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Research Article

CO_2 Storage Properties of Nanostructured Carbons by a Microwave Plasma Reactor

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Nanostructured carbon was successfully produced by methane cracking in a relatively low-energy cold plasma reactor designed in-house. A followed thermal treatment was carried out to further enhance its porosity. The modified plasma carbon was then employed for CO_2 adsorption at 25°C. The as-synthesized plasma carbon and the modified carbon were characterized by BET surface area/pore size analyzer, Raman spectra, and transmission electron microscopy (TEM). The results show thermal modification pronouncedly improves BET surface area and porosity of PC due to opening up of accessible micro-/mesopores in the graphitic structure and by the removal of amorphous carbons around the graphite surface. The modified PC displays a higher adsorption capacity at 25°C than that of the commercial activated carbon reported. The low hydrogen storage capacity of the modified PC indicates that it can be considered for CO_2 removal in syngas.

1. Introduction

Climate change resulting from the emission of greenhouse gases, especially CO_2, has become widespread concern in recent years. The International Panel on Climate Change (IPCC) estimated the CO_2 levels would range from 10 Gt to ~250 Gt of CO_2 by 2100 [1]. CO_2 capture and storage methods based on the low cost and energy-efficient requirements are crucial for achieving a substantial reduction of CO_2, thereby stalling global warming. Consequently, much effort has been made over the last decade to develop various chemical and physical methods for CO_2 capture and separation [2–4]. Among these approaches, porous or nanosized solid adsorbents have been widely investigated as a medium for CO_2 capture and separation, as researchers attempt to exploit their large accessible surface areas and large pore volumes. Various amines compounds [5–7], metal oxides [8, 9], amine containing polymers [10], zeolites [11], and porous carbons [12, 13] are identified as efficient CO_2 capture sorbents. Porous carbon materials have been actively considered as CO_2 sorbent, due to their highly developed porosity, extended surface area, surface chemistry, and thermal stability [14]. Commercially porous carbon structures are generated in carbon precursors through physical or chemical modification. In industrial practice, thermal modification is most frequently carried out by burning off some of the raw carbon to create micropores [15, 16]. The thermal modification usually takes place at temperature between 700 and 1000°C in steam or CO_2. Donnet et al. have summarized the physical methods of activation that involves primary carbonization (below 700°C) followed by controlled gasification under the action of oxidizing gases at high temperature, up to 1100°C [17]. Hence, the desirable activated carbon with respect to surface area can be produced through controlling activation conditions, for example, activation temperature and time. Sekirifa et al. conducted an investigation of pyrolysis and thermal activation between 700 and 900°C [18]. The BET surface area of the resulting product is increasing from 502 to 604 m^2/g with increasing temperature of treatment.

Previous studies have been carried out on the use of activated carbons [19], carbon fibers, carbon nanotubes, metal-carbon composites, and nitrogen-doped carbons as adsorbents for CO_2 capture [12, 13, 20–22]. Carbon based materials display a comparatively high adsorption capacity for CO_2 capture over a wide range of operating conditions. However, their performance in CO_2 capture is determined by both their textural and surface properties. Wickramaratne and Jaroniec [19] studied CO_2 adsorption on microporous

carbon in relation to the pore size and proved micropores smaller than 1 nm are responsible for high CO_2 adsorption at 1 bar.

In our previous study, we successfully produced nano-sized carbons with a mixture of microstructures by a self-designed microwave plasma reactor via methane cracking, which was referred to as plasma carbon (PC) [23]. The PC consists of structures of spherical particles and graphene sheets. The goal of this study is to improve the porosity of PC by the thermal modification process and investigate the CO_2 storage capacity of the modified PC.

2. Experimental Methods

The experimental setup was discussed in a previous paper [23]. A microwave plasma torch system was designed and assembled using a magnetron with a maximum power of 6 kW produced by the power supply. The microwave radiation passed through a three-stub tuner and was then fed into a waveguide, which was connected to a cavity. A quartz tube with a diameter of 3.4 cm connected with a sample collector at the end was inserted into the nozzle and intersected with the waveguide. Under the operating conditions used in this paper, a gas mixture of 12 L/min of N_2 and 0.75 L/min of CH_4 was fed into the discharge zone by the nozzle. The applied microwave power was set up at 2000 W. N_2 also acted as a carrier gas and was known as buffer gas when cracking methane in the microwave plasma reactor. Carbon products were collected in the sample collector at the end of quartz tube.

