Full Length Article

Nitrogen-doped porous carbons with ultrahigh specific surface area as bifunctional materials for dye removal of wastewater and supercapacitors

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ABSTRACT

In this work, the nitrogen-doped porous carbon (PCM-K) with ultrahigh specific surface areas has been prepared successfully by using biomass pine nut shell as a precursor. The as-synthesized PCM-K exhibits an ultrahigh specific surface area of $3376.1 \, m^2 \cdot g^{-1}$, a large pore volume of $1.655 \, cm^3 \cdot g^{-1}$ and a high nitrogen content of 6.25%. By exploring the removal ability of PCM-K for cationic dye methylene blue (MB) in wastewater, and examining the effects of various experimental factors, such as contact time, initial dye concentration, adsorbent dosage and temperature on the MB removal from wastewater, it is found that the PCM-K not only exhibits excellent MB adsorption capacity of $766.9 \, mg \cdot g^{-1}$, which is higher than $704.3 \, mg \cdot g^{-1}$ of rhodamine B and $408.7 \, mg \cdot g^{-1}$ of methyl orange, but also shows almost 100% removal efficiency of MB from wastewater. Owing to the high nitrogen content, the PCM-K also exhibits excellent electrochemical performance as supercapacitors. Galvanostatic charging–discharging measurements showed that the specific capacitance of PCM-K in a three-electrode system reaches $376.4 \, F \cdot g^{-1}$ in 6 M KOH and at a current density of $0.1 \, A \cdot g^{-1}$. The excellent dye removal and electrochemical performances suggest that the biomass-derived nitrogen-doped porous carbons is a promising candidate for wastewater treatment and energy storage.

1. Introduction

Nanoporous carbons as versatile materials have attracted great attention in many fields, such as gas adsorption and separation [1–3], catalyst support [4–8], electrochemical capacitors (ECs) [9–12], and adsorbent for dye removal [13–16] as well as fuel cells, owing to their high surface area, good chemical and thermal stabilities [17]. Recently, biomass wastes were considered as a preferable precursor for synthesis of porous carbons, because these materials are cheaper and abundantly available, compared to the precursors of metal-organic frameworks (MOFs) and mesoporous zeolites. It is worth noting that nitrogen-doped porous carbon has received global interest and is still a hot topic [18–20], because the doping of nitrogen atoms in the carbon framework can adjust efficiently the physical properties of the carbon material by redistributing the overall electron density [21–23]. Therefore, it is very significant to prepare the nitrogen-doped carbons with ultrahigh specific surface area (SSA) and high nitrogen content.

Dyes are widely used in various industries such as electroplating, textiles, rubber, pharmacies, paint, tanneries, plastics and food processing [24], and discharging of organic dye wastewater from these industries without proper treatment will result in severe environmental problems to aquatic animals and human beings [25]. Methylene blue (MB) is a cationic dye with various applications in chemistry, biology, medical science and dyeing industries, and its long term exposure can cause vomiting, nausea, anemia and hypertension. Rhodamine B (RhB) and methyl orange (MO) are also common dyes and they are toxic and carcinogenic generally. Therefore, effective removal of these toxic dyes from wastewater before discharging to the environment has been more and more important.

Many approaches have been proposed for the removal of dyes from wastewater, such as adsorption [26], chemical coagulation [27], photocatalytic degradation [28], membrane separation [29], ion exchange [30], and electrochemical treatments [31]. Among these techniques, adsorption is regarded as one of the competitive methods for the removal of noxious dyes from wastewater owing to its high efficiency, economic feasibility and environmentally friendly. Activated carbon with high surface area and tunable pore structure, has been widely used as adsorbents in industrial process. As so far, various biomass-derived porous carbons have been reported for removing dye molecules from the wastewater. Chen et al. used H_3PO_4 activation to convert NaOH-

pretreated rice husks into activated carbons at 500 °C under nitrogen atmosphere, and found that the adsorption amount of MB is 578 mg·g^{-1} [32]. Reffas et al. prepared ACs by activation of coffee grounds at 450 °C and found that its MB adsorption amount is 350 mg·g^{-1} [33]. Hasan adopted tomato processing waste as adsorbents for the removal of MB and its adsorption amount is 400 mg·g^{-1} [34]. Alexandro et al. used flamboyant pods as carbon sources to prepare porous carbons and found that its adsorption amount of MB reached 890 mg·g^{-1} [35].

In recent years, there has been an urgent demand for energy storage materials due to the decrease of fossil fuel resources and the environmental impact of fuel combustion [36]. As one of the most widely used energy storage devices, supercapacitors, including electric double layer capacitors [37] and pseudo-capacitors which is a Faradic process relying on redox reactions [38], have drawn significant attention due to their high power density, fast charging–discharging rates and longer cycle life [39]. Nowadays, biomass-derived porous carbons as supercapacitor electrode materials have attracted more attention due to its high SSA, well-developed porous structure, high electrical conductivity and electrochemical stability. Up to now, a variety of waste biomass materials, including celtuce leaves [40], coconut shell [41], entermorpha prolifera [42] and feather of animal [43] have been utilized as precursors to prepare porous carbon materials, which have shown great potential as electrode materials for supercapacitors.

Pine nut shell is abundantly available and sustainable, and it may be good precursors for the preparation of porous carbons. In this work, we use biomass pine nut shell as precursors to synthesize the nitrogen-doped porous carbon with ultrahigh SSA. Then, we systematically characterize the as-synthesized nitrogen-doped porous carbons, and further explore the multifunctional applications of the nitrogen-doped carbons in the removal of MB from wastewater and in supercapacitor electrodes. Finally, the conclusions are drawn and discussion is addressed.

