

Short Communication

Worm-like Hierarchical Porous Carbon Derived from Bio-renewable Lignin with High CO₂ Capture Capacity

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The worm-like hierarchical pore structure carbon material was successfully prepared by a pyrolysis process. Bio-renewable lignin was introduced as the industrially available precursor. The hierarchical porous property and worm-like channel were characterized by nitrogen adsorption-desorption isotherms and TEM. Characterization results indicated that the carbon materials exhibited microporous and mesoporous structures with worm-like frameworks. CO₂ capture tests approved that the worm-like hierarchical porous carbon showed excellent adsorption capacity of 26.2mg/g. In addition, the worm-like porous carbon shows a lower impedance.

Keywords: Carbon materials; Microstructure; Worm-like channel; CO₂ capture;

1. INTRODUCTION

With the increasing evidences of global warming and its correlation to anthropogenic carbon dioxide (CO₂) emissions, the National Research Council and the Intergovernmental Panel on Climate Change are strongly advocating reductions in carbon emissions. Thus, effective CO₂ capture has very important practical significance. The solid adsorbents was considered to be an alternative lower energy consumption technology for CO₂ capture compare to liquid adsorbents. Several types of solid adsorbents have been proposed for CO₂ capture, including carbon materials, aminated mesoporous silicas, and microporous organic polymers [1-4]. Among these adsorbents, carbon material has been considered as the superior physisorbents for CO₂ because of low cost, high adsorption capacity and selectivity, easy regeneration, and long term stability [5].

To date, carbon materials with hierarchical pore frameworks, various synthesis approaches, such as chemical activation [6, 7], pyrolysis polymers process [5, 8], and carbonization process [9],

had been developed to fabricate hierarchical pore carbon (HPC) materials. The chemical activation often required use of chemical reagents as activators, such as KOH, ZnCl₂, or H₃PO₃, but the production equipment will be subject to corrosion by these chemical agents, and secondary pollution also will be produced. The pyrolysis polymers process were used petroleum based chemicals as carbon sources, such as phenolic resin, benzene and pyridine, these carbon sources were not only toxic but also scarcity in near future [10]. Therefore, it is crucial to find environmentally friendly synthetic routes and renewable carbon sources.

Lignin, a non-toxic and carbon-rich renewable resource, is usually a waste discharged from paper and biomass bioethanol factories [11]. There are numerous reports on the use of lignin for the preparation of activated carbon [12], carbon fiber [13], and tin-walled graphite carbon [14]. Nevertheless, to the best of our knowledge, there is no hierarchical pore carbon with worm-like frameworks prepared by lignin. Herein, in this article, we report a low-cost and environment-friendly method for preparing hierarchical pore carbon by a carbonization process using lignin as the carbon source. The physicochemical properties of the sample was performed on transmission electron microscopy (TEM), X-ray diffraction (XRD) and nitrogen adsorption-desorption isotherms. The electrochemical performance of the sample was evaluated by electrochemical impedance spectroscopy (EIS). Furthermore, the CO₂ adsorption capacity of the hierarchical pore carbon was investigated.

2. EXPERIMENTAL

Alkali lignin was purchased from Nanjing Forestry University, Prof. Liu group. All the chemicals were used as received without further purification. The hierarchical pore carbon is synthesized by a low temperature carbonization reaction. Briefly, 30 g lignin (20wt% water solution) was added into 10 g hexadecyl trimethyl ammonium bromide. After stirring for 60 min, the dark-brown oligomer was further polymerized at 100 °C for 12 h, and then peeled off, pyrolyzed at 900 °C for 3 h with a ramping rate of 5 °C /min under Argon flow. The produced sample was denoted as HPC. Activated carbon (AC, Jiangsu ZhuXi activated Carbon Co., Ltd) was used as the reference material.

The morphology and physical characteristics of HPC was examined by transmission electron microscopy (TEM, JEOL JEM-2010), X-ray powder diffractometer diffraction (XRD, CuK1 radiation, $\lambda=1.5406 \text{ \AA}$), and the surface area and pore volume were determined by nitrogen sorption isotherms (ASAP 2000). Electrochemical experiments were performed on the electrochemical workstation (CHI660E). The CO₂ adsorption isotherms were performed on a simultaneous differential scanning calorimetry-thermal gravimetric analysis (DSC-TGA) under ambient pressure (1.0 atm).

3. RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of HPC. The strong diffraction peak at $2\theta=26.2^\circ$ and the three weak diffraction peaks at $2\theta=42.2^\circ$, 53.8° and 77.9° can be indexed as (100), (004) and (110) diffraction planes of the graphite (JCPDS Card No. 75-1621). The porous nature of the HPC was

evaluated by N₂ uptake measured at 77 K (Fig. 1b). The isotherms exhibit a clear type-IV hysteresis loop at a relative pressure of 0.4-0.75, suggesting the mesoporous pore nature of the HPC as-prepared. In addition, another strong uptake of the HPC is located at P/P₀ 0.01-0.03 demonstrating the micropores characteristics. The BET surface areas and pore volumes of HPC are 466.1m²·g⁻¹ and 0.61cm³·g⁻¹, respectively. The pore size distribution and average pore-size obtained by BJH method applying the adsorption branches of the isotherm are shown in Fig. 1b (inset), three peaks distributed at 0.56, 1.1 and 3.5 nm could be clearly observed, proving its hierarchical pore character, such structure may be beneficial for gas storage and adsorption [5]. The BET surface areas and pore volumes of active carbon (AC) are 653.9 m²/g and 0.47 cm³/g, respectively.