The literature indicates that the thermal treatment of carbon at a higher temperature in the range between 700 and 1000°C in steam or CO_2 leads to more efficient removal of amorphous/loose carbon and hence a larger surface area [24]. Therefore, a relatively high temperature for the thermal modification was selected in order to compare with literature. Here, a 50 mg plasma carbon was loaded in a thermal furnace, heated up to 950°C, under flowing N_2 gas at 80 mL/min, and then CO_2 gas was introduced to the furnace at a flow rate of 80 mL/min for 120 min. After the treatment, the samples were cooled to room temperature under N_2 gas flow and then kept in the glove box for further characterization.

The produced carbon powder particles were dispersed in acetone and cleaned with an ultrasonicator to remove possible organic impurities from the carbon particles, which were subsequently filtered, and then dried in a vacuum oven at 160°C for 2 h. The microstructure of the modified carbon samples was characterized by a transmission electron microscope (TEM), JEOL JEM 2000-EX, and a high-resolution transmission electron microscope (HRTEM), TECNAI, FEI Company. BET surface area and porosity of each sample were determined from argon adsorption at 77 K using a surface area/pore size analyzer, Quantachrome AUTOSORB-1. The modified carbon samples were degassed for 8 h at 573 K to remove any moisture or adsorbed contaminants that may be present in the materials. The BET surface areas of the samples were determined using the BET equation imbedded in the manufacturer-supplied software. The pore size distribution was evaluated by the density functional theory (DFT) method [25, 26]. The total pore volume V was estimated by converting the amount of argon gas adsorbed (expressed in cm^3/g STP) to the corresponding liquid volume of the adsorbate at a relative pressure of 0.99. The properties of carbon structures were also analyzed by a Renishaw inVia Raman spectroscopy using a 514.5 nm Ar Laser.

Table 1: Physical properties of plasma carbons.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)[a]	Pore size (nm)[b]
As-synthesized PC	114	0.2055	7.2
Modified PC	459	0.5496	4.8

[a] V_p is the total pore volume, derived from the amount of vapor adsorbed at $P/P_0 = 0.96$.
[b] Average pore width, calculated by $4V_p/S_{BET}$.

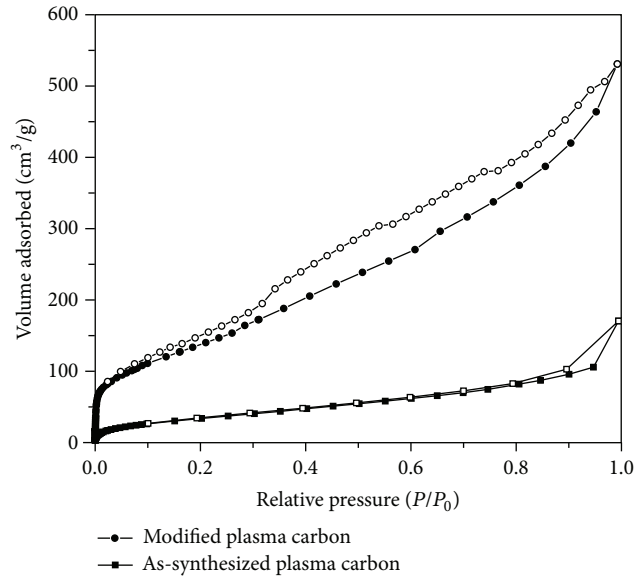


Figure 1: Argon isotherms of as-synthesized PC and modified PC at 77 K.

3. Results and Discussion

BET surface area and porosity of the synthesized plasma carbon and the modified plasma carbon were determined from the argon isotherm (Figure 1). The values of BET surface area, pore volumes, and pore size are summarized in Table 1. The argon isotherm of the as-synthesized PC exhibits types III and V characteristics according to the IUPAC classification of adsorption isotherms, which are characteristic week affinities of adsorbents to adsorbates [27], as a result of the coexistence of mesoporous and macroporous surfaces [28]; in the current case, the macropores are mainly due to the packing of the carbon powder particles [23]. From the isotherm curve of the modified plasma carbon, the presence of a steep increase at very low relative pressure P/P_0 reflects the generation of micropores after thermal treatment. The hysteresis loop can be observed at a high relative pressure from 0.3 to 1.0, which can be related to capillary condensation on mesopores. According to IUPAC

