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Confined space reduced graphite oxide doped with sulfur as metal-free oxygen reduction catalyst

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ABSTRACT

Reduced GO in confined space of silica gel nanopores doped with sulfur shows high catalytic activity for oxygen reduction reaction (ORR) in alkaline medium and exhibits a superior tolerance to the presence of methanol. Even though the partially reduced GO with hydroquinone structures is a good catalysts for ORR, it shows instability in KOH. The good performance of S-doped material is linked to the coexistence of sulfur and oxygen on the surface in equal atomic quantities and a unique porosity being the replica of the silica pores. The former leads to the positive charge on the carbon atoms, which are the reaction sites. Hydrophobicity of the surface and small pores enhance adsorption of O_2.

1. Introduction

Research efforts have recently been focused on the introduction of heteroatoms to graphene in order to increase its catalytic activity in oxygen reduction reaction (ORR), which is of paramount importance for development of new energy sources [1]. As in the case of activated carbons, the treatment with hydrogen sulfide [2] or organic sulfides [3] has been applied to graphite oxide (GO) leading to the formation of thiophenic, sulfones or sulfoxides functionalities. Our latest study of activated carbon modified with sulfur demonstrated their unusually high activity for oxidation reactions [4] along with the visible light photoactivity [5].

Following our recent line of research, we have partially reduced GO in confined space of silica gel pores, doped it with sulfur and evaluated its performance in oxygen reduction reactions (ORR) in neutral electrolyte with the possible application in microbial fuel cell [6]. Even though the results showed a high catalytic activity for ORR on reduced GO and that one modified with sulfur with an apparent insensitivity for methanol oxidation, an introduction of sulfur did not notably increase the performance in that particular system. The high catalytic activity was linked to the presence of oxygen and sulfur functional groups, to hydrophobicity and to the specific texture consisting of micro and mesopores being the replicate of the silica matrix porosity.

Since the alkaline fuel cell are much more common than microbial ones [6–13], the objective of this study is to evaluate catalytic activity of our unique materials for oxygen reduction reactions in a strongly alkaline medium. Qiao and co-workers [11] and Yang et al. [2] recently have demonstrated the effect of sulfur incorporated to graphene layers on the enhancement in the performance of GO in ORR. Although in both approaches silica was used as a template, our methodology differs in the application of commercial silica gel of a defined porosity as a matrix for a partial reduction of GO (obtained using Hummers method [14]) at 800 °C.

2. Experimental

2.1. Materials

Graphite oxide (GO) was synthesized by the oxidation of graphite (Sigma–Aldrich) using the Hummers method [14]. The dry silica gel (grade 22, 60–200 mesh, Sigma–Aldrich) (7.0 g) was immersed in the well dispersed GO suspension

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(3 wt.%) and stirred for 24 h. Then the composite was filtrated, dried and carbonized under nitrogen at 800 °C for 1 h. After carbonization the inorganic matrices were removed using 48% HF. The resulting material was washed in distilled water to reach constant pH at around 5.0. The sample obtained is referred to as RGO.

To introduce sulfur to the graphene matrix, the initial material (RGO) was heated at 800 °C in hydrogen sulfide for three hours (1000 ppm of H_2S balanced in nitrogen, flow rate 150 mL/min), in a horizontal furnace. The heating rate was 10 °C/min. The material obtained is referred to as RGOS.

The surface feature of the modified GO addressed in this paper was extensively studied in Ref. [6]. For the clarity of the discussion some data is introduced to this paper.

2.2. Electrochemical characterization

The performance of our materials for electrochemical oxygen reduction reaction was investigated in 0.1 M KOH using three-electrode cell with the Ag/AgCl/KCl (3 M) as a reference electrode. The measurements of cyclic voltammetry and chronoamperometry were carried out on VersaSTAT MC (AMETEK, Princeton Applied Research) within the potential window of 0.19 V to −1.0 V with the scanning rate of 5 mV/s (cyclic voltammetry). The working electrode was prepared by mixing the active material with polyvinylidene fluoride (PVDF) (9:1) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on a Ti foil (current collector) with the total surface area of 1 cm^2 of an active material. Linear sweep voltammograms (LSV) were obtained in 0.1 KOH

