IUPAC classification, all the samples exhibit reversible type IV isotherms along with a hysteresis loop, which is one of the main characteristics of mesoporous materials. Furthermore, for all of the NCNTs samples, the N_2 adsorption isotherms have a sharp knee occurring at relative pressure (P/P_0) below 0.01, showing the strictly microporous nature. Compared to pristine MWCNTs, the nitrogen uptake of NCNTs clearly increases, indicating the formation of increasing porosity when PPy is employed as both nitrogen and carbon source and after $ZnCl_2$ activation. The textural properties of the MWCNTs and NCNTs (i.e., specific surface area and pore structure parameters) are summarized in Table 1. It can be seen that the specific surface area of the NCNTs ranges from 680 to 862 m^2 g^{-1}, larger than that of the MWCNTs (233 m^2 g^{-1}); this is mainly due to the increase of the micropore volumes. Clearly, with the increase in the micropore volumes, both the specific surface area and

Table 1. Pore structure parameters and N/C ratio for pristine MWCNTs and NCNTs

Samples	S_{BET}[a] (m^2 g^{-1})	V_{Mi}[b] (cm^3 g^{-1})	V_{Me}[c] (cm^3 g^{-1})	V_T[d] (cm^3 g^{-1})	F_M[e] (%)	AD[f] (nm)	N/C ratio	N (wt%)
MWCNTs	233	0.007	0.961	0.968	0.7	16.6	0.005	0.43
CNP-0.05	680	0.217	0.598	0.815	26.6	4.80	0.035	3.25
CNP-0.1	690	0.228	0.517	0.745	30.6	4.32	0.105	8.48
CNP-0.2	862	0.321	0.339	0.660	48.6	3.06	0.114	8.90
CNP-0.5	823	0.285	0.569	0.854	33.4	4.15	0.071	6.13

[a] Specific surface area (m^2/g): BET equation ($p/p_0 = 0.05–0.1$).
[b] Micropore volume (cm^3/g): DR equation.
[c] Mesopore volume (cm^3/g): BJH equations.
[d] Total pore volume (cm^3/g): V_{ads} $(P/P_0 = 0.995) \times 0.001547$.
[e] Fraction of micropores (%).
[f] Average pore diameter (Å): $2 \times S_{BET} / V_{ads}$.

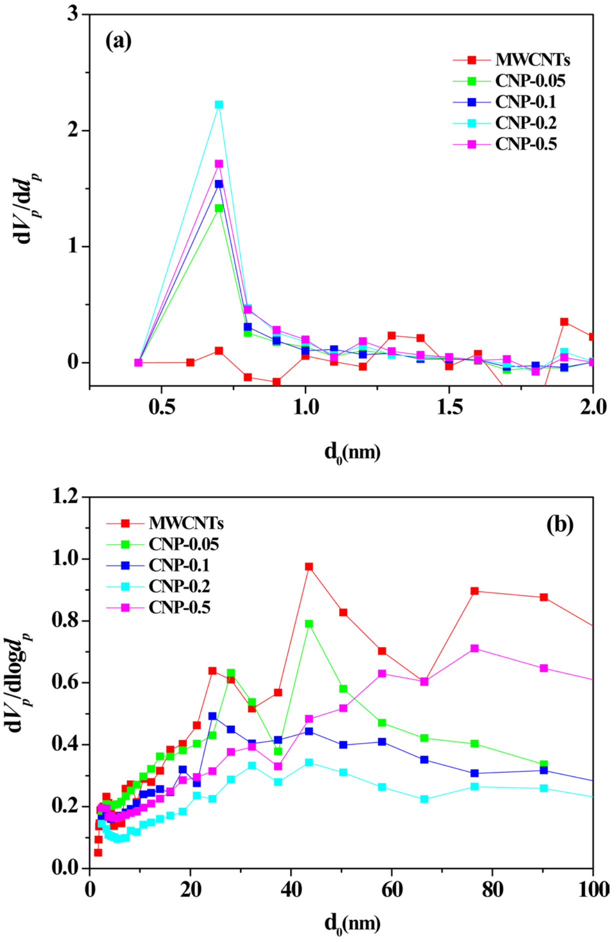

Fig. 2. Pore size distributions of pristine MWCNTs and NCNTs: (a) micropore size distribution and (b) mesopore size distribution.

