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Tailoring microporosity and nitrogen content in carbons for achieving high uptake of CO_2 at ambient conditions

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Abstract A series of nitrogen-containing carbon spheres (CS) was prepared using the modified Stöber method. These CS were synthesized by using resorcinol and formaldehyde as carbon precursors, melamine as nitrogen precursor and ammonia as a polymerization reaction catalyst. Hydrothermal treatment followed by activation of these polymer spheres resulted in highly porous nitrogen-containing CS. Elemental analysis and N_2 adsorption showed that the aforementioned CS exhibited high surface area (reaching 1,610 m^2/g) with large fraction of fine micropores (volume of micropores smaller than 1 nm was estimated to be 0.40 cm^3/g) and comparatively high nitrogen content (about 4.0 at.%). Interestingly, high CO_2 adsorption capacities, 4.4 and 6.9 mmol/g, were obtained for these CS at 1 bar and two temperatures, 25 and 0 °C, respectively.

Keywords CO_2 adsorption · Activated carbon spheres · Nitrogen-containing carbon spheres · CO_2 activation

1 Introduction

Global warming is one of the most studied atmospheric phenomena during past decade; there is a common believe that it is mainly due to greenhouse gases such as CO_2, water vapor, N_2O, and CH_4. Among them CO_2 is probably the main contributor to the global warming. The reduction of carbon dioxide emissions has attracted a great attention because this gas is considered as one of the most destructive anthropogenic contributors for both global warming and climate change. In the last few years, the CO_2 amount in atmosphere continued to increase with an alarming rate. The main contributors to this increase are vehicular emissions, fossil-fired power plants, deforestation and chemical processes. It was shown that 77 % of anthropogenic greenhouse gas emission comes from fossil fuel-fire power plants (coal, petroleum, and natural gas) totaling 38 Gt in 2004; it is predicted that this number will grow in the future and about 50 % increase is expected by 2030 (D'Alessandro et al. 2010; Samanta et al. 2012).

In the recent years, various types of porous adsorbents, including metal organic frameworks (MOF), zeolites, silica, metal oxides, and carbon materials have been investigated for CO_2 capture (An et al. 2010; Liu et al. 2012a; Grajciar et al. 2012; Zukal et al. 2011; Broda and Müller 2012; Sevilla and Fuertes 2011). Among them, carbon materials gained much attention because they exhibit several advantages in comparison to the aforementioned other porous materials. Namely, carbon materials: (1) possess better chemical and physical properties (namely, higher resistance to water due to hydrophobicity, higher thermal stability, controllable pore structure, high surface area, and chemical resistance to both alkali and acidic media), (2) can be easily prepared at low cost, and (3) can be regenerated at low energy requirement. Thus, these materials are the most studied adsorbents towards CO_2 capture. Most of these studies have been carried out with a special emphasis on the development of carbon materials with high surface area, fine micropores, and large nitrogen content (Wang and Yang 2012; Yang et al. 2012; Xing et al. 2012). Many of these reports deal with introduction of either one or two of the aforementioned properties. Recently, we experimentally showed that the carbons with fine micropores

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(<1 nm) are responsible for high CO_2 adsorption at one bar (Wickramaratne and Jaroniec 2013a, b. This finding is in an excellent agreement with experimental and computer modeling studies reported by Presser et al. (2011), Hu et al. (2011), Yang and Zhong (2004). Another set of reports deal with nitrogen-containing microporous carbons for CO_2 capture, claiming that these carbons exhibit unprecedented CO_2 adsorption capacities and selectivity over nitrogen at flue gas conditions, which is at 25 °C and 0.2 bar (Zhao et al. 2012). There are mainly two methods available for introduction of nitrogen into carbon matrix: (1) by using nitrogen-containing carbon precursors in the synthesis, and (2) by passing ammonia through carbons at high temperatures (Gu et al. 2013; Liu et al. 2011b). The former method is commonly used for the synthesis of nitrogen-containing carbons.

