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Enhanced capacitance of a nitrogen-containing carbon-based nanocomposite via noncovalent functionalization method

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A B S T R A C T

Ordered carbon (OC) with large surface area was prepared via replication by using Santa Barbara Amorphous-15 as a template and sucrose as a carbon precursor. The prepared OC was then noncovalently functionalized with Basic Red 2 dye precursor (BR2) to obtain OC–BR2, a nitrogen-containing carbon-based nanocomposite with enhanced electrical properties. The functionalization was explained through adsorption isotherm, kinetic, and thermodynamic studies performed under variable conditions. The electrochemical performance test results demonstrated that the nanocomposite presents enhanced capacitance (48.4%) compared with the original OC, with maximum specific capacitance of 227 F g^{-1} at 0.5 A g^{-1} in 1 M KOH electrolyte.

Introduction

Ordered carbon (OC) development has gained tremendous attention because of the resultant ordered structure and the large specific surface area, large pore volume, chemical inertness, high mechanical stability, and conductivity of the final material [1–3]. OC is used in various applications, including adsorption, catalysis, energy storage, and electrochemistry, because of its distinct advantages over traditional porous materials, such as zeolites, activated carbon, and metal oxides. Well-aligned OC channels act as highways for smooth electron and ion transport and exhibit excellent performance as electrochemical double-layer capacitors [4]. Thus, OC appears to be a promising electrode material for electrochemical capacitors with high energy density storage capabilities.

Previous studies have demonstrated that the applications of OC are influenced by its structure and surface chemical properties [5–7]. Various surface modification techniques, such as noncovalent and covalent functionalization, have been performed to boost the electrochemical performance of the carbon material [4,8–10]. These processes alter the electronic structures of the carbon material, enhancing its surface polarity, electrical conductivity, and electron-donor properties [3,11]. The presence of electrochemically active surface functional species provides additional pseudo-capacitance to the energy storage mechanism through the redox process. In this study, we selected a basic dye, Basic Red 2 (BR2), to noncovalently functionalize OC and form an electrochemically active OC-based nanocomposite, OC–BR2. BR2 is a water soluble nitrogen (N)-containing compound (Fig. 1) that forms positively charged ions when dissolved in water to provide electrochemically active sites. Introduction of N-containing functional species generally creates basic properties that can enhance interactions between the carbon surface and acid molecules. In addition, N-functionalized carbon-based materials exhibit high affinity to water molecules, which means improved hydrophilic properties in aqueous electrolytes [12].

Modification of the OC surface through adsorption-induced noncovalent BR2 functionalization is an interesting endeavour. Adsorption refers to the adhesion of molecules (adsorbate) on the surface of a solid (adsorbent). The current study was designed to examine the adsorption capacity of OC over BR2 in aqueous solution. Optimum adsorption conditions were determined by

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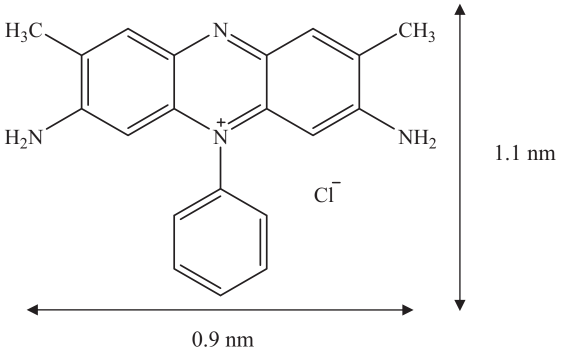

Fig. 1. Molecular structure and dimensions of BR2.

varying the solution pH, OC loading, and contact time. Adsorption experimental data were plotted according to the Freundlich and Langmuir adsorption models, and kinetic and thermodynamic studies were conducted to determine the enthalpy of adsorption. The influence of surface functional species was investigated to increase the specific capacitance and hydrophilic properties of the resultant OC–BR2 nanocomposite in electrochemical performance tests.

The template replication method includes the following processes: (i) complete infiltration of the pores of the hard template with a carbon precursor, (ii) inert atmosphere carbonization of the carbon precursor inside hard template pores, and (iii) hard template dissolution of the carbon/silica composite [12]. Santa Barbara Amorphous-15 (SBA-15) was used in this study to prepare OC. SBA-15 consists of a silica framework with a mesoporous structure, interconnected micropores, and secondary mesopores in its pore walls [14]. The OC prepared using this method is a true replicate of the mesoporous structure of SBA-15 with a high surface area of up to 900 $m^2 g^{-1}$ and large pore volumes. Compared with traditional adsorbent materials, OC offers more advantages because of its large specific surface area, narrow pore size distribution, chemical inertness, high thermal stability, and tunable pore size [15,16]. The presence of wider pores facilitates functionalization with N-containing aromatic molecules [15]. Different pore geometries of OC have been synthesized by employing ordered mesoporous silicas as hard templates. The pore dimensions of the prepared OC are influenced by the structure of the hard template, such as MCM-41 and MCM-48 [17,18]. However, OC prepared using MCM-48 undergoes symmetry changes because MCM-48 does not possess small complementary interconnected pores [13]. In addition, the ordered hexagonal mesoporous structure of MCM-41 is not suitable in OC replication because of the disordered structure of the obtained microporous carbon [15].

