



Template-free synthesis of N-doped carbon with pillared-layered pores as bifunctional materials for supercapacitor and environmental applications



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ABSTRACT

Cross-linked, N-doped, pillared-layered porous carbons (NCs) were prepared via a one-pot, template-free pyrolysis process at 600 (NC600), 700 (NC700) and 800 °C (NC800), which have bifunctional applications in supercapacitors and environmental remediation. NC700 displays a high surface area (2118 m² g⁻¹) and a specific capacitance of 305 F g⁻¹ at 0.2 A g⁻¹ in a two-electrode setup. The maximum energy density of NC700 was 20.4 W h/kg at a power density of 139 W kg⁻¹ and 89.1% capacitance was retained after 10000 cycles of charge-discharge at 5 A g⁻¹. For water remediation, NC800 displayed high adsorption capacities towards flame retardant tetrabromobisphenol A (TBBPA, 372 mg g⁻¹) and antibiotic sulfa-chloropyridazine (SCP, 288 mg g⁻¹) solutions, while NC700 showed the most efficient SCP oxidation removal. These results suggest low-cost and green carbon materials as electrodes in flexible energy storage devices, metal-free adsorbents as well as catalysts for high efficient removal of emerging contaminants in aqueous solution.

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1. Introduction

Recently, the development of renewable energy resources to alleviate environmental issues from the over-depletion of fossil fuels has accelerated intensive research efforts on technologies such as electrical energy storage devices [1,2]. As the promising devices in this community, electrical double layer capacitors, also known as supercapacitors, have drawn enormous attention due to the capability to deliver a high power density with a long cycling life [3,4]. Supercapacitors play a pivotal role in clean-energy device systems, ranging from lighting on roads, electrical motors in hybrid electric vehicles, lasers, and portable electronics, to name a few [1,5,6]. Because of their low cost, high specific surface areas and well-developed porous structure, porous activated carbons have been considered as the first candidate electrode materials for supercapacitors [7]. Direct pyrolysis to synthesize porous carbons without any further activation process represents the most

promising method for a large-scale production [8]. Until now, such reports are rather limited. For coping with a commercial market guidance, the search is still on to exploit high-surface-area porous carbon materials with a facile synthesis method [9].

Apart from energy, environment issue is another serious challenge that humanity will face with the development of human society. It is noted that severe threat has been posed to the planet Earth and mankind by fresh water contamination [10]. Emerging water contaminants such as SCP antibiotics used in human medicine and aquaculture, or TBBPA, a commercial flame retardant in plastics and electronics, have induced highly toxic effects on aquatic life and human health [10,11]. Hopefully, porous carbons bring in new prospects as metal-free materials for the management of these pollutants in effluents [11]. On one hand, high-surface-area porous carbons can remove the target pollutants by physical adsorption. On the other hand, they can be applied in advanced oxidation processes (AOPs) by activation of some superoxides such as persulfate (S₂O₈²⁻, PS) for complete removal of these organics [12]. Glaze in 1987 proposed that AOPs are tied to the production of hydroxyl radicals, which bring out the oxidation of organic compounds [13]. Since the 1990s, various radical species including sulfate radicals, superoxide anion radical, hydrogen peroxide, and

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singlet oxygen have been proposed [14]. The mechanisms of different AOPs in the work were also studied in terms of the radical species.

We recently found that sodium bicarbonate is an excellent in-situ porogen for synthesis of N-doped, pillared-layered porous carbons (NCs) in which the pore structure can be tuned by changing the amount and species of doping agents [15]. However, the critical influences of synthesis temperature on the physicochemical properties and microstructure of these porous carbons were not explored. In this work, NCs are studied at varying synthesis temperatures of 600, 700 and 800 °C. The process is one-step, time-saving, and mild without harsh treatments such as KOH activation, which is extensively used in the activation process of carbon materials [16–18], or HF washing for multistep hard-template routes [19]. The synthesized pillared-layered porous carbons were proved to be well-defined bifunctional materials in supercapacitors and environmental catalysis.

2. Experimental details

2.1. Sample preparation

Briefly, glucose (1.8 g), sodium bicarbonate (1.8 g), and urea (1.8 g) were dissolved in 60 mL deionized water to form a transparent aqueous solution, which was then put in an oven without stirring and heated at 100 °C for 24 h until dried. Subsequently, the remained mixture was annealed at 600, 700 and 800 °C, respectively, for 2 h in a tubular furnace under nitrogen atmosphere with a heating rate of 5 °C min⁻¹. Finally, to remove residual inorganic salts, the obtained carbon materials were washed with water as well as ethanol, and then dried at 80 °C. The collected samples were denoted as NC600, NC700 and NC800, respectively.

