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Nitrogen doped hierarchically porous carbon derived from glucosamine hydrochloride for CO_2 adsorption

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ABSTRACT

Hydrothermal carbonization (HTC) of biomass is an attractive and sustainable method for the preparation of carbonaceous materials. In this work, nitrogen doped carbon with a hierarchically porous strucutre was successfully prepared through the HTC of glucosamine hydrochloride and the subsequent KOH activation. The resultant carbons were characterized with different techniques, and the effects of activation conditions on the porous structure were also discussed. The carbons showed outstanding CO_2 adsorption properties, a high CO_2 uptake of 4.5 mmol/g was achieved at 298 K and 1 bar. In order to analyze the influences of nitrogen doping, a pristine carbon sample with very close pore size distribution characteristics but higher porosity was also synthesized with glucose as the carbon precursor. The corresponding CO_2 uptake at 298 K and 1 bar was 3.4 mmol/g. Our results revealed that the presence of ultramicropores was an essential prerequisite for CO_2 adsorption at ambient conditions, while nitrogen doping showed positive effects on both CO_2 uptake and the adsorption selectivity over N_2.

1. Introduction

The progressive increase of CO_2 concentration in the atmosphere has become an important contributor to global warming. To tackle this issue, carbon capture and storage technology has been proposed as one of the most promising and practical strategy, where CO_2 is first captured from power plants, then compressed and transported, and finally stored [1]. For the capture of CO_2, amine scrubbing is currently the mature technology, utilizing the chemical reactions between amines and CO_2 [2]. However, the regeneration of the amine solution requires the heating of the system and creates serious energy consumption. In this context, the development of alternative methods triggers huge research interests. Solid adsorbents employing chemisorption or physisorption have been intensively investigated in recent years. For instance, metal oxides form metal carbonates with CO_2 through chemical reactions [3]; porous materials such as activated carbons [4] and metal–organic frameworks (MOFs) [5] adsorb CO_2 through van der Waals interactions.

Porous carbon as gas adsorbent has a long history due to virtues such as outstanding stability, high specific surface area and low manufacturing cost. Although various methods for the production of porous carbons have been developed, hydrothermal carbonization (HTC) of biomass materials represents a more sustainable approach towards various carbonaceous materials [6]. Biomass materials are very attractive carbon precursors because they are abundant, renewable and cheap. In HTC process, biomass precursor is dissolved or dispersed in water and then treated at a relatively low temperature under autogeneous pressure [7]. The carbohydrates of biomass undergo dehydration and polymerization reactions, the generated hydrochar generally exhibits very high and tunable content of oxygen-containing functional groups [8]. One main drawback of HTC is that the hydrochar usually has a low porosity [9], which necessitates the further activation treatment to yield a more developed porous structure.

Nitrogen doping is a very powerful tool of enriching the functionality of carbon materials. Nitrogen doped carbons have been widely investigated in different fields [10]. Promising results on their CO_2 adsorption performances have also been reported, nitrogen doping exerts positive influences on both the CO_2 uptake and the adsorption selectivity over other gases [11,12]. For instance, nitrogen doped carbon prepared from the physical activation of mesoporous polyacrylonitrile monolith exhibited exceptionally high CO_2 uptake of 5.14 mmol/g under ambient conditions [13]; in another report, microporous nitrogen doped carbons derived from covalent organic polymers also showed superior adsorption properties, the carbon

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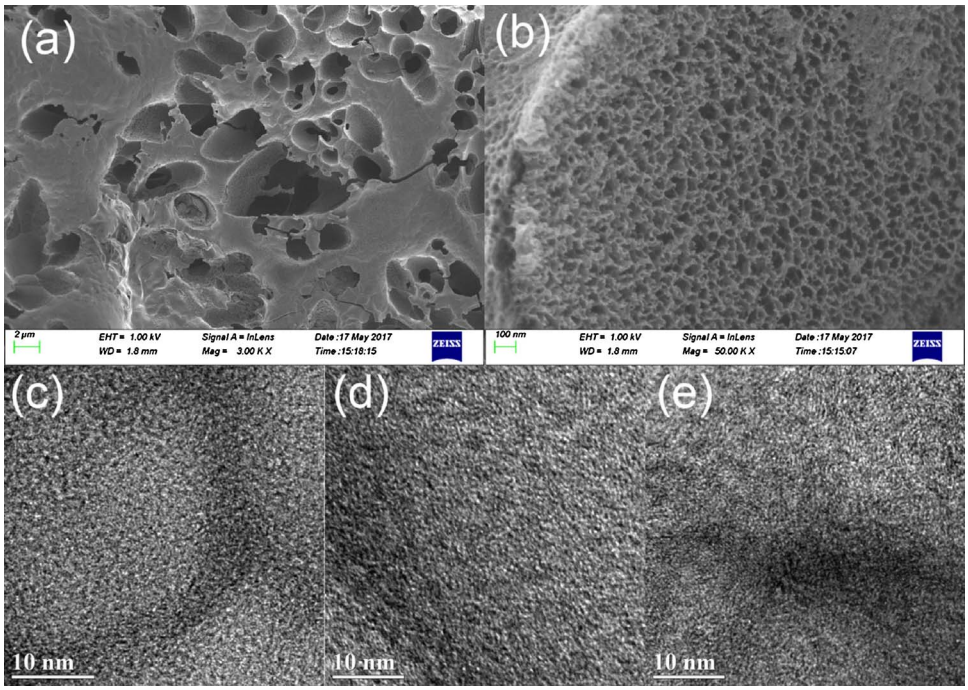