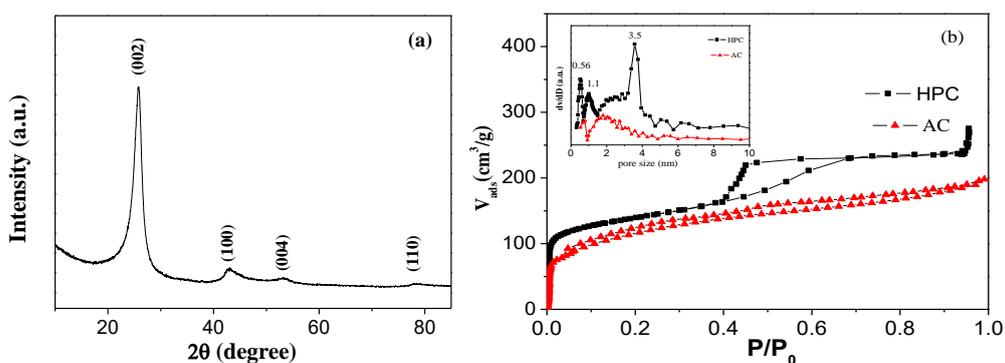


Figure 1. (a) XRD pattern of HPC and (b) N₂ adsorption-desorption isotherms of HPC and AC

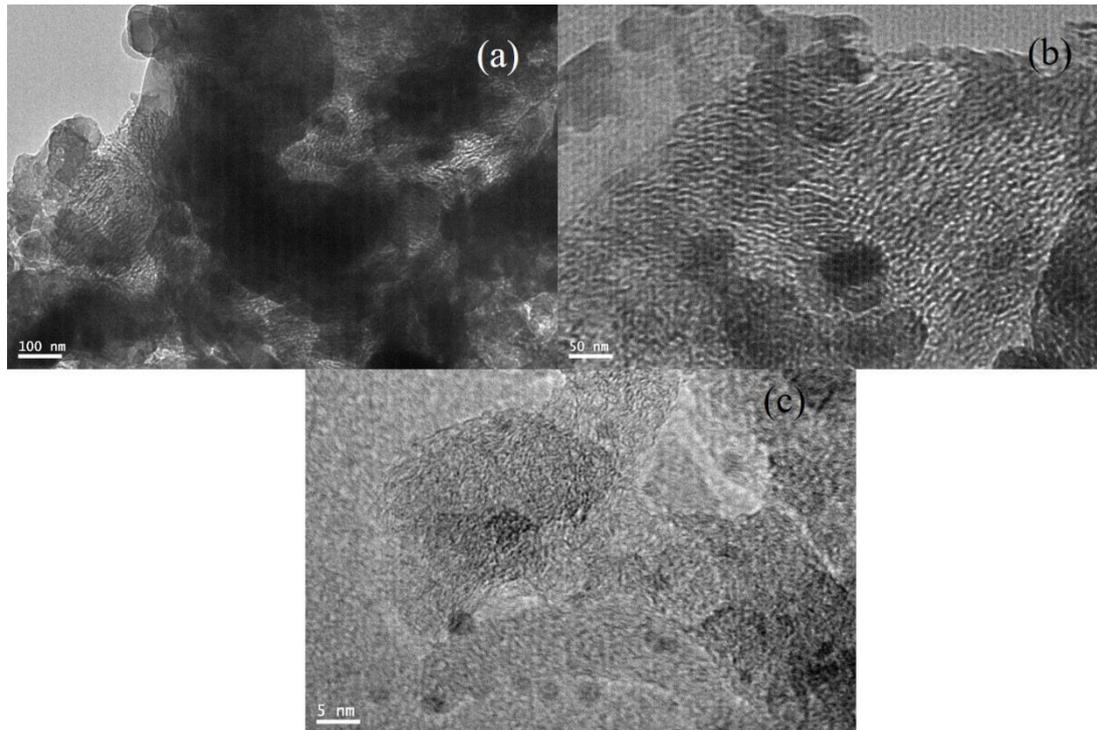


Figure 2. TEM image of the HPC

More detailed morphologies and pore structures of the HPC is further characterized by using TEM. From Fig.2a and 2b can be seen that HPC has an array of worm-like channels. Lots of channels on the surface of HPC are presented. Fig.2c shows that the HPC possesses a well-defined graphite structure, the result is well in agreement with the XRD.

