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Facile synthesis of boron and nitrogen-doped graphene as efficient electrocatalyst for the oxygen reduction reaction in alkaline media

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ABSTRACT

Boron-doped graphene and nitrogen-doped graphene have been respectively synthesized by a facile thermal solid-state reaction of graphene oxide with boric acid and urea. The morphology and structure of the doped graphene have been characterized by the scanning electron microscopy, infrared spectroscopy, ultraviolet visible spectroscopy and X-ray photoelectron spectroscopy, while the electrocatalytic activity toward oxygen reduction reaction has been evaluated by the cyclic voltammetry. It has been shown that the morphology, structure, doping level and fashions of graphene could be finely tuned by the thermal treatment conditions, and which have substantial effects on the activity of oxygen reduction reaction. The boron-doped graphene and nitrogen-doped graphene calcined at 700 °C demonstrate excellent electrocatalytic oxygen reduction activities as the appropriate introduction of boron and nitrogen functional groups in graphene, which might be promising for low temperature fuel cell applications.

1. Introduction

Proton exchange membrane fuel cells are able to transform chemical energy of the fuel into electrical energy via oxidation–reduction reaction of the oxidant such as oxygen, and are considered ideal power sources for future mobile and stationary applications due to their high energy efficiency, high power density, as well as low/zero emissions [1,2]. For fuel cells, the performance depends largely on the oxygen reduction reaction, which is substantially affected by the activity of the cathode catalyst. Since the sluggish kinetics of the oxygen reduction process, platinum and its alloys are usually used as electrocatalysts to promote the chemical reaction. However, the Pt-based catalyst suffers from crossover and poisoning effects which compromise the efficiency of fuel cells, and the high cost and scarcity of Pt intrinsically limit the large scale production and commercialization of Pt-loaded fuel cells [3–6]. Therefore, several alternative non-precious ORR electrocatalysts have been researched and developed,

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such as the transition metal nitrogen-containing complexes, the transition metal chalcogenides, and the metal-free doped carbon materials [1,3]. The doped carbon materials, for example by boron, nitrogen, phosphorus and sulfur doping, have attracted intense attention because they demonstrate high catalytic activity, high long-term durability and excellent tolerance to poisoning toward the ORR reaction, and are considered to have great potential as a rising category of potential candidates for the replacement of Pt-based catalysts [7–11].

Graphene and its derivatives represent a novel classic of two dimensional carbon nanomaterials, and the planar atomic-thick graphene exhibits unique electronic, mechanical, and thermal properties [12]. Meanwhile, doping with heteroatoms can further modulate the structure, electronic, and physicochemical properties of graphene. For example, boron-doped graphene and nitrogen-doped graphene can be obtained by introducing B or N atoms into the graphene lattice, and the conversion between the p-type and n-type semiconductor of graphene can be realized [13–15]. For the N-doped electron-rich carbon nanostructures, it has been found that the π electrons of carbon can be activated by the conjugation with the lone-pair electrons of N dopants, and the oxygen molecules can get effectively reduced on the neighboring positively charged carbon atoms [16]. For the B-doped electron-deficient carbon nanotubes (CNTs), the π electrons can also be activated for use in oxygen reduction reaction, with the vacant orbital of B conjugation with the π system of carbon to extract the electrons, and oxygen molecules can be effectively reduced on the positively charged boron sites [17]. Therefore, both electron-rich (as N) and electron-deficient (as B) dopants are favorable to break the electroneutrality of sp^2 carbon to create charged sites for O_2 adsorption and effective reduction activity.

To prepare the boron-doped graphene and nitrogen-doped graphene, the arc discharge method has been used, for

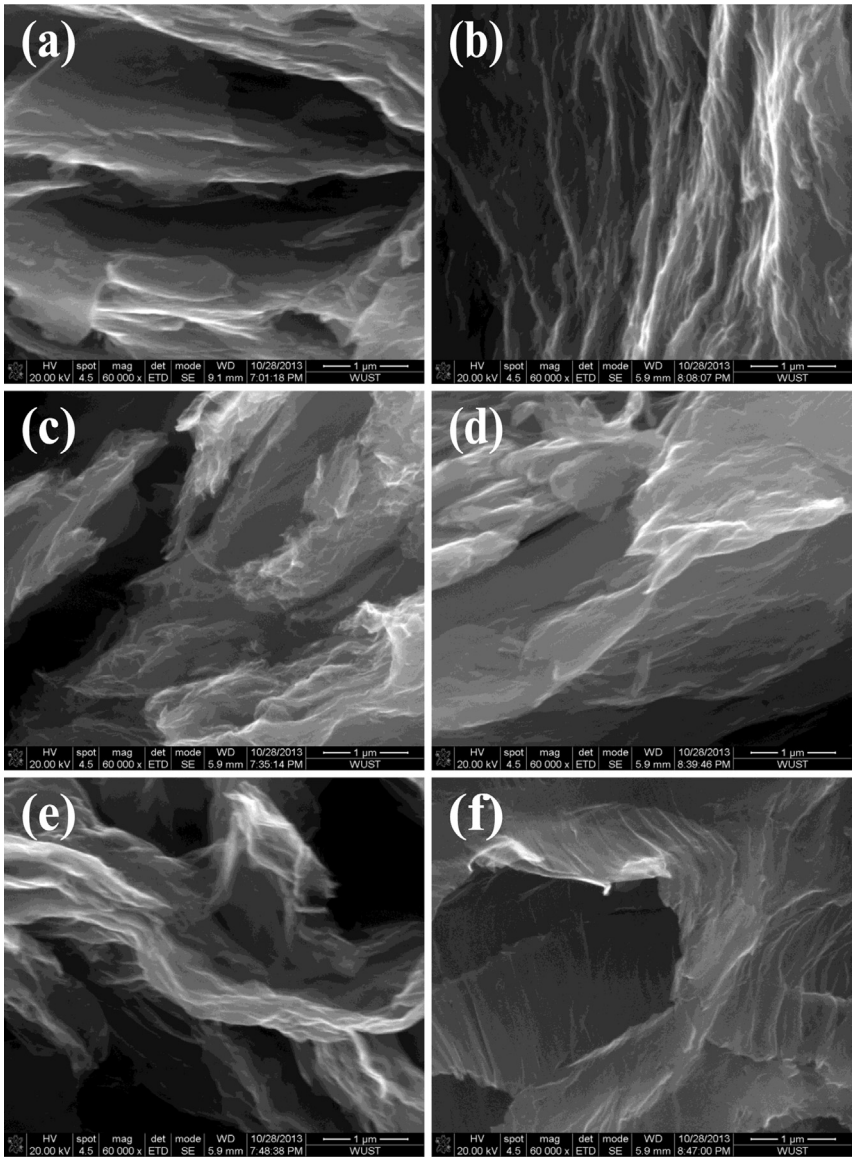

Fig. 1 – SEM images of nitrogen-doped graphene calcined at 200 °C (a), 400 °C (c), 700 °C (e) and boron-doped graphene calcined at 200 °C (b), 400 °C (d), 700 °C (f).