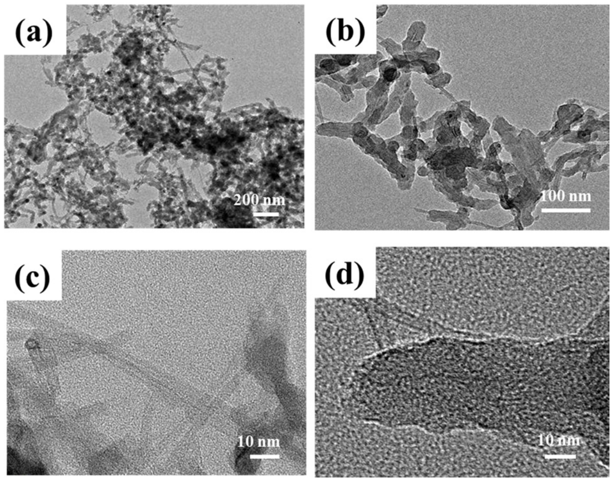

Fig. 3. TEM image of NCNTs (CNP-0.2).

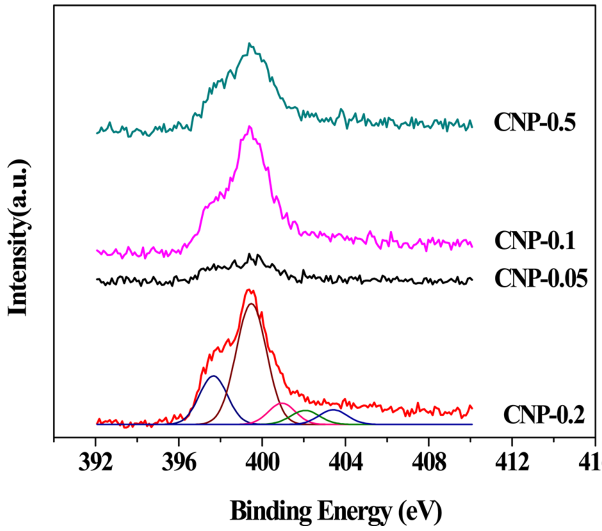

Fig. 4. XPS N1s region for NCNTs.

total pore volume are increased. Particularly, when PPy content varies from 0.05 to 0.1, this increase is sharper. Generally, the micropore volumes and fraction of micropores increase when higher amounts of PPy are employed. Only sample CNP-0.5 exhibits decrease in both specific surface area and fraction of micropores when the PPy content was from 0.2 to 0.5; these decreases are attributed to micropore enlargement, leading to a broader pore size distribution.

Fig. 2 shows the pore size distributions of the pristine MWCNTs and NCNTs. The micropore and mesopore size distributions were calculated by the HK method and BJH method. As shown in Fig. 2a, the synthesized NCNT samples demonstrate one single narrow peak centered at around 7 Å. The microporosity of the NCNTs can obviously be finely controlled by PPy addition and $ZnCl_2$ chemical activation, allowing the preparation of NCNTs with different pore size distributions. Fig. 2b shows the mesopore size distribution of MWCNTs and NCNTs. It can be observed that the obtained NCNTs primarily consist of mesopores and macropores less than 100 nm in diameter. Under low PPy content (i.e., 0.05, 0.1, and 0.2 M), all of the as-prepared samples exhibit a decrease of mesopores. However, when PPy content is up to 0.5 M, the mesopores show a slight increase caused by micropore enlargement, which is consistent with the data listed in Table 1.

