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Facile green synthesis of nitrogen-doped porous carbon and its use for electrocatalysis towards nitrobenzene and hydrazine

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ABSTRACT

By using eco-friendly polydopamine as carbon and nitrogen precursor and commercial hydrophilic nano-$CaCO_3$ as hard-template; a one step, cost-effective and green method to synthesize nitrogen-doped porous carbon (NPC) is presented. A series of NPC samples with different nitrogen contents have been reported. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectra (EDX), fourier transform infrared spectroscopy (IR), Raman spectroscopy, X-ray diffraction (XRD), nitrogen adsorption-desorption and X-ray photoelectron spectra (XPS) were employed for characterizations of NPC. The influence of BET surface area and different amounts of N-bonding configurations of NPC for the electrocatalysis towards nitrobenzene (NB) and hydrazine (N_2H_4) were investigated in detail. Results indicated that NPC with largest BET surface area and highest amounts of pyrrolic N and graphitic N showed improved electrocatalytic activity for NB and N_2H_4 in neutral solution.

1. Introduction

Nowadays, porous carbon catalysts have been attracting special focus mainly due to their promising applications for electrocatalytic and electrochemical analysis [1,2]. Nevertheless, single-phased carbon material is limited in performance gradually because of their intrinsic weaker material properties in electrocatalytic ability. In order to improve the electrocatalytic ability of porous carbon catalysts, researchers have been devoted to introduce precious metals or metal oxides to carbon materials [3,4]. However, the limited reserves and high cost of noble metals have been raised as major issues to be addressed. As a result, incorporation of heteroatoms (e.g., N, B, P, and S) into carbon materials so as to modify their surface and physicochemical properties has been investigated in recent years [5–8]. Among them, N-containing carbon materials have received considerable attentions due to the strong electron donor nature of nitrogen which should promote enhancement in π bonding, leading to improved stability, electron transfer rate, and hence durability of the carbon supports during electrocatalytic processes [9–11]. Up to now, a variety of N-containing porous carbon materials has been reported. The nitrogen groups, for example, the pyrrolic N [12,13] and graphitic N [14,15], have been demonstrated to play a critical role in promoting the electrocatalytic activity towards small molecules or oxygen reduction reaction. Despite their high electrocatalytic activity, there still exist some problems; for instance, porous carbon in these works is usually prepared by nanocasting using colloid [16] or mesoporous [17] silica as a hard template. The involved silica template fabrication is often time-consuming, and in some cases, costly and usually includes the use of extremely toxic and corrosive HF to remove these templates. It makes this method unpractical and difficult to find applications in reality. In addition, the nitrogen precursors in the previous works including ethylenediamine [18], ammonium hydroxide [19] and melamine [20] are poisonous to humans, and the preparation processes of those N-doped porous carbon (NPC) materials are complex. Consequently, it remains a challenge to develop a facile, cost-effective and green method to prepare NPC materials simultaneously with great electrocatalytic activity.

Among various of nanostructured hard templates for the preparation of porous carbon, commercial hydrophilic nano-$CaCO_3$ with unique mechanical and optical properties is one of the most abundant industrialized nanomaterials with cheap price (ca. \$500 ton^{-1}) [21]. At present, both the surface polarity and particle size of the nano-$CaCO_3$ can be well-tuned in industrial production, making it possible to meet the needs of various carbon precursors. Moreover, it is easy and relatively safe to remove the calcium template with diluted HCl instead of the corrosive HF. As a N-containing polymer, polydopamine (PDA) can be formed on any type and shape of

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surface at slightly basic pH without any polymerization initiator. In addition, PDA has been demonstrated to have a high carbonization yield recently due to its similar structure to phenolic resin [22]. These unique properties of PDA inspired us to select PDA as the eco-friendly nitrogen and carbon precursor in the present work.

Nitrobenzene (NB) is an important raw material and solvent in the fields of manufacturing of aniline, dye, pesticide, explosives, shoes and floor metal polishes. As a toxic and suspected carcinogenic compound, even at low concentrations, NB released to environment may pose a great threat to human health [23]. Hydrazine (N_2H_4) is widely used in areas of pharmaceutical intermediates, fuel cells, manufacture of rocket propellants, pesticides, explosives, and textile dyes [24]. It has been reported that N_2H_4 and its derivatives have adverse health effects [25]. Therefore, the rapid and accurate detection of NB and N_2H_4 is of great significance. There are various techniques including fluorescence, chromatography, colorimetric, spectrophotometry and electrochemistry methods for the detection of NB [26–29] and N_2H_4 [30–33]. Among these analytical techniques, electrochemical detection is distinctive for its high sensitivity, low-cost, easy operation and real-time detection. Therefore, developing efficient electrocatalyst for sensitive electrochemical detection of NB and N_2H_4 remains very important.

Herein, using polydopamine as carbon and nitrogen precursor and commercial hydrophilic nano-$CaCO_3$ as hard-template, we developed a one step, cost-effective and green synthesis approach for the fabrication of NPC. NB and N_2H_4 were used as the probes to demonstrate the electrochemical performance of the prepared electrocatalyst. The electrochemical results showed that NPC exhibited high electrocatalytic activity towards NB and N_2H_4 in neutral solution.