Herein, we report the successful noncovalent surface functionalization of OC prepared using an SBA-15 template replication strategy. The optimum functionalization conditions were determined, and the effect of surface functional species was evaluated according to the results of electrochemical performance tests.

Materials and method

Materials

The directing agent with a triblock copolymer structure, Pluronic 123 ($EO_{20}PO_{70}EO_{20}$ = 5800), tetraethyl orthosilicate (TEOS, silica source), and sucrose (carbon source) were purchased from Sigma-Aldrich (Germany). BR2 (C.I = 50240; Mol. wt. = 350.85 g mol^{-1}) was obtained from Sigma-Aldrich (Germany) and used as a basic dye. The molecular dimensions of BR2 are approximately 0.9 nm × 1.1 nm according to the Gaussian 03 software package [19]. All other chemicals employed for material preparation and BR2 functionalization were purchased from QReC^{TM}, Merck, Sigma-Aldrich, and RCI Labscan Ltd. and used without further purification. Distilled water was used to prepare all of the solutions in this study. For electrochemical testing, polyvinylidene fluoride (PVDF) and carbon black (Super P, conductive) were obtained from Sigma-Aldrich (Germany) and Alfa Aesar (UK), respectively.

Preparation of OC–BR2 nanocomposite

Synthesis of SBA-15 template

SBA-15 was synthesized via the procedure reported by Zhao et al. [20] with some modifications. Pluronic P123 (4.0 g) was initially dissolved in 120 mL of 2 M HCl solution and 30 mL of water. TEOS (8.5 g) was then added to the solution and stirred at 35 °C for 20 h. The mixture was aged at 80 °C for another 24 h. Then, the solid product was recovered, washed, and dried at 60 °C. The Pluronic P123 surfactant was cast off the as-synthesized solid using a 200 mL Soxhlet extractor in ethanol–water mixture (50 wt.%) for 18 h.

Synthesis of OC

OC was synthesized using sucrose as carbon source according to the procedure reported by Ryoo et al. [21]. Sucrose (1.25 g) was dissolved in H_2SO_4 solution, and 1.0 g of SBA-15 template was added to the solution. The homogeneous paste was heated up to 100 °C for 6 h, followed by another 6 h of heating at 160 °C. The product was again mixed with sucrose (0.8 g) and H_2SO_4 solution. The mixture was then heated as before. The final product was carbonized at 800 °C under an inert ambience for 1 h. Finally, the carbon/SBA-15 composite was treated with 10 wt.% HF, washed, dried, and stored for further use.

Characterization of OC

The textural properties, such as surface area, pore volume, and pore size distribution, of the SBA-15 template and OC were analyzed by nitrogen adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2010 volumetric adsorption analyzer. All samples were outgassed at 130 °C for 12 h prior to analysis to remove physisorbed species from the sample surfaces. Specific surface areas were determined from Brunauer–Emmet–Teller (BET) plots, and pore size distributions were estimated by using the Barrett–Joyner–Halenda (BJH) method from the desorption branch. X-ray diffraction (XRD) patterns of the SBA-15 template and OC were recorded on a Siemens D5005 X-ray diffractometer using a Cu $K\alpha$ radiation source (λ = 1.5406 Å, step size = 0.01°) over the 2θ angle range of 0.5–8°. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were performed on a Hitachi SU8020 scanning electron microscope and a JEOL JEM-2001 electron microscope, respectively. Ground samples for TEM measurements were sonicated in ethanol for 2–5 min and then deposited onto a carbon-coated copper grid. The surface functional species of OC were determined through X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra DLD; USA) in a vacuum of 2×10^{-9} mbar. The zeta potential of the OC suspension was measured at 25 °C using a Zetasizer Nano system (ZSP, Malvern, UK). This instrument automatically calculates the electrophoretic mobility of the particles and converts it to a zeta potential according to the Smoluchowski model. The pH of the OC suspension, which consisted of 0.05 g of OC in 100 mL of water, was adjusted from 2 to 10 using HCl and NaOH solutions.