TEM images of CNP-0.2 are provided as a typical representation to further investigate its morphology and structure (Fig.3). As shown in Fig. 3, the CNP-0.2 sample shows a rough surface and fibrous structure; fibers are overlapped by a compact carbon layer, increasing the total diameter to about 30 to 60 nm, indicating that the carbon layer is over 10 to 30 nm. These results confirm that, after PPy polymerization and $ZnCl_2$ activation, the MWNTs can act as excellent substrates for the formation of NCNTs with uniform core–shell structure. X-ray photoelectron spectroscopy (XPS) of N1s also was performed to study the form of nitrogen in the carbon matrix. As can be seen in Fig. 4, the four as-obtained samples show similar shapes, mainly pyridinic–like and pyrrolic-/pyridonic-like N (398.2±0.1 and 400.0±0.1, respectively). It is worth noting that the pyrrolic-/pyridonic-like N is most abundant among different nitrogen functionalities, which contribute greatly to CO_2 capture

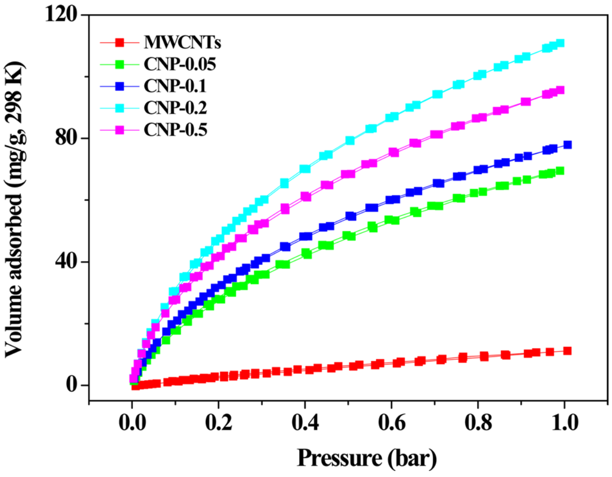

Fig. 5. CO_2/298 K sorption isotherms of pristine MWCNTs and NCNTs.

[22]. Furthermore, as determined by XPS, the nitrogen content of the NCNT samples ranges from 3.25 to 8.9 wt%, higher than that of the MWNTs (i.e., 0.43 wt%) (see Table 1). Thus, it is obvious that N-enriched MWNTs are obtained successfully after PPy polymerization.

Fig. 5 shows the CO_2 adsorption isotherms obtained at 298 K for the MWCNTs and prepared NCNTs. It can be seen that MWCNTs with low surface area and surface porosity exhibit the lowest CO_2 adsorption capacity and almost reach the saturation condition for CO_2 uptake at pressures varying from 0.0 to 1.0 bar. Owing to the presence of nitrogen-containing basic groups induced by PPy and abundant microporosity caused by $ZnCl_2$ activation, all of prepared NCNTs show improved CO_2 adsorption capacity. It is worth mentioning that CNP-0.2 shows the largest CO_2 uptake capacity (i.e., 110 mg g^{-1}), which might be ascribed to the large fraction of narrower micropores (<1 nm), as well as high nitrogen content. This is consistent with recent research that has suggested that high specific surface area and total pore volume do not directly contribute to high CO_2 adsorption capacity, and that narrower micropores (<1 nm) and incorporated heteroatoms such as N are more effective [23-25]. The narrower micropores improve the interaction between CO_2 molecules and the surface of the carbon solid adsorbents and thus enhance the CO_2 uptake capacity [26]. Furthermore, nitrogen-containing basic groups also increase the CO_2 adsorption capacity and selectivity by different mechanisms (i.e., acid–base interaction, Van der Waals interaction, and hydrogen-bonding interactions) [27,28].

In summary, we have prepared a series of NCNTs using MWCNTs and PPy as carbon sources and $ZnCl_2$ as the activation agent. The existence of PPy and $ZnCl_2$ allows a high N content and large micropore (<1 nm) distribution in the prepared NCNTs. Among all of the as-prepared samples, the CNP-0.2 sample shows the highest CO_2 adsorption capacity of 110 mg g^{-1}, indicating that the pore size and distribution of NCNTs lead to feasible contact with CO_2; the presence of a high percentage of N groups on the NCNTs could have resulted in further stabilization of the surface effects. The improved performance of the NCNTs is attributed to the graphitic porous carbon layers and basic nitrogen-containing functional groups, which result in further stabilization of molecular CO_2 on the NCNT surface.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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References

[1] Bai BC, Kim EA, Lee CW, Lee YS, Im JS. Effects of surface chemical properties of activated carbon fibers modified by liquid oxidation for CO_2 adsorption. Appl Surf Sci, **353**, 158 (2015). https://doi.org/10.1016/j.apsusc.2015.06.046.