Our recent studies showed that the cysteine-assisted Stöber synthesis could be employed to obtain polymeric spheres with nitrogen- and sulfur-containing groups. However, these groups were decomposed during carbonization process, and the resulting carbons possessed only trace amounts of heteroatoms (Wickramaratne et al. 2013). It was shown that nitrogen-containing carbon spheres (CS) can also be obtained by reaction between resorcinol and hexamethylenetetramine in the presence of citric acid as catalysts. However, these CS exhibited also relatively small amount of nitrogen ranging from 1.3 to 3.1 % (Liu et al. 2012b). Su et al. (2011) also reported the synthesis of polypyrrole-derived nitrogen containing microporous CS with unprecedented nitrogen doping (~12.5 %). However, these carbons possessed very low specific surface areas ranging from 12 to 36 m^2/g. Further, this group showed that the KOH activation of these carbons caused a substantial increase in the specific surface area up to 1,080 m^2/g, but the nitrogen content dropped below 2.2 %. In addition, microporous polymer spheres were obtained by melamine-assisted synthesis; however, no data on either nitrogen content or CO_2 adsorption capacity are provided for these particles (Zhong et al. 2012). The nitrogen-containing carbons (non-spherical) obtained from melamine–formaldehyde were also studied for adsorption, catalysis and energy-related applications (Candelaria et al. 2012; Lv et al. 2013); however, these carbons exhibited relatively low specific surface areas (<260 m^2/g).

In current study, we report the synthesis of nitrogen-containing highly porous CS using Stöber synthesis in the presence of melamine, which acted as nitrogen precursor. It is shown that the resulting polymer spheres are nitrogen rich and their carbonization in flowing nitrogen produces nitrogen-containing CS. Additional carbon dioxide activation of these spheres was performed to increase both the surface area and microporosity. The elemental analysis (EA) confirmed the presence of nitrogen in the CS (up to ~4 %) and nitrogen adsorption revealed their high surface area and enhanced microporosity. Further, these carbons showed a comparatively high CO_2 adsorption capacity, respectively, 4.4 and 6.9 mmol/g at 25 and 0 °C under atmospheric pressure (1 bar). Interestingly, it is shown that very high CO_2 adsorption (up to 1.5 mmol/g) can be achieved at flue gas conditions (25 °C and 0.2 bar).

2 Experimental

2.1 Chemicals

Resorcinol [$C_6H_4(OH)_2$; 98 %], melamine ($C_3H_6N_6$; 99 %) and formaldehyde (HCHO, 37 %), were purchased from Acros Organics. Ammonium hydroxide (NH_4OH; 29.2 %) was acquired from fisher chemicals.

2.2 Synthesis of carbon spheres

Nitrogen-containing carbon spheres (CS) were synthesized using a slightly modified recipe reported by Liu et al. (2011a). A detailed synthesis was follows: an aqueous-alcoholic solution was prepared by mixing 16 mL of ethanol and 40 mL of distilled water at 30 °C. Subsequently, 0.2 mL of 29.2 wt% ammonia was added under continuous stirring. Then, various amounts of resorcinol and melamine (R-0.3 g and M-0.1 g, R-0.2 g and M-0.2 g, and finally R-0.1 g and M-0.3 g were used to achieve the total mass of resorcinol and melamine in the synthesis mixture equal to 0.4 g) were added to the mixture and stirred until a complete dissolution. Next, 0.6 mL of 37 wt% formaldehyde was added slowly to the solution and stirred for 24 h at 30 °C. Finally, the reaction mixture was transferred to a 125 mL-capacity Teflon container and placed in a sealed metal autoclave vessel, which was placed in an oven at 100 °C for 24 h. The solid product (polymer spheres) was obtained by centrifugation and dried at 100 °C for 12 h.