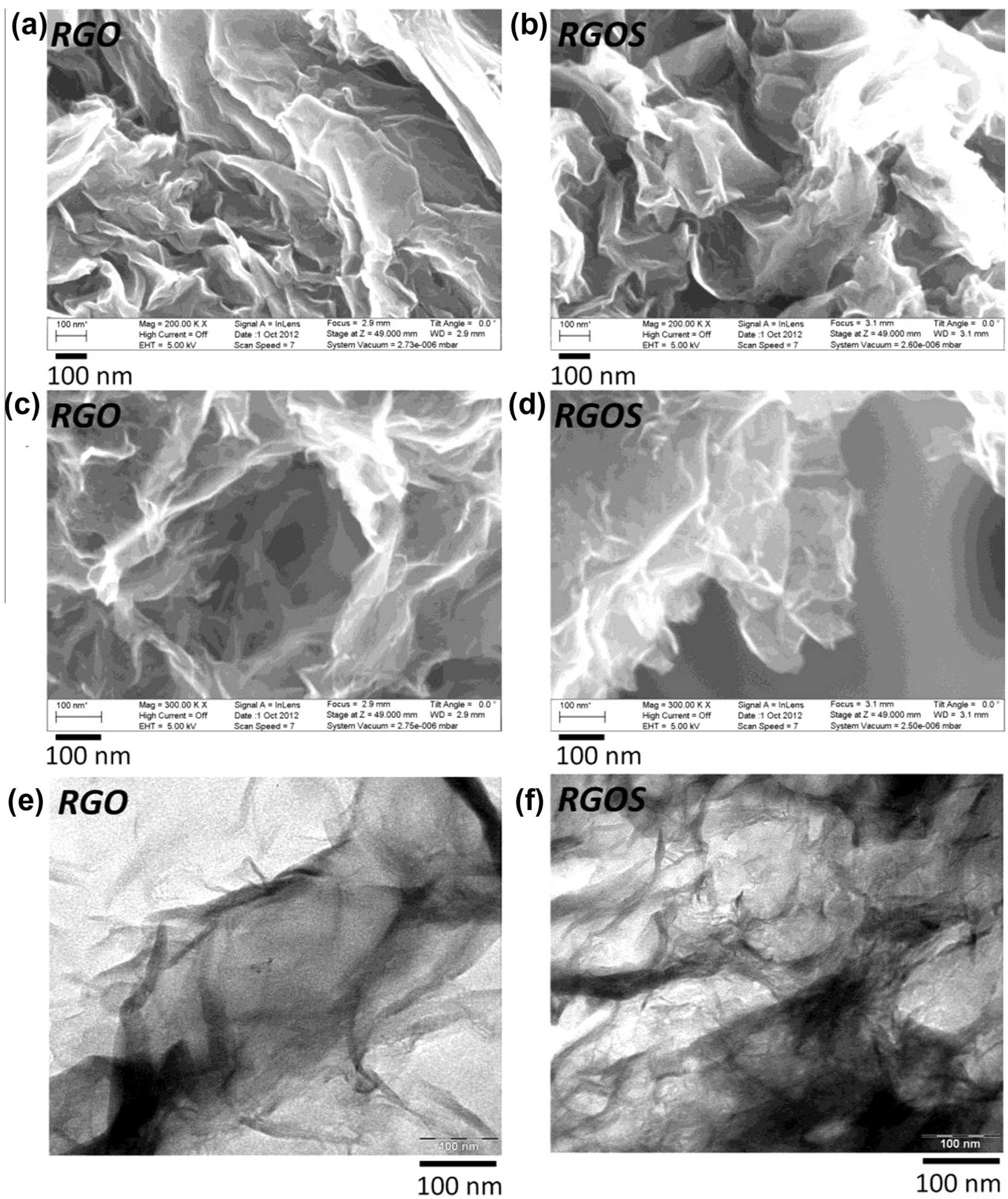

Fig. 1 – Textural characterization of the materials studied: (a–d) SEM; and (e, f) TEM images, respectively.