[2] Xing W, Liu C, Zhou ZY, Zhang L, Zhou J, Zhuo SP, Yan ZF, Gao H, Wang GQ, Qiao SZ. Superior CO_2 uptake of N-doped activated carbon through hydrogen-bonding interaction. Energy Environ Sci, **5**, 7323 (2012). https://doi.org/10.1039/c2ee21653a.

[3] Jeon DH, Bae ST, Park SJ. Preparation and characterization of chemically activated carbon materials for CO_2 capture. Carbon Lett, **17**, 85 (2016). https://doi.org/10.5714/cl.2016.17.1.085.

[4] Ullah R, Atilhan M, Anaya B, Al-Muhtaseb S, Aparicio S, Patel H, Thirion D, Yavuz CT. Investigation of Ester and Amide Linker based porous organic polymers for carbon dioxide capture and separation at wide temperatures and pressures. ACS Appl Mater Interfaces, **8**, 20772 (2016). https://doi.org/10.1021/acsami.6b05927.

[5] Heo YJ, Le MUT, Park SJ. Investigation of carbon dioxide adsorption by nitrogen-doped carbons synthesized from cubic MCM-48 mesoporous silica. Carbon Lett, **18**, 62 (2016). https://doi.org/10.5714/cl.2016.18.062.

[6] Yu JM, Xie LH, Li JR, Ma YG, Seminario JM, Balbuena PB. CO_2 capture and separations using MOFs: computational and experimental studies. Chem Rev, **117**, 9674 (2017). https://doi.org/10.1021/acs.chemrev.6b00626.

[7] Basnayake SA, Su J, Zou XD, Balkus KJ. Carbonate-based zeolitic imidazolate frame work for highly selective CO_2 capture. Inorg Chem, **54**, 1816 (2015). https://doi.org/10.1021/ic5027174.

[8] Kim S, Lee YM. Rigid and microporous polymers for gas separation membranes. Prog Polym Sci, **43**, 1 (2015). https://doi.org/10.1016/j.progpolymsci.2014.10.005.

[9] Yuan H, Meng LY, Park SJ. KOH-activated graphite nanofibers as CO_2 adsorbents. Carbon Lett, **19**, 99 (2016). https://doi.org/10.5714/cl.2016.19.099.

[10] Hwang DG, Jeong E, Lee SG. Density functional theory study of CH_4 and CO_2 adsorption by fluorinated graphene. Carbon Lett, **20**, 81 (2016). https://doi.org/10.5714/cl.2016.20.081.

[11] Chandra V, Yu SU, Kim SH, Yoon YS, Kim DY, Kwon AH, Meyy-

appan M, Kim KS. Highly selective CO_2 capture on N-doped carbon produced by chemical activation of polypyrrole functionalized graphene sheets. Chem Commun, **48**, 735 (2012). https://doi.org/10.1039/c1cc15599g.

[12] Wang Q, Luo JZ, Zhong ZY, Borgna A. CO_2 capture by solid adsorbents and their applications: current status and new trends. Energy Environ Sci, **4**, 42 (2011). https://doi.org/10.1039/c0ee00064g.

[13] Kim JH, Kim DY, Jeong E, Lee YS. Characteristics of fluorinated CNTs added carbon foams. Appl Surf Sci, **360**, 1009 (2016). https://doi.org/10.1016/j.apsusc.2015.11.111.

[14] Tourani S, Khorasheh F, Rashidi AM, Safekordi AA. Hydro-purification of crude terephthalic acid using palladium catalyst supported on multi-wall carbon nanotubes. J Ind Eng Chem, **28**, 202 (2015). https://doi.org/10.1016/j.jiec.2015.02.015.

[15] Kim HS, Jung Y, Kim S. Capacitance behaviors of conducting polymer-coated graphene nanosheets composite electrodes containing multi-walled carbon nanotubes as additives. Carbon Lett, **23**, 63 (2017). https://doi.org/10.5714/CL.2017.23.063.