2. Experimental

2.1. Reagents

Commercial hydrophilic nano-$CaCO_3$ was purchased from Shanxi Xintai NanoMater. Co., Ltd. Dopamine hydrochloride (DA), hydrochloric acid (HCl, 37.5%), NB, N_2H_4 and Nafion (5 wt%) were purchased from Sigma-Aldrich, while 2-amino-2-hydroxymethylpropane-1,3-diol (Tris, $C_4H_{11}NO_3$) were purchased from Sinopharm Chemical Reagent Co. Ltd. The 0.1 M phosphate buffer solution (PBS pH 7.0), which was made up from NaH_2PO_4, Na_2HPO_4 and H_3PO_4, was employed as a supporting electrolyte. All other chemicals were at least of analytical grade. Aqueous solutions were prepared with double-distilled water and stored in the shade.

2.2. Apparatus

Electrochemical experiments were performed on a CHI 830B electrochemical workstation (CH Instruments, China) connected to a personal computer. A three-electrode configuration was employed, consisting of a bare or modified glassy carbon electrode (GCE, 3 mm diameter) serving as a working electrode, whereas an Ag/AgCl (in saturated KCl solution) and a platinum wire served as the reference and counter electrodes, respectively. Infrared (IR) spectra of the samples were recorded with Nicolet Magna 560 FT-IR spectrometer with a KBr plate. X-ray diffraction (XRD) patterns were obtained on an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu Kα radiation (k = 0.15406 nm). Raman spectroscopy patterns were obtained using a confocal microprobe Raman system (HR800, Jobin Yvon). Nitrogen adsorption-desorption isotherms were performed on ASAP 2020 (Micromeritics, USA). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size was obtained from the desorption branch of the isotherm by the Barrett-Joyner-Halenda method. The total pore volume was determined from the amount of liquid nitrogen adsorbed at a relative pressure of about 0.99. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. Scanning electron microscopy (SEM) images were determined with a Philips XL-30 ESEM equipped with an Energy-dispersive X-ray (EDX) analyzer. X-ray Photoelectron Spectroscopy (XPS) was measured using Thermo ESCA LAB spectrometer (USA).

2.3. Preparation of NPC

NPC was synthesized by using the commercial hydrophilic nano-$CaCO_3$ as the template and PDA as the carbon and nitrogen precursor. In brief, 1 g of DA was dissolved in 500 mL of Tris-HCl (pH 8.5, 10 mM) buffer solution. Next, different amounts of $CaCO_3$ (NPC-1: 2.333 g; NPC-2: 1 g; NPC-3: 0.428 g $CaCO_3$) were added, and the mixture solution was stirred at room temperature for 24 h to form PDA/$CaCO_3$ nanocomposite. The obtained nanocomposite was centrifuged (7000 rpm, 5 min) and washed with fresh Tris-HCl buffer three times to remove the tan colored solution, followed by drying in vacuum at 70 °C overnight. Then the nanocomposite was collected and calcined for 2 h at 700 °C in N_2. Finally, the NPC was obtained after removing the template with 2 M HCl.

2.4. Preparation of the modified electrodes

GCE was polished before each experiment with 1, 0.3 and 0.05 μm alumina power, respectively, rinsed thoroughly with double-distilled water between each polishing step, and then sonicated successively in 1:1 nitric acid, absolute alcohol, and double-distilled water and dried in air. To prepare the modified electrodes, approximately 1 h of ultrasonication was necessary to disperse 2 mg of NPC into a mixture of 0.1 mL (5 wt%) Nafion and 0.9 mL distilled water. After dropping 5 μL of the suspension onto the bare electrode surface, the electrode was dried in air at laboratory temperature.

3. Results and discussion

3.1. Characterization of NPC

The morphologies of nano-$CaCO_3$ and NPC-2 are characterized by SEM in Fig. 1A and 1B, respectively. The particle size of the nano-$CaCO_3$ is ca. 40-110 nm as shown in Fig. 1A. The NPC-2 exhibits adhesive and roughly spherical pores mainly on the borderline between mesopores and macropores, that is, 35-100 nm. It is in good agreement with the particle size distribution of nano-$CaCO_3$. The TEM image of NPC-2 (Fig. 1 C) also shows adhesive and roughly spherical pore structure. EDX spectrum is obtained to determine the composition of NPC-2 (Fig. 1D). The EDX spectrum of NPC-2 shows peaks corresponding to the elements of C, N and O (the other elements are derived from the indium tin oxide glass), which confirms the successfully doping of nitrogen into porous carbon.

Fig. 2A exhibits FT-IR spectra of NPC. The typical absorption peak at 1550 cm^{-1} is attributed to the C = C/C = N stretching vibrations [15], and the band centered around 1245 cm^{-1} is related to aromatic C-N stretching bond [34]. The result proves that NPC has been successfully prepared using PDA as carbon and nitrogen precursor. The NPC-2 sample was further analyzed by XRD in the wide-angle region (Fig. 2B). There are two diffraction peaks located at around 25° and 43°, which can be assigned, respectively, to the (002) and (101) planes of graphitic carbon. The high intensity peak at (002) suggests that NPC-2 exhibits graphitic features to some extent [35,36]. This phenomenon is further supported by Raman spectrum