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Synthesis of Layered MnO_2 Nanosheets for Enhanced Oxygen Reduction Reaction Catalytic Activity

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ABSTRACT

In this study, a novel layered manganese oxide (MnO_2) nanosheets was prepared by using a facile method with graphene oxide as the template, and its electrocatalytic performance was studied. The results of cyclic voltammograms (CV) and the rotating disk electrode (RDE) measurements show that the MnO_2 nanosheets possess excellent electrocatalytic activity for oxygen reduction reaction (ORR) in alkaline medium. The electron transfer number of the nanosheets electrode was measured to be 3.4, which lied between the two-electron and four-electron processes, suggesting that the oxygen reduction on nanosheets might proceed by a coexisting pathway involving the two-electron and four-electron transfer.

1. Introduction

The conversion efficiencies of most fuel cells and metal-air batteries are close associated with the catalytic activity of the applied catalysts. Platinum has been commonly used to catalyze oxygen reduction reaction attributed to its excellent catalytic activity [1]. However, the high cost and limited availability constrain its commercial application. MnO_2 has recently emerged as a promising alternative to platinum, attributed to its low cost, great chemical stability, and comparative catalytic activity toward ORR [2–5]. Especially, MnO_2 has excellent ORR electrocatalytic activity in alkaline media, through a redox-mediation mechanism or sequential disproportionations of the O_2 reduction intermediates [6,7]. The MnO_2 electrocatalytic reactivity typically increases with its enhanced hydration degree and surface area [8,9]. Compared with manganese oxide in bulk material, its nano-material counterparts such as nanosheets have significantly higher catalytic activity [10–12]. Since the catalytic process of ORR catalyzed by MnO_x involves the reduction and oxidation of surface manganese oxide and its crystal defects, the number and activity of crystal defects significantly affect the catalytic performance [13]. In this article, we hypothesized that a distortion of MnO_2 nanosheets might increase the surface area and the number of active sites in the catalyst, and thus improve its catalytic activity.

Here we aimed to investigate the catalytic activity of a novel MnO_2 nanosheets for ORR in alkaline solution. Cyclic voltammogram (CV) and rotating disk electrode (RDE) measurements were used to characterize the ORR electrocatalytic activity of MnO_2 nanosheets. To the best of our knowledge, this might be the first report on the catalysis of ORR by MnO_2 nanosheets synthesized by facile redox method.

2. Materials and methods

MnO_2 nanosheets was prepared using graphene oxide as template, and the graphene oxide (GO) was prepared from flake graphite using the modified Hummers method. In brief, 1.0 g graphite (average particle diameter of 20 μm, 99.95% purity, purchased from Qingdao Tianhe Graphite Co. Ltd., China), 1.0 g $NaNO_3$ and 46 mL H_2SO_4 were mixed and stirred in a three-neck flask in an ice-bath for 15 min. Then, 8 g $KMnO_4$ was slowly added to the solution. The solution was transferred to a 35 ± 5 °C water bath, and stirred for about 2 h. After that, 80 mL distilled water was slowly added to the solution with stirring. The resultant mixture was stirred for 1 h at 90 ± 5 °C water bath, and then 200 mL distilled water was added. Later, 6 mL H_2O_2 (30%) was slowly dosed.

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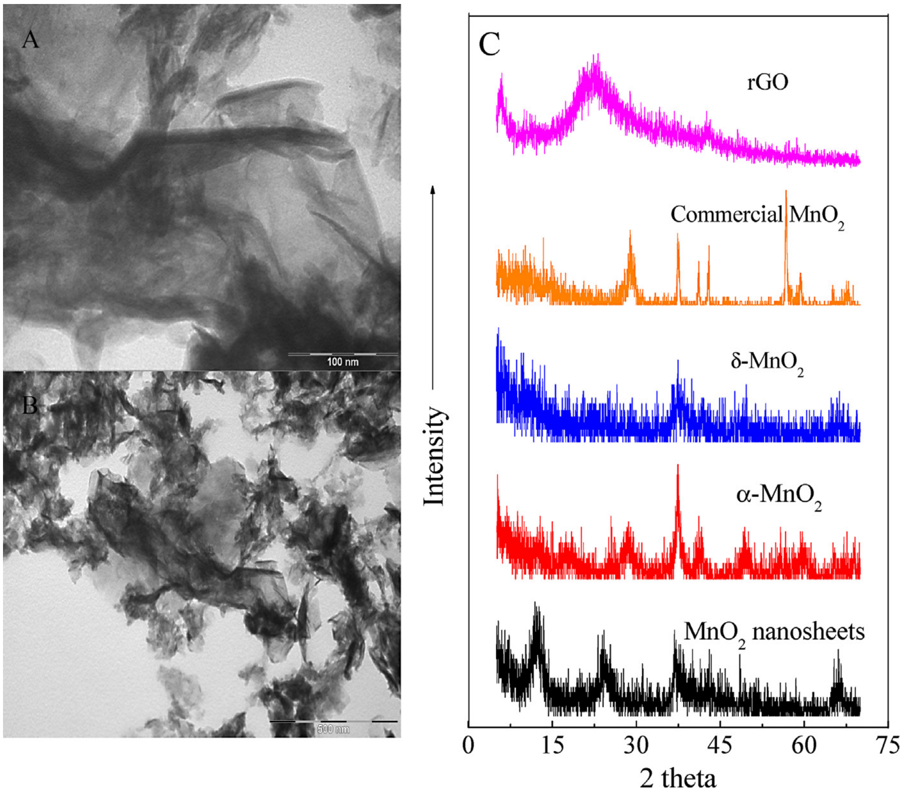