2. Experimental

2.1. Reagents

The pine nut shell used in the experiment was obtained from mountain specialty product wholesaler in Yichun City of China. Melamine (C$_3$N$_3$(NH$_2$)$_3$) and Chitosan ((C$_6$H$_{11}$NO$_4$)$_n$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium hydroxide was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemical reagents were analytical grade and used as received without further purification. Deionized water was used in all treatment processes.

2.2. Synthesis of nitrogen-doped porous carbons

Pine nut shell was washed with distilled water to eliminate the impurities (dust and water soluble substances), and dried at 110 °C overnight in an oven. The dried biomass was milled and sieved to 300 μm particle size. The treated pine nut shell powder was put into the magnetic boat and carbonized at 400 °C for 120 min under a flow of argon gas, and the char of pine nut shell was obtained. After that, the char, potassium hydroxide, melamine and chitosan were evenly mixed at a mass ratio of 1:2:1.5:1.5 in a solid grinding manner. Among them, potassium hydroxide, as a physical activating agent, facilitated the formation of microporous structure of the carbon powder of pine nut shell, while melamine and chitosan provide nitrogen sources. Then carbonization was performed in a horizontal tube furnace. The temperatures rose steadily from room temperature to the target temperatures of 800 °C with a heating rate of 5 °C·min^{-1} and held for 140 min at this carbonization temperature in argon atmosphere. After cooling down to room temperature, the obtained carbon materials was washed with 1 M HCl followed by distilled water several times to remove residual KOH until the pH of the supernatant remained neutral and dried at 60 °C for 12 h. The product was denoted as PCM-K. In contrast, the

directly calcined carbon material was named as P-K without the addition of melamine and chitosan in the synthesis process.

2.3. Characterizations

The morphologies of the samples were obtained by using a JSM-6701F instrument. X-ray powder diffraction (XRD) patterns were obtained on an XRD analyzer (XRD, D8 ADVANCE type (BRUKER-Germany)). Raman spectra were recorded on a LabRAM Aramis Raman Spectrometer (HORIBA JobinYvon) with a 532 nm laser source. X-ray photoelectron spectroscopy (XPS) was carried out to characterize the surface elemental compositions on a ThermoFisher ESCALAB 250 X-ray photoelectron spectroscopy equipped with twin anode Mg Ka X-ray sources. The surface functional groups of the prepared porous carbons were detected using a Nicolet 8700 Fourier transform infrared (FTIR) spectrometer with the wavenumbers range from 4000 to 400 cm^{-1}. The Zeta potentials of the samples were determined by using a Zetasizer Nano (Malvern) at a pH range of 2–8. The powders were dispersed by sonication in water with a concentration of 0.5 mg/10 mL and the dispersion was used for Zeta potential measurements. Nitrogen adsorption-desorption isotherms at 77 K were measured by ASAP 2020 analyzer (Micromeritics, U.S.A). The SSA was calculated using the Brunauer–Emmett-Teller (BET) equation. Pore size distribution was obtained by the non-local density functional theory (NL-DFT). Elemental analysis (C, N, and O) was performed on a Thermo Fisher scientific Elemental Analyzer (Ea1112, Beijing Research Institute of Chemical Industry, SINOPEC).

2.4. Adsorption experiments

MB, an organic cationic dye, was used to evaluate the adsorption capacity of the as-synthesized samples. RhB and MO were also used to examine adsorption properties of the samples for different types of dye molecules.

Aqueous stock solutions of MB (C$_{16}$H$_{18}$N$_3$SCl, MW: 373.9), RhB (C$_{28}$H$_{31}$ClN$_2$O$_3$, MW: 479.01) and MO (C$_{14}$H$_{14}$N$_3$SO$_3$ Na, MW: 327.33) with 1000 ppm concentration were prepared in advance, and work solutions with different concentrations of dyes were prepared by diluting the stock solution with deionized water. Batch experiments of adsorption were carried out in 250 mL Erlenmeyer flasks under agitation (150 round per minute (rpm)). The effects of some important parameters, such as sample amount (10–25 mg), contact time (1–120 min), initial concentration (50–500 ppm) and temperature (25–55 °C), on dye adsorption were investigated. In general, a certain amount of sample was added into the 250 mL Erlenmeyer flask contained 100 mL dye solution of known concentration. The adsorption mixture was continually stirred over a given period of time. Then, the solutions were separated from the adsorbents with a syringe filter. The concentrations of MB, RhB and MO were measured using a UV–vis spectrophotometer (TU-1901) at wavelengths of 665, 554 and 464 nm, respectively, which correspond to the maximum adsorption of the dyes.

For kinetic experiments, 20 mg of the as-prepared PCM-K was dispersed into 100 mL MB solution with 100 ppm concentration. For isotherm experiments, 20 mg of the as-prepared PCM-K was put in 100 mL MB solutions with different concentrations (50–500 ppm). For thermodynamic experiments, 20 mg of the as-prepared PCM-K was added into 100 mL MB solution with 400 ppm concentration at different temperatures (25–55 °C).

The percentage of dye removal and the adsorption capacity of dyes were calculated by following two equations:

$$R_e = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

$$q_t = \frac{C_0 - C_t}{W} \times V \tag{2}$$