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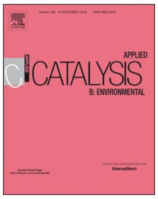

Bone char-derived metal-free N- and S-co-doped nanoporous carbon and its efficient electrocatalytic activity for hydrazine oxidation

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ABSTRACT

Bone char (BC) was successfully used, for the first time, both as a self-template/a pore-former and a precursor of heteroatoms (N and S atoms) during carbonization of sucrose, allowing for the synthesis of nanoporous N- and S-co-doped carbon (NSC) material possessing high surface area and excellent electrocatalytic activity. BC's ability to help with the formation of nanopores in the carbon material was indirectly confirmed by making a control material, denoted as pyrolyzed sucrose or PS, under the same condition but without including BC in the reaction media. N_2 gas porosimetry showed that NSC had a very large BET surface area (1108 $m^2\ g^{-1}$), which is about 60% higher than that of PS (443 $m^2\ g^{-1}$). Comparison of the SEM images of the two materials also indicated some differences in their textural and morphological features. XPS analysis showed that NSC had a higher content of S (2.29%) than PS (0.21%) and that the S atoms were distributed mostly in the form of thiophenic moieties (32.3% for the PS and 59.2% for the NSC). Although some of the S groups were originated from sulfuric acid, which was used for the dehydration of sucrose during the synthesis of the materials, this result indicated that BC was the major source of the S dopant atoms in NSC as well as the major reason for the formation of thiophenic groups in this material. Furthermore, while PS's structure did not have N dopants, NSC's lattice had about 1.39% of N dopant atoms that existed in the form of pyridinic, pyrrolic and graphitic groups and that were also originated from BC. X-ray diffraction and Raman spectroscopy revealed that NSC's lattice had a higher density of defects than PS. Owing to its high surface area and optimal density of heteroatom dopant groups and defect sites, NSC exhibited excellent electrocatalytic activity toward the hydrazine oxidation reaction (HzOR), or the lowest overpotential ever reported for this reaction, along with a high current density. Besides making it among the most efficient electrocatalysts for HzOR, its electrocatalytic performance can make this metal-free material a good alternative to the conventional metal-based electrocatalysts that are commonly used in HzOR-based fuel cells.

1. Introduction

The increase in energy demand worldwide has long prompted the scientific and engineering community to find alternative energy sources that can reduce our reliance on fossil fuels [1]. As part of this effort, substantial attention has focused on direct liquid fuel cells (DLFCs), which can convert chemical energy sources such as ethanol, methanol, dihydrogen (H_2), low molecular weight hydrocarbons, and others into electrical energy [2,3]. However, for these promising energy systems to efficiently generate electrical energy directly from chemical fuels, they require advanced, effective catalysts, which can efficiently promote the half-reactions involved at the electrodes of the fuel cells [4].

Most catalytic active materials used at the anode and cathode in many conventional fuel cells contain less earth-abundant noble metals such as Pt and Ir; consequently, fuel cells are currently expensive and hard to scale up for large-scale commercial applications [2]. This also means, less costly and sustainable fuel cells catalysts should be developed in order for fuel cells to become viable for large-scale applications and make major differences in our renewable energy landscapes [2]. Non-noble metal-based alternative catalysts that have been widely investigated in recent years to replace conventional fuel cell catalysts include non-precious metals and metal alloys. Such materials have been reported to effectively catalyze reactions such as the oxygen reduction reaction (ORR) [5,6], the ethanol oxidation reaction (EOR) [7], the

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hydrogen evolution reaction (HER) [8], the hydrazine oxidation reaction (HzOR) [9,10], etc. There have also been several reports in the literature, where various metals and metallic alloys in supported forms on other materials, mainly carbons and metal oxides, could serve as catalysts for these types of reactions [11–13]. In fact, many commercially used catalysts for various reactions are available in supported forms, except that they comprise noble metals (*e.g.*, Pt/C) [7,14]. Many of them are synthesized by anchoring or "heterogenizing" catalytically active metallic species on solid-state support materials. However, the use of metals and metallic alloys as catalysts even in supported forms still presents some challenges especially in electrocatalysis, due to the possible dissolution, corrosion, poisoning, sintering and/or agglomeration of the metals in the catalysts [15]. This is often what leads to the reduction in activity or the complete failure of these catalysts over time.

In addition to various bare noble metals and metal alloys and their supported variants, heteroatom-doped carbon-based materials (*e.g.*, N-doped carbons) containing metals have been considered as promising electrocatalysts for many reactions [2]. Studies have indicated that the catalytic activities of these materials, for the most part, stem from their chemical dopant groups and the perturbation of the electron configurations in their lattice as a result of the heteroatom dopant atoms. Additionally, in the presence of some supported metals, the dopant groups of many such materials form highly catalytically active sites [16]. However, these catalysts too have some drawbacks such as high cost of synthesis, low selectivity to desired products and poor stability, besides the sintering, leaching and corrosion problems mentioned above [17].

Hence, considerable efforts have recently been directed toward the development of metal-free carbon materials for application as catalysts in various catalytic processes [2]. To make carbon materials effective electrocatalysts, generally their carbon lattices should be doped with the right types of heteroatom dopants or dopant moieties. In particular, doping carbon structures with elements such as N and S atoms makes these materials highly electrocatalytically active. This is because N and S dopant atoms easily modulate the conjugated sp^2-sp^2 linkages, π-orbital electron delocalization, and electron distribution in the structures of these materials. These, in turn, generate positively and negatively charged groups on the materials that are often effective in adsorbing reactants or intermediates, desorbing the products, and promoting the overall conversions of the reactants into desired products [17,18]. The dopants also improve the steps associated with bond breakages in the reactants or bond formations in the products during electrocatalysis [17]. So, materials that can help these processes and provide the right balance of adsorption and desorption processes with less energy barriers are highly desirable in electrocatalysis.