Thermal treatment of the resulting polymeric spheres was performed in flowing nitrogen in the tube furnace using a heating rate of 2 °C/min up to 350 °C, dwell for 4 h, and resuming heating rate of 5 °C/min up to the respective final temperature (either 600 or 800 °C) and dwell for 2 h. The resulting carbon materials were labeled as CSx-T, where "CS" refers to carbon spheres, "x" indicates the amount of the melamine used in the reaction (0.1, 0.2 and 0.3 g of melamine were denoted by x = 1, 2 and 3, respectively), and "T" refers to the initial number of the three digit carbonization temperature: for instance, for the carbons obtained at 600 and 800 °C were denoted with T = 6 and 8, respectively.

The post-synthesis activation of the CS was performed using previously reported conditions (Górka and Jaroniec

2011) to achieve the optimal structural properties for adsorption applications. This activation was carried out as follows: A ceramic boat with 0.10 g of CS was placed in a ceramic tube furnace under flowing nitrogen with a heating rate of 10 °C/ min up to 850 °C. After the required temperature was reached, the activating gas was introduced to the tube furnace (50 cm^3/min) for 4 h and then switched back to nitrogen to prevent further activation during the cool down process. The resulting activated CS are denoted as CSx-T-CD, where "x" and "T" represent melamine amount and the initial number of the carbonization temperature (as discussed in the previous paragraph), respectively, and "CD" refers to carbon dioxide activation, which was performed at 850 °C.

2.3 Characterization

Nitrogen adsorption isotherms were measured at −196 °C on ASAP 2010 volumetric adsorption analyzers manufactured by Micromeritics, Inc. (Norcross, GA, USA) using nitrogen of 99.998 % purity. CO_2 adsorption isotherms were obtained at both 0 and 25 °C on ASAP 2020 volumetric adsorption analyzer manufactured by Micromeritics, Inc. Before adsorption measurements, each sample was degassed under vacuum for at least 2 h at 200 °C. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05–0.20. Pore size distributions (PSD) were calculated from nitrogen adsorption data by the DFT method provided by Micromeritics. The X-ray diffraction (XRD) measurements were recorded for the carbonized samples using a PANanalytical, Inc. X'Pert Pro Multi-Purpose Diffractometer (MPD) with Cu Kα radiation (1.5406 Å) at an operating voltage of 45 kV. TEM images were obtained using FEI Tecnai F20ST/STEM instrument operated at 200 keV. The preparation of samples for TEM analysis involved their sonication in ethanol for 2–5 min and deposition on a 400 mesh lacey carbon coated copper grid. The percentages of carbon, nitrogen, sulfur, and hydrogen were obtained using a LECO TruSpec Micro elemental analyzer. SEM images were obtained using Hitachi S-2600N scanning electron microscope.

3 Results and discussion

The main goal of this study was to investigate the role of both nitrogen and fine micropores in carbons towards CO_2 adsorption. A series of nitrogen-containing CS was synthesized by using Stöber method in the presence of melamine, which acted as a nitrogen precursor. The EA data show that the nitrogen content in these carbons can be increased by increasing melamine amount (see Table 1). Namely, for the carbons obtained at 600 °C the nitrogen content can be increased from 2.6 to 2.9, and 4.0, simply by increasing the amount of melamine from 0.1 to 0.2 and 0.3 g, respectively. Further, it was shown that both higher temperature carbonization (800 °C) and activation lowered the nitrogen content as compared to the carbons obtained at 600 °C. It is obvious that both high temperature carbonization and high temperature activation prompted the loss of nitrogen-containing moieties. The nitrogen content obtained for CS3-8 and CS3-6-CD are 2.6 and 2.9, respectively. Interestingly, activated carbons possessed higher nitrogen content than the respective carbons carbonized at 800 °C. There are two possible explanations: (1)

