Ultra-high surface area and nitrogen-rich porous carbons prepared by a low-temperature activation method with superior gas selective adsorption and outstanding supercapacitance performance

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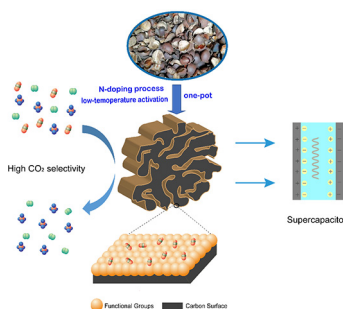[b] School of Resource, Environmental and Chemical Engineering, Nanchang University, Nanchang 330031, Jiangxi, PR China
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HIGHLIGHTS

- Ultra-high surface area and rich nitrogen functionality porous carbon.
- Low-temperature and N-doping one-pot method.
- Outstanding gas-mixture selective adsorption ability.
- Excellent supercapacitance with superior rate retention.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Ultra-high surface area and nitrogen-rich porous carbons are prepared via a low-temperature and one-pot N-doping method. The obtained carbons exhibited large surface area of $2965.7\,m^2\,g^{-1}$ and high N-doping level of 6.6 at%, endowing them as efficient gas-mixture selective adsorbents and excellent supercapacitor electrodes. By optimizing the ratio of porogen/carbon or activation temperature, the as-prepared N-rich microporous carbons possessed outstanding mixed-gas selectivities of CO_2/N_2 (77.9), CO_2/CH_4 (12.8), and CH_4/N_2 (4.9) at 298 K and 1 bar. Furthermore, three samples with almost identical surface properties were successfully prepared by judicious selection of activation conditions, thus the favorable effect of pyrrole/pyridine (N-5) species on gas-mixture separation could be clearly demonstrated. Moreover, as supercapacitor electrodes, the N-doped materials displayed extremely high supercapacitance of $350.2\,F\,g^{-1}$ at a current density of $0.5\,A\,g^{-1}$ in a 6 M KOH electrolyte solution with superior rate retention of 74.2% at $10\,A\,g^{-1}$ and 98% capacitance retention after 8000 cycles.

1. Introduction

The hierarchical nanoporous carbons have attracted considerable attentions due to their large surface area, excellent physicochemical and thermal stability, low manufactory cost, and structure tunability [1,2]. Benefiting from these exceptional features, porous carbons are promising materials for gas storage/separation [3], catalyst supports [4], additives [5], and electrode materials [6]. Recent investigations showed that the pressure/vacuum swing adsorption (P/VSA) processes employing solid adsorbents are expected to mitigate the CO_2 concentration in the atmosphere by selectively capture CO_2 from stationary power plants and other greenhouse gas sources [7,8]. This has led to the bloom of solid porous adsorbents investigations, which aims at high CO_2 capacity, excellent gas selectivity, and structure stability. Whereas, there still are crucial challenges for improving the commercial feasibility of carbon capture and sequestration (CCS). On the other hand, supercapacitors, as advanced energy storage devices, have advantages such as high power density, excellent cyclic performance and less environmental pollution, which was regarded as the next generation energy-storage systems for electronics and hybrid vehicles [9,10]. The unique properties of porous carbons, such as hierarchical pore system, large surface area, controllable pore size, and chemical inertness, endow them preferred choice for electrical double-layer capacitors (EDLCs).

However, pristine nanoporous carbons displayed poor CO_2 adsorption capacities, low gas separation abilities, and inferior supercapacitive behaviors, due to their scarce gas adsorption sites, poor specific gas identification ability, and absent pseudocapacitance-inducing heteroatoms. Recently, chemically incorporating heteroatoms into carbon frameworks has attracted much attention, due to its ability to tailor physical and chemical surface properties [11–13]. It is widely shared that integration of nitrogen atoms into carbon frameworks could significantly improve the surface polarity, electric conductivity, and electron-donor affinity [14,15]. The electronegative N species, such as pyridinic, pyrrolic, quaternary and oxidized nitrogen, have preferred interaction with CO_2 over nonpolar N_2 [16], thus enhancing the CO_2 uptake and gas-mixture selectivity. In terms of supercapacitors, researches have demonstrated that the electronic structure of carbon are changed after N doping and lead to enhanced charge carrier density, quantum capacitance, and interfacial capacitance [17]. For instance, Rana *et al.* reported soya derived N-doped carbon with surface area of 1072 m^2 g^{-1} and N content (up to 5.3 wt%), showing a CO_2 adsorption capacity of 3.2 mmol g^{-1} at 25 °C and electrochemical capacitance of 193 F g^{-1} at 0.5 A g^{-1} [18]. Moreover, well-established chemical and physical activation methods, including template method, gas (water vapor, CO_2, and NH_3)-etching method, and chemical method, allow the production of porous carbons with large surface areas (above 1000 m^2 g^{-1}) [19,20]. Especially for KOH-activation method, it is the most common manufactory route to produce micropore-rich, high pore volume, and large surface area porous carbons [21]. Whereas, this method suffers intrinsic drawbacks such as high activation temperature, severe corrosive nature, and low carbon yields. Thus, it is highly urgent to develop a novel activation agent to produce porous carbon in mild activation conditions. Sodium amide ($NaNH_2$) is an emerging activation and N-doping agent, which could produce highly porous carbons in relatively low activation temperature and serve as N source at the same time [22,23].