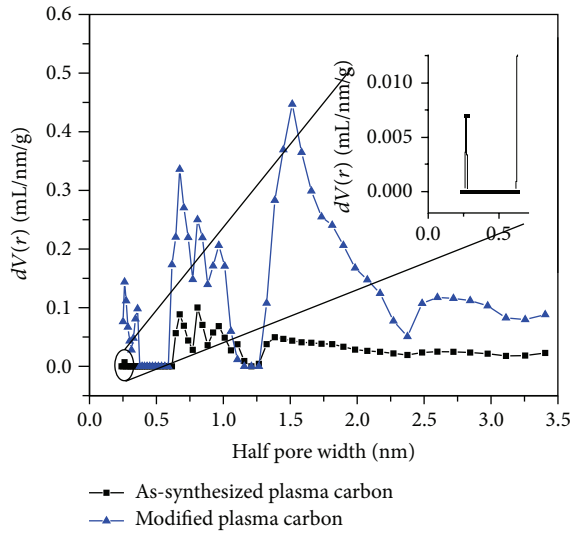
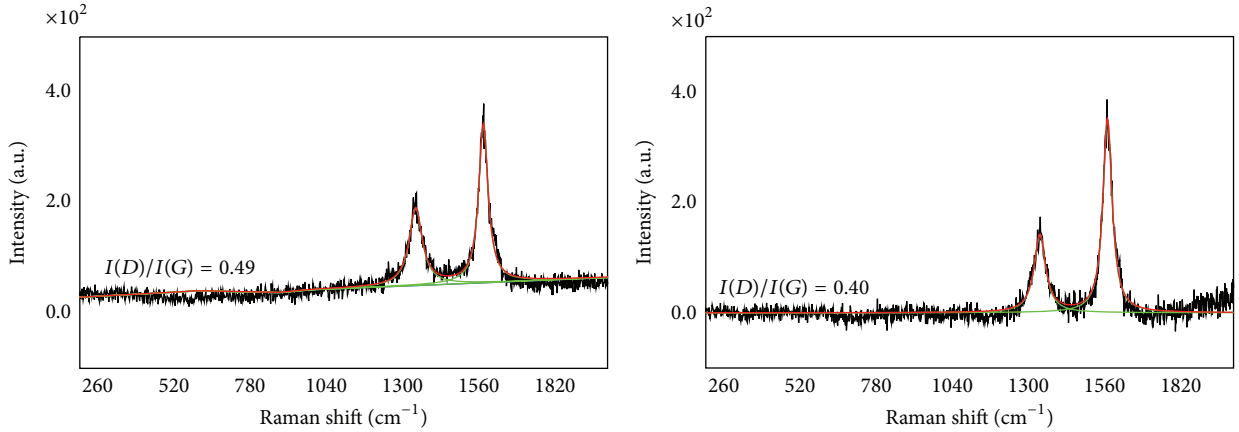


FIGURE 2: Pore size distributions of as-synthesized PC and modified PC, using the DFT model.



(a) As-synthesized PC (b) Modified PC

FIGURE 3: Raman spectrum of as-synthesised PC (left) and modified PC (right).

classifications, isotherms of the modified plasma carbon can be labeled as type II or type IV, which corresponds to a mesoporous material. Moreover, the argon uptake of the modified plasma carbon rapidly increases with the relative pressure, which also indicates that the mesoporous structure is developed with the thermal treatment process, due to the breakup of some of ultramicropores (<1 nm) and the opening up of accessible mesopores.

Figure 2 presents the pore size distributions for the as-synthesized PC and modified PC by the DFT method. It can be seen that the porosity has been strongly developed through the thermal modification. For example, the as-synthesized PC shows two peaks at 0.26 and 0.8 nm, respectively. After thermal modification, more micropores are generated at 0.3 nm and 0.8 nm, and also some micropores are broken and developed to mesopores at 1.5 nm. The modification is beneficial to the generation and development of the blocked micro- and mesopores in the as-synthesized PC.