Table 1 Adsorption parameters and particle size for the samples studied

Sample	D_{PS} (nm)	S_{BET} (m^2/g)	V_{total} (cm^3/g)	PV_{1nm} (cm^3/g)	n_{CO2} (mmol/g) 25 °C	0 °C	N%	N/C %
PS1	–	–	–	–	–	–	8.1	13.7
PS2	–	–	–	–	–	–	13.3	23.8
PS3	–	–	–	–	–	–	19.8	37.4
CS1-6	500*	593	0.25	0.20	3.5	–	2.6	2.9
CS2-6	430*	575	0.24	0.19	2.5	–	2.9	3.2
CS3-6	390*	555	0.24	0.18	2.6	3.9	4.0	4.6
CS1-6-CD	450^+	1,610	0.64	0.40	4.4	6.9	2.3	2.5
CS2-6-CD	390^+	1,207	0.48	0.36	4.2	–	2.3	2.6
CS3-6-CD	330^+	1,123	0.44	0.34	4.0	6.2	2.9	3.4
CS1-8	–	698	0.26	0.24	3.7	–	1.6	1.7
CS2-8	–	641	0.25	0.23	3.5	–	2.1	2.3
CS3-8	–	495	0.21	0.16	–	–	2.6	2.9

Notation: D_{ps} is the mode particle size obtained from TEM and SEM images; V_{total} is the single point pore volume calculated from adsorption isotherm at P/P_o=0.98; S_{BET} is the BET specific surface area obtained from the adsorption data in the P/P_o range from 0.05 to 0.2; PV_{1nm} is the volume of micropores below 1 nm; n_{CO2} is the CO_2 adsorption capacity at 25 and 0 °C and 1 bar; superscripts * and $^+$ in the second column refer to the mode sizes of particles obtained from TEM and SEM images, respectively; and PS represents the as-synthesized polymer spheres

the nitrogen-containing moieties are relatively stable at CO_2 environment than in nitrogen atmosphere at higher temperatures and/or (2) the amount of carbon decomposition during the activation process is comparatively higher than that during carbonization in nitrogen, which may result in higher N% in the case of activated carbons. The N/C atomic ratio and N% data are listed in Table 1.

Nitrogen adsorption isotherms measured for carbon and activated CS are shown in Fig. 1. All isotherms are type I, which is revealed by distinct adsorption plateau, indicating the presence of highly microporous structure. The surface area of the carbons obtained at 600 and 800 °C varies from 550 to 600 and 490–700 m^2/g, respectively. As can be seen from Table 1, the CS-6 series of carbon exhibits somewhat similar surface area, indicating that the increment of melamine in the reaction mixture did not disturb much the formation of microporous structure at low temperature carbonization. However, in the case of CS3-8 the surface area is lower as compared to CS3-6, whereas CS1-8 showed relatively high surface area as compared to CS1-6. It is possible that in the case of CS1-8 the decomposition of nitrogen-containing moieties at high temperature carbonization caused an increase in microporosity, while in the case of CS3-8 this process was too rapid, which led to the partial deterioration of the microporous structure. The surface area of the activated carbons studied range from 1,100 to 1,600 m^2/g, which indicates about 600–1,000 m^2/g enhancement as compared to the respective non-activated carbons; of course, this enlargement in the surface area is mainly due to the creation of additional micropores during activation process. It was shown previously that the enhancement in the surface area could reach up to 1,600 m^2/g for activated CS (Wickramaratne and Jaroniec 2013b). The smaller surface area enhancement observed for nitrogen-containing activated CS observed in this study is probably due to the presence of melamine-generated moieties, which can be decomposed during activation, leading to larger pores (>1 nm) and/or partial collapse of the microporous structure. The PSD and cumulative pore volume curves obtained from N_2 adsorption by density functional theory (DFT) method for slit-like pore geometry for both carbons and activated carbons are shown in Fig. 2. Figure 2a shows the incremental pore volume against pore size for the CS-6 and CS-8 series of carbons. As can be seen all samples exhibited fine micropores; namely CS1-8 possessed large fraction of fine micropores as compared to CS1-6. However, CS3-8 possessed a slightly smaller amount of fine micropores as compared to CS3-6. Figure 2b shows clearly that activated carbons possessed both fine micropores (<1 nm) and larger micropores (1 nm < x <2 nm) as well as larger volume (PV_{1nm}) of micropores below one nm than the respective non-activated carbons. Namely, PV_{1nm} for CS1-6-CD is 0.40 cm^3/g as compared to 0.20 cm^3/g for CS1-6. The basic adsorption and