Fig. 1. (A) High resolution TEM image of the MnO$_2$ nanosheets; (B) Low resolution TEM image of the MnO$_2$ nanosheets; (C) XRD patterns of MnO$_2$ nanosheets, α-MnO$_2$, δ-MnO$_2$, commercial MnO$_2$ and rGO.

Once H_2O_2 was added, the color of the solution turned from dark brown to pale brown yellowish. The warm solution was filtered and rinsed with 100 mL Milli-Q water. The filter cake was vacuum dried and the dark brown GO powder could be obtained. Then, 5 mL of $KMnO_4$ solution (16 g L^{-1}) was added into 100 mL graphene oxide suspension (about 0.1 g L^{-1}). The mixture was kept in 60 °C water bath for 15 h. The resulted materials were rinsed with deionized water and the layered MnO$_2$ nanosheets were obtained. The morphology of the MnO$_2$ nanosheets was characterized with transmission electron microscopy (TEM) (JEM-2011, JEOL, Japan). The N_2-BET surface area was obtained with a DIL-402 C surface area analyzer using N_2. The crystal properties of the dried precipitates were identified using an 18 kW rotating anode X-ray diffractometer (MAP18AHF, MAC Sci. Co., Japan). For comparison, other crystalline MnO$_2$ nanoparticles were also prepared. Nanoparticles of α-MnO$_2$ were synthesized through redox reaction between stoichiometric quantities of $MnSO_4$ and $KMnO_4$ in aqueous medium [14]. Nanoparticles of δ-MnO$_2$ were prepared following the same synthesis route as that of α-MnO$_2$, but with doubled stoichiometric amount of $KMnO_4$ [15]. Commercial MnO$_2$ particles (Sinopharm chemical reagent Co., Ltd) after ball-milling were directly used as catalyst. Their N_2-BET surface areas and ORR catalytic activities were measured.

Glassy carbon (GC) electrodes (5 mm diameter, Gaoss Union Inc.) were polished with alumina slurry on a microcloth, and subsequently rinsed with ultrapure water and ethanol. The electrodes were then sonicated in ultrapure water for 10 min to remove bound particles, rinsed with ultrapure water, and then dried under nitrogen atmosphere. To prepare the working electrode, catalyst ink was prepared by mixing 0.8 mg catalyst with 5 μL Nafion solution (5%) and 1 mL deionized water under ultrasonication. Then, 20 μL of the suspension was dropped onto the GC surface and dried at room temperature to form a well-dispersed catalyst film on the electrode.

Electrochemical measurements were conducted in a three-electrode cell, with the catalytic electrode as the working electrode, a KCl-saturated Ag/AgCl electrode as the reference electrode and a platinum foil as the counter electrode. The measurements, including CV and RDE, were performed at room temperature in 0.1 M KOH solution. The solution was purged with high purity nitrogen or oxygen for at least 30 min prior to the measurement. CV was performed within a potential range of -0.7 to +0.3 V (vs Ag/AgCl) and at a scan rate of 10 mV s^{-1} (CHI660, Chenhua Instrument Co., China). For the RDE voltammogram measurement (Pine Research Instrumentation Inc., USA), the potential range and scan rate were +0.1 to -0.7 V (vs Ag/AgCl) and 10 mV s^{-1} respectively.

3. Results and discussion

The TEM images with high and low resolutions (Fig. 1A, 1B) show the monolayer MnO$_2$ nanosheets and its agglomerated wrinkled layer-structure respectively. These morphological observations clearly indicate that the synthesized MnO$_2$ nanosheets consisted of randomly aggregated thin sheets with a wrinkled and distorted structure. However, α-MnO$_2$ and δ-MnO$_2$ were all composed of spherical aggregates of nanoparticles (data not shown), which were in consistent with previous reported results [15]. Table 1 shows that the N_2-BET surface area of MnO$_2$ nanosheets reached 157 m^2 g^{-1}, much higher than that of α-MnO$_2$, δ-MnO$_2$ and commercial MnO$_2$ [16]. The high surface area of MnO$_2$ nanosheets could enable more active sites for the contact between catalyst and electrolyte. All the broad diffraction peaks of the MnO$_2$ nanosheets (Fig. 1C) were attributed to MnO$_2$ (JCPDS No. 72-1982), and it was also considered to be in a poorly crystalline phase. According to the previous results [13], such a poorly crystalline material could be regarded as containing enormous structure distortion with more active sites. Unlike the nanosheets patterns, broad peaks at 11.9 and 37.2 for α-MnO$_2$ and at 37.2 and 66.1 for δ-MnO$_2$ are presented (Fig. 1C),