[16] Hao GP, Li WC, Qian D, Lu AH. Rapid synthesis of nitrogen-doped porous carbon monolith for CO_2 capture. Adv Mater, **22**, 853 (2010). https://doi.org/10.1002/adma.200903765.

[17] Fatemi S, Vesali-Naseh M, Cyrus M, Hashemi J. Improving CO_2/CH_4 adsorptive selectivity of carbon nanotubes by functionalization with nitrogen-containing groups. Chem Eng Res Des, **89**, 1669 (2011). https://doi.org/10.1016/j.cherd.2010.10.002.

[18] Wang MR, Hu LT, Lei XK, Fang J, Lai YQ. Pre-surface functionalization of commercial conductive carbon for effective N doping as a highly efficient electrocatalyst. Mater Lett, **207**, 33 (2017). https://doi.org/10.1016/j.matlet.2017.07.047.

[19] Ren XM, Li H, Chen J, Wei LJ, Modak A, Yang HQ, Yang QH. N-doped porous carbons with exceptionally high CO_2 selectivity for CO_2 capture. Carbon, **114**, 473 (2017). https://doi.org/10.1016/j.carbon.2016.12.056.

[20] Adeniran B, Mokaya R. Is N-doping in porous carbons beneficial for CO_2 storage? Experimental demonstration of the relative effects of pore size and N-doping. Chem Mater, **28**, 994 (2016). https://doi.org/10.1021/acs.chemmater.5b05020.

[21] Molyanyan E, Aghamiri S, Talaie MR, Iraji N. Experimental study of pure and mixtures of CO_2 and CH_4 adsorption on modified carbon nanotubes. Int J Environ Sci Technol, **13**, 2001 (2016). https://doi.org/10.1007/s13762-016-0989-0.

[22] Li Y, Zou B, Hu CW, Cao MH. Nitrogen-doped porous carbon nanofiber webs for efficient CO_2 capture and conversion. Carbon, **99**, 79 (2016). https://doi.org/10.1016/j.carbon.2015.11.074.

[23] Wickramaratne NP, Xu JT, Wang M, Zhu L, Dai LM, Jaroniec M. Nitrogen enriched porous carbon spheres: attractive materials for supercapacitor electrodes and CO_2 adsorption. Chem Mater, **26**, 2820 (2014). https://doi.org/10.1021/cm5001895.

[24] Babu DJ, Bruns M, Schneider R, Gerthsen D, Schneider JJ. Understanding the influence of N-doping on the CO_2 adsorption characteristics in carbon nanomaterials. J Phys Chem C, **121**, 616 (2017). https://doi.org/10.1021/acs.jpcc.6b11686.

[25] Geng Z, Xiao QF, Lv H, Li B, Wu HB, Lu YF, Zhang CM. One-step synthesis of microporous carbon monoliths derived from biomass with high nitrogen doping content for highly selective CO_2 capture. Sci Rep, **6**, 30049 (2016). https://doi.org/10.1038/srep30049.

[26] To JWF, He JJ, Mei JG, Haghpanah R, Chen Z, Kurosawa T, Chen SC, Bae WG, Pan LJ, Tok JBH, et al. Hierarchical N-doped carbon as CO_2 adsorbent with high CO_2 selectivity from rationally designed polypyrrole precursor. J Am Chem Soc, **138**, 1001 (2016). https://doi.org/10.1021/jacs.5b11955.

[27] Ma XC, Li LQ, Wang SB, Lu MM, Li HL, Ma WW, Keener TC. Ammonia-treated porous carbon derived from ZIF-8 for enhanced CO_2 adsorption. Appl Surf Sci, **369**, 390 (2016). https://doi.org/10.1016/j.apsusc.2016.01.274.

[28] Lim G, Lee KB, Ham HC. Effect of N-containing functional groups on CO_2 adsorption of carbonaceous materials: a density functional theory approach. J Phys Chem C, **120**, 8087 (2016). https://doi.org/10.1021/acs.jpcc.5b12090.