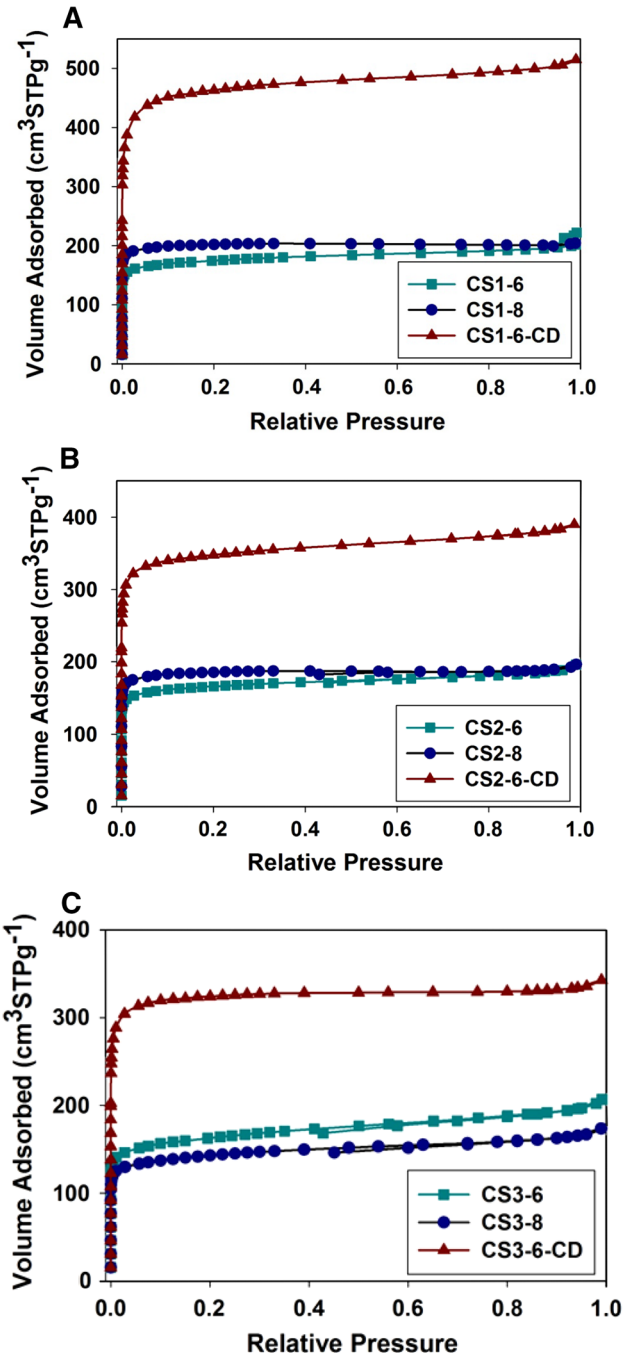

Fig. 1 Nitrogen adsorption isotherms for CS1 (**a**), CS2 (**b**), and CS3 (**c**) carbons and activated carbons studied

structural parameters for these materials are shown in Table 1.

Transmission electron microscopy (TEM) and scanning electron microcopy (SEM) analysis were used to investigate the morphology of the carbons studied. The TEM and SEM images (Fig. 3) showed spherical morphology with mode particle size ranging from 390 to 500 and 330–450 nm for the carbons obtained at 600 °C and