Biomass-derived porous carbons are intensively investigated due to their low costs, wide availability, and energy/environmental security. Till now, various biomass-derived porous carbons, such as cotton [24], celtuce leaves [25] and chitosan [26], displayed great application potential as solid-state adsorbents and supercapacitor electrodes. However, developing multifunctional materials with excellent CO_2 adsorption capacity and electrochemical properties for supercapacitors *via* direct activation of biomass is still very challenging. For instance, our previous work demonstrated algae-derived porous carbons with a

moderate CO_2 uptake of 3.9 mmol g^{-1} at 298 K and supercapacitance of 287.7 F g^{-1} at 0.2 A g^{-1} in 6 M KOH aqueous solution [27]. Meanwhile, tea oil is a unique natural high-grade edible oil original from China, the oil-tea seed shell (OTSS) are regarded as biowaste and a huge amount of OTSS are discarded locally or directly burned every year. Thus, based on our previous work, we further investigate OTSS as novel biomass precursor to prepare high-performance multifunctional nanoporous carbon materials with low-temperature activation and one-step N-doping method.

Keeping these pros and cons in mind, in this work we report a simple and green route to synthesis hierarchical and N-rich (up to 6.6 at %) microporous carbons with ultra-high specific surface areas as well as suitable pore size from waste OTSS through direct activation with solid $NaNH_2$, which acts as both porogen and nitrogen source. The pore size and surface area of obtained materials can be adjusted by optimizing the carbonization temperature and the porogen/OTSS ratio. Benefiting from these advantages, the obtained samples exhibited excellent CO_2 adsorption and electronical performances. For instance, the obtained carbons with excellent CO_2 uptake of 3.5 mmol g^{-1} showed outstanding CO_2/N_2, CO_2/CH_4, and CH_4/N_2 selectivity of 77.9, 12.8, and 4.9 at 298 K and 1 bar, respectively. Furthermore, the dominate role of the effective pyrrole/pyridine (N-5) on porous carbon surface in CO_2-containing gas mixture separations was elucidated. Moreover, it displayed an outstanding capacitance of 350.2 F g^{-1} at 0.5 A g^{-1} in a 6 M KOH electrolyte solution, with excellent rate capability (74.2% at 10 A g^{-1}) and unprecedented cycling stability (98% after 8000 cycles). Thus, the OTSS derived N-doped porous carbons with high surface area and adequate doping of heteroatoms are suitable for multiple applications of CO_2 adsorption and supercapacitor applications with very high efficiencies.

2. Materials and methods

2.1. Materials

The OTSS used in this study was kindly provided by Hunan Academy of Forestry of China and was crushed to 40 mesh (< 0.45 mm) before activation. Sodium amide ($NaNH_2$) was purchased from Aladdin reagent co., Ltd. Hydrochloric acid (HCl) was purchased from Xilong Scientific Co., Ltd. All chemicals were used as received without any further purification.

2.2. Preparation of N-rich and hierarchical nanoporous OTSS-X-Y

The typical synthesis procedure of N-rich and hierarchical nanoporous OTSS-X-Y was shown as below. The dry OTSS powder was carbonized at 550 °C for 1 h under N_2 flow with a flow rate of 300 mL min^{-1} to produce OTSS-C. Afterwards, 1 g of OTSS-C was grinded with $NaNH_2$ (OTSS/$NaNH_2$ = 1/1, 1/2 and 1/3 by weight ratios) manually. Subsequently, the mixtures were heated in a tubular furnace to a target temperature of 350–650 °C at a heating rate of 10 °C min^{-1} in N_2 atmosphere and hold this temperature for 1 h. The obtained sample was washed with deionized water until neutral, then dried in a vacuum oven at 70 °C for 12 h. The as-synthesized porous carbons were denoted as OTSS-X-Y, where X represents the $NaNH_2$/OTSS mass ratio, and Y denotes the activation temperature in °C.

2.3. Material characterization and adsorption measurements

Scanning electron microscopy (SEM) images were taken in a JSM-6701F instrument. Transmission electron microscopic (TEM) images were acquired on a JEM-2100 microscope. Powder X-ray diffraction (XRD) patterns were collected using a PANalytical empyrean series2 diffractometer with Cu-Ka radiation, at room temperature, with a step size of 0.0167°, a scan time of 15 s per step, and 2θ ranging from 5 to 90°. Raman spectra were collected using a HR Evolution Raman