Fig. 1. (a, b) SEM images of GA-600; (c–e) TEM images of GA-600, GA-650 and GA-700, respectively.

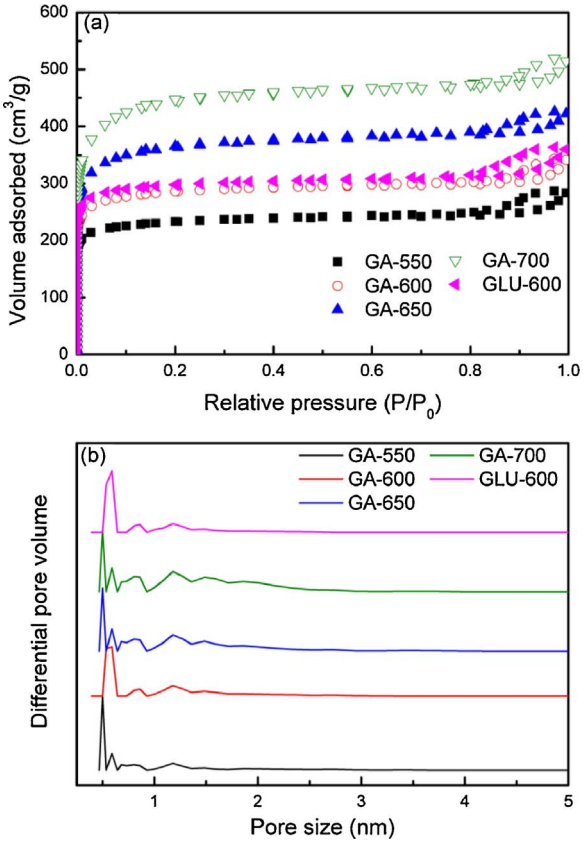

Fig. 2. (a) Nitrogen adsorption–desorption isotherms of the carbon materials at 77 K, and (b) PSD curves calculated by DFT.

demonstrated a high CO_2/CH_4 selectivity of 41.4 at 1 bar [14]. Nitrogen doped carbons can be obtained by the direct carbonization of nitrogen-rich precursors, although the post-treatment of carbons with nitrogen-containing chemicals such as NH_3 is also frequently used [15]. The preparation of nitrogen doped carbon from nitrogen containing biomass is thus of particular significance.

Table 1
Porous characteristics and nitrogen content obtained from XPS tests of different carbons.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_t (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{ultra} (cm^3/g)	Nitrogen content (wt %)
GA-550	778	633	0.44	0.30	0.14	0.21	5.5
GA-600	962	779	0.53	0.36	0.17	0.24	5.3
GA-650	1229	936	0.65	0.43	0.22	0.21	3.3
GA-700	1513	1089	0.80	0.50	0.30	0.21	3.1
GLU-600	999	840	0.56	0.39	0.17	0.28	/

Glucosamine can be easily produced from naturally abundant chitin, the hydrochloride or sulfate is more frequently used due to the instability of glucosamine itself [16,17]. As a sustainable and low cost precursor, glucosamine hydrochloride has been successfully employed as the precursor of nitrogen doped carbons [18,19], which was applied in batteries [20], supercapacitors [21,22] and catalysis [23]. In the current work, we synthesized nitrogen doped carbons with carefully controlled porous structure from glucosamine hydrochloride. Glucosamine hydrochloride was subjected to HTC process, the obtained hydrochar was then activated with KOH. The carbon product showed a high CO_2 uptake of 4.5 mmol/g at 298 K and 1 bar, effects of nitrogen doping and porous characteristics on CO_2 adsorption properties were also discussed.

2. Experimental section

2.1. Sample preparation

The nitrogen doped carbons were prepared by HTC of glucosamine hydrochloride and subsequent activation with KOH. 5 g of glucosamine hydrochloride was dissolved in 50 ml of deionized water, the solution was placed in a 100 ml autoclave and heated at 200 °C for 6 h. The yielded hydrochar was filtered and washed with deionized water repeatedly, then dried at 100 °C. For the activation process, 0.5 g of the dried hydrochar was thoroughly mixed with 1.0 g of KOH in an agate mortar. The mixture was placed in a tube furnace under flowing nitrogen (60 ml/min). The tube furnace was produced by AnHui BEQ Technology CO., Ltd (BTF-1200C-S), and the volume of the quartz tube