2.2. Material characterizations

The morphologies of all the samples were revealed by scanning electron microscopy (SEM, FEI Verios XHR 460) and transmission electron microscopy (TEM, JEOL 2100). X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Axis Ultra DLD system under ultra-high vacuum (UHV) conditions. Kratos Vision and Casa XPS software were adopted to process the obtained XPS spectra and all spectra were calibrated based on a primary C 1s component at 284.6 eV. Raman spectroscopy was characterized on WITec alpha 300RA+. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were estimated by N₂ adsorption on a Micromeritics Tristar 3000.

2.3. Electrochemical measurements

In a typical electrochemical measurement, 2 mg carbon powder was dispersed in a mixture of 500 μL isopropanol and 25 μL of Nafion[®] 117 solution by ultra-sonication. To prepare the working electrode, 10 μL of the dispersion (containing 36 μg of catalyst) was deposited on a glassy carbon electrode (5.0 mm in diameter) and dried in air. Electrochemical measurements were performed on a Gamry electrochemical workstation (Reference 3000) in 6 M NaOH solution using a standard three-electrode configuration with Ag/AgCl (4 M KCl) as the reference electrode and a Pt wire as the counter electrode. The electrochemical performance comparison of the samples were evaluated by electrochemical impedance spectroscopy (EIS) tests from 10 mHz to 100 KHz.

As an alternative approach to analyze the supercapacitor frequency behavior, the real and imaginary parts of the capacitance

were analyzed using the EIS data based on the following equations:

$$Z(\omega) = \frac{1}{j\omega C(\omega)} \quad (1)$$

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (2)$$

$$C'(\omega) = -\frac{Z''(\omega)}{\omega|Z(\omega)|^2} \quad (3)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (4)$$

where $C'(\omega)$ and $C''(\omega)$ represent the real and imaginary parts of the accessible capacitance, respectively.

Two-electrode system tests were carried out using two nearly identical (symmetric by size and weight) electrodes assembled with a separator between them. The working electrode consists of NC700, acetylene black and polytetrafluoroethylene in a weight ratio of 80:10:10. The area of the electrodes is about 1 × 1 cm² with a mass loading of 2.8–3.6 mg. Nickel foam was used as the current collector. Cyclic voltammetry (CV), Galvanostatic charge-discharge tests (GCD), EIS and cycling stability tests of the device were carried out in 6 M NaOH solution. The specific capacitance of a single electrode (C_s , F g⁻¹) was calculated from the GCD discharge curve based on:

$$C_s = \frac{4I \cdot \Delta t}{m \cdot \Delta V} \quad (5)$$

Where m (mg) is the total mass loading of the active materials on both electrodes; ΔV (V) refers to the discharge voltage range excluding the IR drop [20]. The energy density (E , W h kg⁻¹) and powder density (P , W kg⁻¹) were calculated based on:

$$E = \frac{1}{8} C_s \cdot (\Delta V)^2 \cdot \frac{1}{3.6} \quad (6)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (7)$$

2.4. Environmental applications

Adsorptive experiments were performed by dispersing 10 mg the carbon samples in 200 mL tetrabromobisphenol A solution (TBBPA, 20 mg L⁻¹) at 25 °C with constant stirring. The concentrations of TBBPA solution at different time intervals were acquired by measuring the integral area of their diffused reflectance spectra collected on a Cary 100 UV–visible spectrophotometer.

Adsorptive experiments of sulfachloropyridazine (SCP) solutions (20 mg L⁻¹, pH 7) were also performed by the similar procedures. At different time intervals, the solution was taken, filtered and then tested using an ultra-high performance liquid chromatography (UHPLC) to determine the SCP concentration.

For SCP oxidative tests at 25 °C, 10 mg carbon sample and 0.35 g potassium persulfate were added together into 200 mL SCP solutions to initiate the reaction. At certain time intervals, 1.0 mL of solution was withdrawn, filtered and quenched instantly by mixing with 0.5 mL of sodium nitrite solution (0.1 M). Each experiment was repeated at least three times and the results were reproducible.

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