To synthesize such types of heteroatom-doped carbon-based materials, researchers have tried various methods as well as several types of precursors. In many cases, graphite and graphene oxide were used as starting materials [20–23], while in many others, more sustainable carbon sources, such as cellulosic paper [18], rice grains [1], yeast cells [12], cotton [3,24], sucrose [25], softwood kraft pulp-derived cellulose nanofibrils [26], etc. were applied. The use of sustainable carbon sources for making these materials is obviously more appealing in order to be able to ultimately scale up the synthesis and the production of catalysts in large scales for fuel cells. However, it is additionally necessary to replace or eliminate the many toxic and non-environmentally friendly chemicals, such as ammonium hydroxide, pyrrole, and *N,N*-dimethylformamide, which are often used for the synthesis of heteroatom-doped carbon materials.

In this report, bone char (BC) is successfully shown, for the first time, to serve as a low-cost precursor of N and S dopant atoms as well as a self-template for the synthesis of high surface area, electrocatalytically active, nanoporous N- and S-co-doped carbon (NSC). For the synthesis of NSC, sucrose was used as the main source of carbon and subjected to carbonization in the presence of BC. The resulting NSC material was found to efficiently electrocatalyze the hydrazine oxidation reaction (HzOR). The benefits of BC in resulting this catalytically active carbon material was indirectly determined by making a control material from sucrose without including BC in the precursor. This material, which was denoted as pyrolyzed sucrose (PS), did not catalyze HzOR as much as NSC did. On the other hand, thanks to BC, NSC showed more catalytically beneficial textural, chemical and morphological features (high surface area and more heteroatom dopants) compared with PS. HzOR, the reaction that the reported materials were tested to catalyze here, is a highly important electrochemical reaction for fuel cells. This is because, if operated against ORR, HzOR generates only environmental-friendly compounds (N_2 and H_2O) while giving off a high theoretical cell voltage (+1.61 V) and producing a high-energy density (5400 W h L^{-1}). In other words, direct hydrazine fuel cells can generate more energy per unit mole than many other DLFCs and typical H_2-powered fuel cells, while producing environmentally friendly by-products [3,9,27].

2. Materials and methods

2.1. Reagents and chemicals

Commercial-grade sucrose (União brand, refined sugar) was purchased from a local supplier of União Company in Brazil. Hydrochloric acid (37%), sulfuric acid (98%), 2-propanol, Nafion (5% in a solution of lower aliphatic alcohols and water, in which 15–20% is water), hydrazine monohydrate (98%) and phosphate buffer saline (10X PBS, pH 6.8) were purchased from Sigma-Aldrich, USA. All the chemicals and reagents were used as received without further purification.

2.2. Synthesis of N- and S-co-doped carbon (NSC)

BC, the material that was employed as a hard-template in the synthesis of the NSC reported herein, was obtained using an optimized synthetic procedure described in our previous report [28]. Then, 1.00 g of BC was mixed with 1.25 g of sucrose, 5.00 g of distilled water, and 0.14 g of sulfuric acid in a polytetrafluoroethylene (PTFE)-coated reactor. The mixture/reactor was kept in oven at 100 °C for 6 h, and then heated to 160 °C and kept at this temperature for 6 h. A dark-colored product was obtained, which was ground to powder using a mortar and pestle. After putting the resulting powder product back inside the reactor, more sucrose (0.80 g), sulfuric acid (0.09 g) and distilled water (5.00 g) were mixed with it. The mixture was then heated under the same conditions as described above. The final product was ground to powder and then put in a crucible and pyrolyzed in a muffle furnace (EDG-S equipment EDG3P 7000) as follows. First, it was heated from room temperature to 450 °C at a heating rate of 5 °C min^{-1} and kept at this temperature for 2 h under a flow of N_2 atmosphere that was let to flow at a rate of 100 cm^3 min^{-1}. After this time, the N_2 atmosphere was replaced by a flow of CO_2 that was also let to flow at the same rate of 100 cm^3 min^{-1}. The furnace temperature was increased from 450 °C to 750 °C at a heating rate of 5 °C min^{-1} and then kept at this temperature for 3 h. After this time, the furnace was programmed to cool down to *ca.* 150 °C in 4 h under a flow of N_2 at a rate of 100 cm^3 min^{-1}. The resulting pyrolyzed material was treated with an aqueous solution of HCl (50 mL, 1.0 mol L^{-1}) in an autoclave at 110 °C for 6 h in order to remove the BC through dissolution. This procedure was performed three times, by replacing the HCl solution with a fresh one. The solid product was washed several times with hot, distilled water (the temperature of which was *ca.* 60 °C) until the pH of the supernatant reached *ca.* 6.5. For each purification step (using acidic solution, followed by distilled water), the supernatant was removed by vacuum filtration with a membrane (Millipore, 0.45 μm). The equilibrium that describes the dissolution of BC in acidic media can be given as follows, Eq. (1) [29].

$$Ca_{10}(OH)_2(PO_4)_6(s) + 8H^+(aq) \rightleftharpoons 10Ca^{2+}(aq) + 6HPO_4{}^{-2}(aq) + 2H_2O \quad (1)$$