Raman spectroscopy was also performed to examine the structural properties of the as-synthesized and modified PC samples, shown in Figures 3(a) and 3(b). In Figures 3(a) and 3(b), two peaks at ~1350 and 1580 cm^{-1} are known as the *D*-band for "disordered" carbon and the *G*-band for graphite [29, 30], respectively. It has been demonstrated that the integral intensity ratio $I(D)/I(G)$ and the full width at half maximum (FWHM) of these bands have a strong correlation to the microstructure of carbonaceous materials [31, 32]. Table 2 shows the $I(D)/I(G)$ and the FWHM of the *D*-band, which were evaluated using the curve fitting of the Raman spectra. A lower ratio of $(I(D)/I(G))$ indicates a higher degree of crystallinity in the modified PC compared to the as-synthesized PC, which might be due to the reaction of disordered carbon with CO_2 at a high temperature [33].

To support the Raman spectroscopy results, TEM observation was conducted as shown in Figure 4. A large amount of amorphous carbon particles can be detected in the as-synthesized PC, shown in Figure 4(a). Figure 4(c) indicates the high-resolution image of the amorphous structure in the selected area in Figure 4(a). After thermal modification, the graphite sheets and graphite particles are more

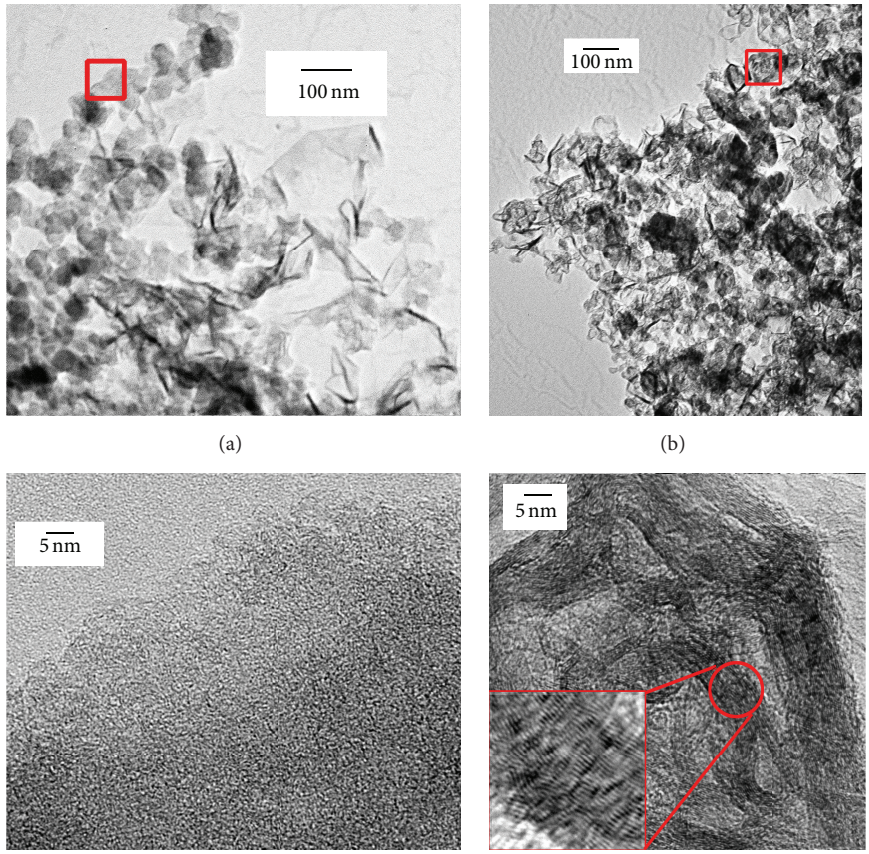


Figure 4: (a) TEM image of as-synthesized PC; (b) TEM image of modified PC; (c) HRTEM image of an amorphous carbon particle, magnified from the selected area in Figure 4(a), and (d) HRTEM image of the graphitic sheets, magnified from the selected area in Figure 4(b).

Table 2: $I(D)/I(G)$ and FWHM of the D-band, evaluated from the Raman spectra.

	$I(D)/I(G)$	FWHM (D) (cm^{-1})
As-synthesized PC	0.49	54
Modified PC	0.40	47

pronounced, which can be seen from Figure 4(b). Figure 4(d) shows a high magnification image of graphitic particles from the selected area in Figure 4(b), which clearly reveals the ordered graphitic sheets. The amorphous structure is more difficult to detect from the TEM image of the modified PC because of the burn-off of amorphous carbon at high temperature.