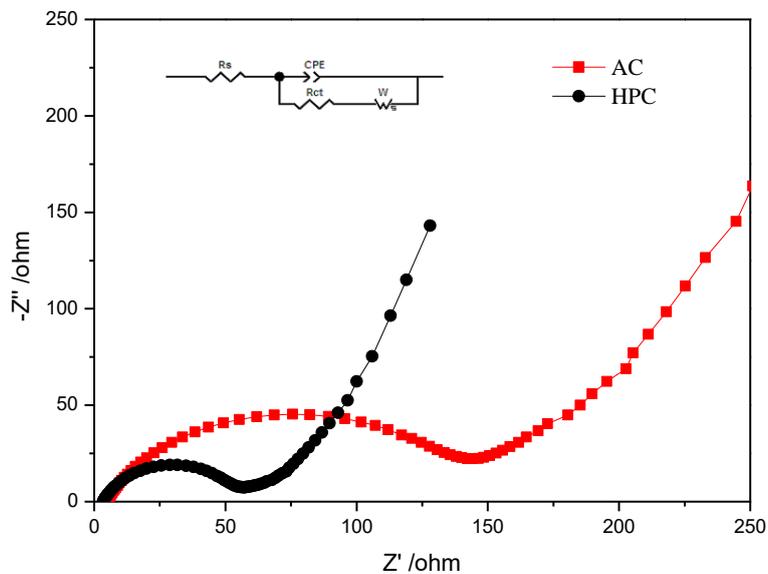


Figure 3. EIS Nyquist plots of the HPC and AC

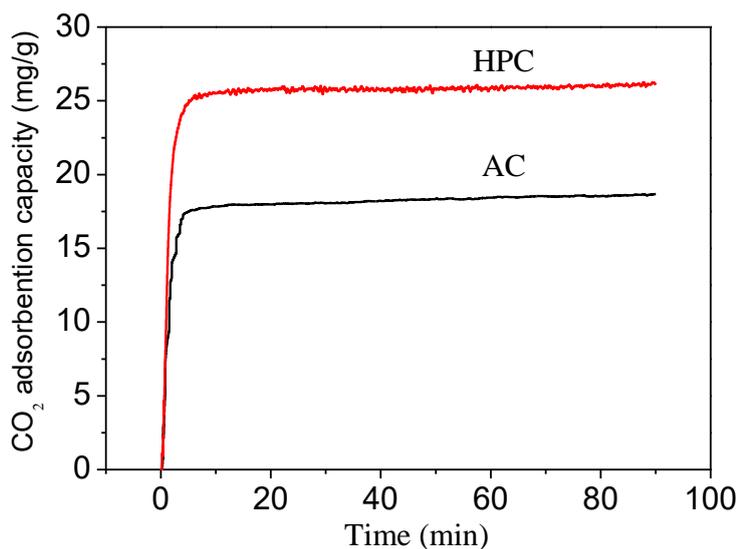


Figure 4. CO₂ adsorption isotherms on the HPC and AC at 30°C

Electrochemical impedance spectroscopy (EIS) measurements were carried out to understand the superior electrochemical performance of HPC and AC. The EIS spectra of the GCNCs were recorded (Fig. 3) and the inset is the equivalent circuit. The two impedance spectra are composed of a depressed semicircle at high frequency and an inclined line segment in the low frequency region. The

semicircle at high frequencies corresponds to the charge-transfer resistance [15]. The diameters of the semicircles are listed in the sequence of AC >HPC, which relate to worm-like hierarchical pore structure favorable for electron transfer. The incline line at low frequency corresponds to the diffusion resistance. Compared with AC, the HPC displays more vertical line at low frequency, which can be attributed to the graphitic layer of high crystallinity and the worm-like hierarchical pore structure. The lower resistance implied the higher conductivity [16], which indicated that the HPC can be used as electrode material.

In order to show the performance of worm-like mesoporous carbon in CO₂ capture, we have also studied activated carbon (AC) adsorption curves (Fig. 4). The substantial worm-like Structure HPC gives rise to a superior CO₂ capture capacity of 26.2 mg/g, much higher than the commercial activated carbon (S_{BET} : 653.9 m²/g, V_{BJH} : 0.47 cm³/g) of only 18.6 mg/g. Despite the much smaller S_{BET} of HPC than the commercial AC, HPC exhibits a higher adsorption capacity, which is ascribed to the synergy effect based on the special worm-like structure of HPC. First, HPC can easily adsorb and condense CO₂ in the hierarchical pore structure. Second, CO₂ is free adsorbed in the worm-like channel. Furthermore, it is assumed that a certain amount of CO₂ may be adsorbed in the inter-layers of HPC.

4. CONCLUSION

In summary, the carbon material with worm-like hierarchical pore structure were successfully prepared by a pyrolysis process. The bio-renewable lignin was used as carbon precursors. TEM and N₂ adsorption-desorption isotherms results all consistently reveal that the HPC have a worm-like channel and hierarchical pore structure. Lower resistance and good electrochemical properties, which indicated the HPC can be used as an electrode material. In addition, the HPC shows ultra-high CO₂ capture capacity up to 26.2 mg/g. The high adsorption performance of HPC can be attributed to the worm-like structure and hierarchical porosity.

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