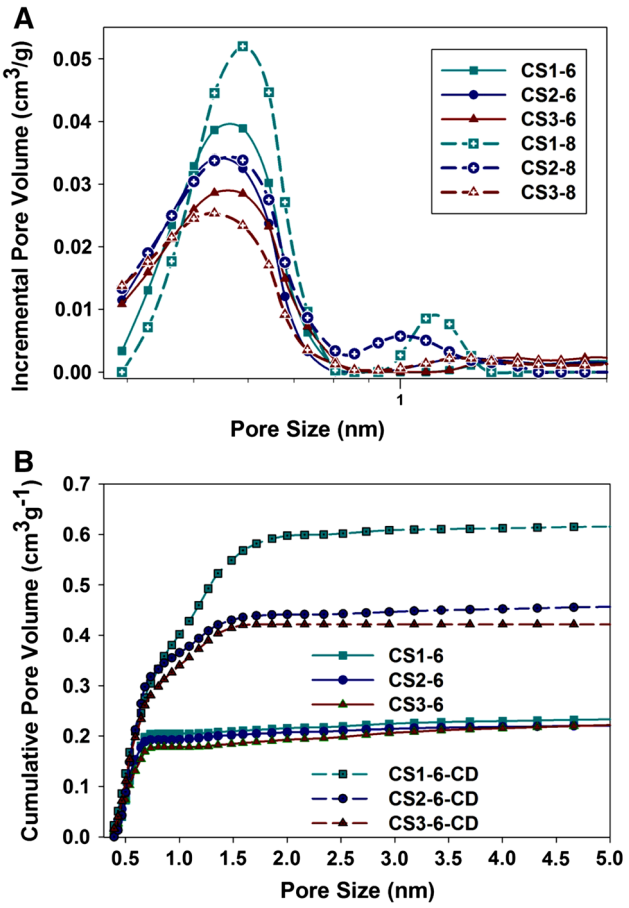

Fig. 2 Incremental (**a**) and cumulative (**b**) pore size distributions for the carbons studied

activated CS, respectively. It is noteworthy that the size of the CS-6 CS decreased with increasing amount of melamine. An increase in the melamine percentage from 25 to 50 and 75 caused a gradual decrease in the particle size from 500, 430, and 390 nm, respectively. The smaller particle size obtained for activated CS with respect to their analogous CS is due to the reduction of the outer surface of CS, which is mainly caused by reaction between CO_2 molecules and the outer carbon surface at higher temperatures. Previous studies showed that the CO_2 activation of CS reduced the size of the resulting activated CS. Further, the particle size of these spheres can be tailored to some degree by controlled activation, for instance, by adjusting the activation time. The wide-angle XRD spectra for the CS studied are shown in Fig. 4. The two broad peaks obtained at $2\theta = 25$ and 44° indicate that no pronounced graphitization occurred during the carbonization and activation (Wickramaratne and Jaroniec 2012, 2013a).

CO_2 adsorption on nitrogen-containing microporous CS was investigated at 25 and 0 °C under atmospheric pressure (1 bar). The CO_2 adsorption isotherms for both activated and non-activated CS are shown in Fig. 5a. For CS-6, CS-8 and CS-6-CD series of carbons the CO_2 adsorption capacity at 25 °C under 1 bar ranges from 2.5 to 3.5, 3.5 to 3.7 and 4.0–4.4, respectively. The CO_2 uptake for CS3-6, CS3-6-CD and CS1-6-CD at 0 °C under 1 bar is 3.9, 6.2 and 6.9 mmol/g, respectively (see Fig. 5b; Table 1). Thus, the activated CS studied exhibited very high CO_2 uptake at both 0 and 25 °C under atmospheric pressure. This is