Figure 5 presents CO_2 sorption isotherm of the modified PC at 25°C. The isotherms are plotted in respect of total pressure with the highest pressure being 1500 kPa. The amount of CO_2 adsorbed increases as the total pressure goes up. It can be observed that the modified PC displays the adsorption capacities of 1.1 mmol/g (5 wt.%) at 1000 kPa and 13.7 mmol/g (60 wt.%) at 1500 kPa. de Andrés et al. [34] reported the CO_2 adsorption capacity of the commercial activated carbon with BET surface area of 1020 m^2/g was 3 wt.%. CO_2 adsorption

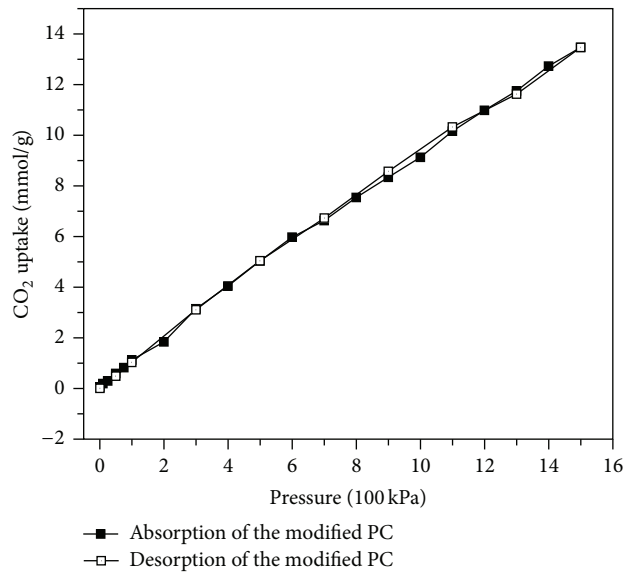


Figure 5: CO_2 isotherm of the modified PC at 25°C; the solid symbols are adsorption and the hollow symbols are desorption processes.

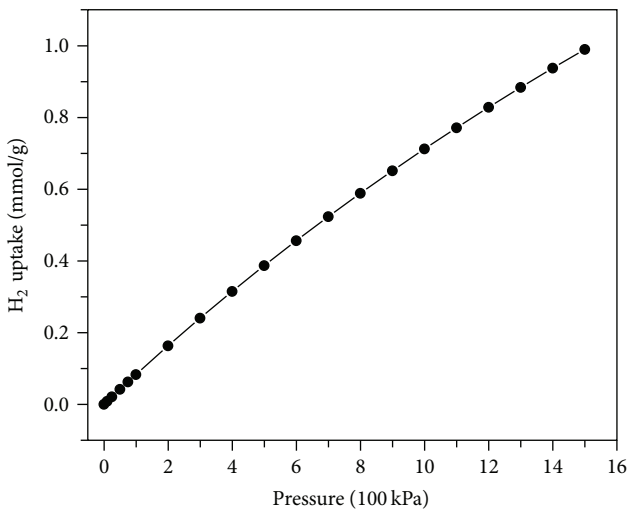


FIGURE 6: H_2 isotherm of the modified PC at 25°C.

capacity of modified PC is higher than that of the commercial activated carbon reported in other works, although the latter has a higher surface area. The possible reason is that the modified PC consists of micropores (<0.7 nm) that are mainly responsible for high CO_2 uptake at lower pressure [35–38]. In addition, due to very low H_2 uptake of the modified PC (Figure 6) at 25°C, the modified PC can be considered for CO_2 removal in syngas.

4. Summary

Nanostructured carbon materials were synthesized by the plasma reactor via methane cracking and further modified by the thermal treatment process. BET isotherm and pore size distribution indicate that the increases in BET surface area and pore volume are due to the generation of micropores, the breakup of some level of micropores to mesopores, and the opening up of accessible porosities in the graphitic carbon regions as the amorphous carbon was removed from the surface. From the Raman and TEM results, it can be concluded that a high degree of crystallinity was obtained and the amorphous carbon was burnt off during the thermal process. CO_2 adsorption experiment showed a large adsorption capacity of 13.5 mmol/g for the modified plasma carbon. The study suggests that the modified plasma carbon with large surface area can be commercially used for CO_2 capture and other applications such as CO_2 removal in syngas, wastewater filer, or gas separation. However, further research is needed on the improvement of its porosity and adsorption capacity through a better control of the plasma methane cracking and modification processes.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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