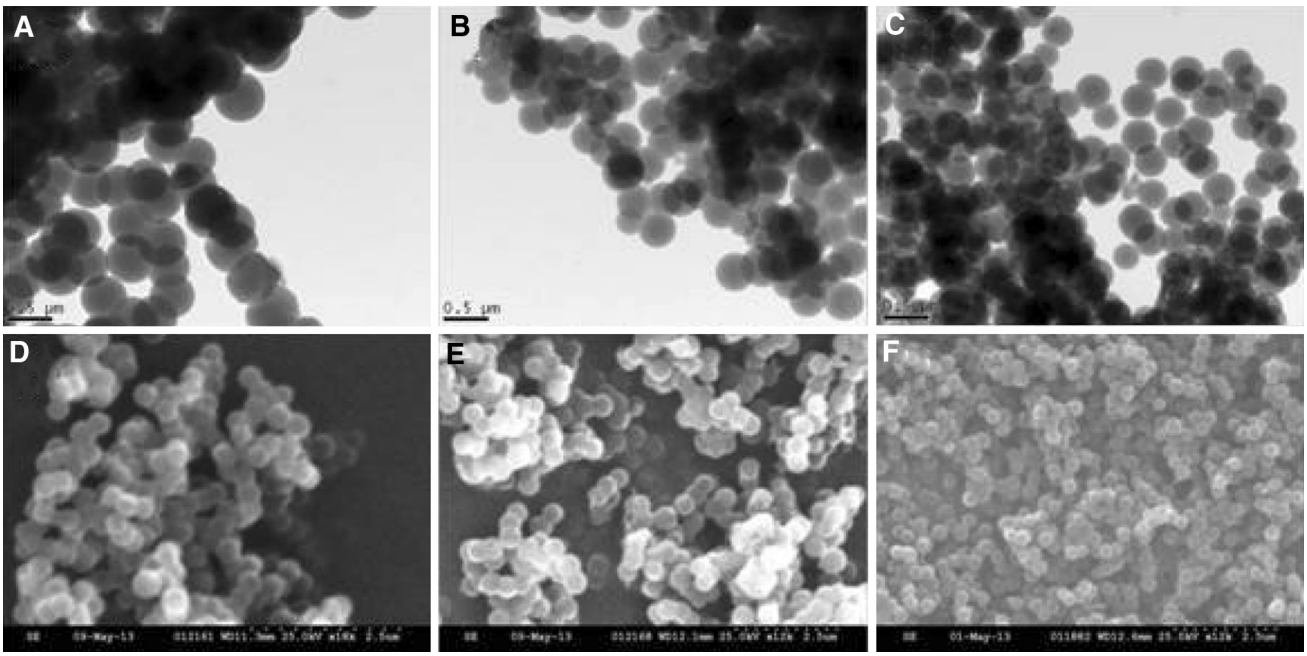

Fig. 3 TEM images of CS1-6 (**a**), CS2-6 (**b**), and CS3-6 (**c**) and SEM images of CS1-6-CD (**d**), CS2-6-CD (**e**), and CS3-6-CD (**f**)

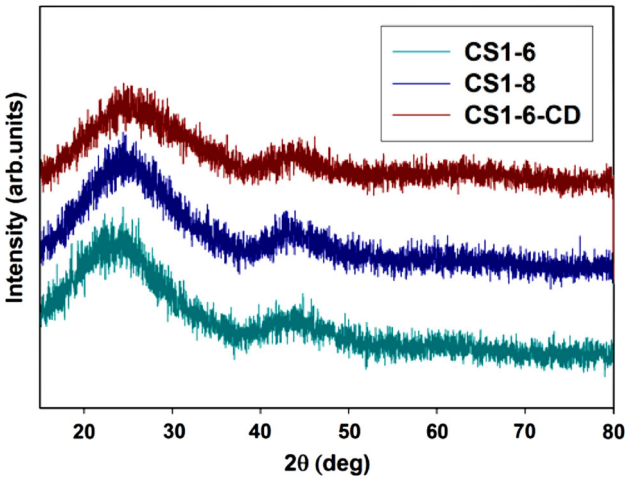

Fig. 4 Wide-angle XRD patterns for CS1 series of carbon samples

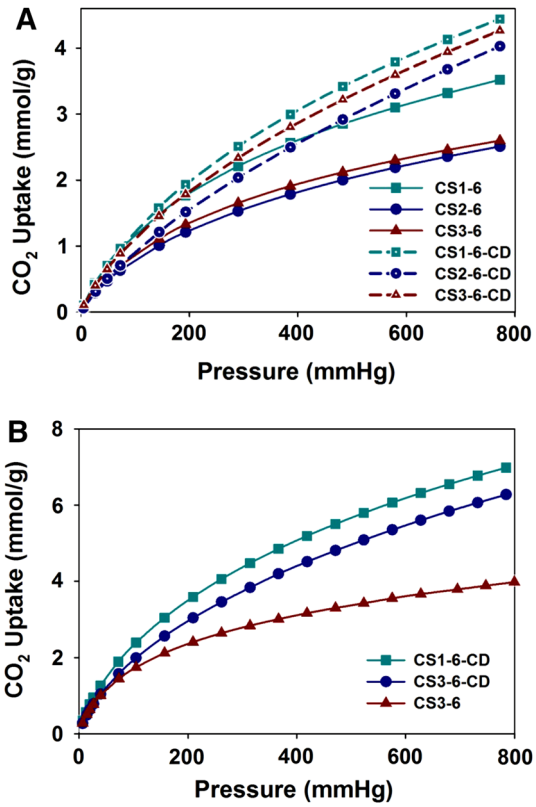

Fig. 5 CO_2 adsorption isotherms for CS-6 and CS-6-CD series of carbons measured at 25 °C (**a**), and for selected carbons measured at 0 °C (**b**)

mainly due to the presence of high fraction of fine micropores, which are responsible for adsorption at ambient conditions. It was shown previously (Wickramaratne and Jaroniec 2013b) that phenolic resin-based CS exhibited comparatively high CO_2 uptake reaching ~2.5 mmol/g at 25 °C and 1 bar. This relatively large CO_2 uptake was

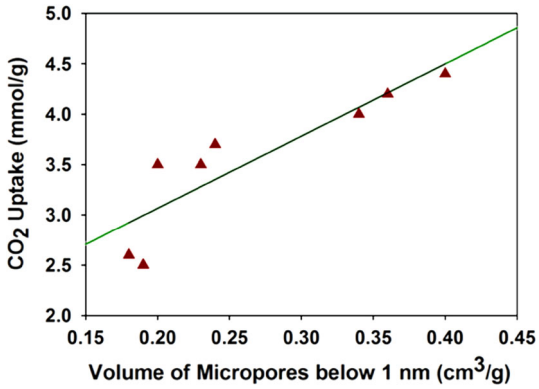

Fig. 6 CO_2 uptake at 25 °C versus the volume of micropores below 1 nm for the carbons studied

mainly due to the presence of high fraction of fine micropores (<1 nm). Interestingly, CS1-6 exhibited very high CO_2 uptake up to 1.5 and 3.0 mmol/g, at 25 and 0 °C under 0.2 bar, respectively, at the flue gas conditions. Such high CO_2 adsorption at low pressure could be attributed to the integration of high nitrogen content and ultra-fine micropores (<0.6 nm) in CS. It was reported that nitrogen-containing carbons are responsible for low pressure CO_2 adsorption (Zhao et al. 2012). In addition, our previous studies showed that ultra-fine micropores are also responsible for low pressure CO_2 uptake (Wickramaratne and Jaroniec 2013a, b). The importance of fine micropores for enhancement of CO_2 adsorption is illustrated by the relationship between the volume of fine micropores (PV_{1nm}) against CO_2 capacity at 1 bar. As shown in Fig. 6, the CO_2 capacity at 1 bar increases with increasing value of PV_{1nm}. However, there is no linear relationship observed between the CO_2 capacity and N%. This study indicates the dominating role of fine micropores in CO_2 capture in relation to the effect of N%, which seems to be less pronounced at lower nitrogen content (below 4 %).

4 Conclusions

A series of highly microporous nitrogen-containing CS was synthesized using a slightly modified Stöber method in the presence of melamine as a nitrogen precursor. Remarkably, these CS exhibited very high CO_2 uptake of 6.9 and 4.4 mmol/g at 0 and 25 °C under 1 bar, respectively. Moreover, these carbons showed very high CO_2 adsorption capacities 1.5 and 3.0 mmol/g at flue gas conditions, 25 and 0 °C under 0.2 bar, respectively. Interestingly, activation of these CS produced highly porous CS with comparatively high loading of nitrogen, making them potentially attractive materials as electrodes for supercapacitors.

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