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Co3O4 nanorods decorated reduced graphene oxide composite for oxygen reduction reaction in alkaline electrolyte

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Abstract
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Keywords
Co3O4, nanorods, electrolyte, reaction, alkaline, decorated, reduced, composite, graphene, reduction, oxide, oxygen

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Co$_3$O$_4$ nanorods decorated reduced graphite oxide composite for oxygen reduction reaction in alkaline electrolyte

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Abstract

Highly uniform Co$_3$O$_4$ nanorods decorated on reduced graphene oxide (rGO) were prepared by a one-pot hydrothermal procedure. During the hydrothermal process, Co$^{2+}$ ions were crystallized to Co$_3$O$_4$ nanorods and simultaneously GO was reduced to rGO to form the Co$_3$O$_4$/rGO hybrid. The Co$_3$O$_4$/rGO hybrid was characterized by scanning electron micrographs, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. The obtained Co$_3$O$_4$/rGO hybrid exhibits excellent electrocatalytic performance for oxygen reduction reaction.

Keywords: Co$_3$O$_4$ nanorods; reduced graphene oxide; oxygen reduction reaction
1. Introduction

The cathodic oxygen reduction reaction (ORR) is one of the key challenges in developing alkaline-based fuel cells and metal-air batteries [1]. Recently, transition metal oxides [2-5] as promising cathodic materials, have received considerable attention due to their high catalytic activity, low cost and environmental friendliness. However, these materials also suffer from some disadvantages, such as relatively poor electrical conductivity and lower electron transfer rate, which limited their applications in real devices. It is well known that graphene exhibits notable electronic conductivity and high surface area, which could be an attractive support for metal oxides to form a new class of nanocomposites for ORR. [6-8] Dai’s group [9-11] reported a series of nanocomposites consisting of Co$_3$O$_4$, Mn$_3$O$_4$, MnCo$_2$O$_4$ nanocrystals deposited on rGO templates as excellent catalysts for ORR. However, it is still a challenge to develop a simple facile deposition approach to prepare quality metal oxide/rGO catalysts for ORR with stable performance. To the best of our knowledge, the fabrication of Co$_3$O$_4$ nanorods decorated on rGO supports for ORR has not yet been reported.

In this work, we report a facile route to prepare a Co$_3$O$_4$ nanorods decorated rGO hybrid through a one-pot hydrothermal approach showing an efficient pathway for charge transfer. The as-prepared Co$_3$O$_4$/rGO exhibits a significant enhancement in electrocatalytic ORR performance in alkaline media, compared with unsupported Co$_3$O$_4$ or pure reduced graphene oxide.
2. Experimental

2.1 Synthesis of $\text{Co}_3\text{O}_4/r\text{GO}$ nanocomposite

Graphene oxide (GO) was synthesized by the modified Hummers method [12]. The $\text{Co}_3\text{O}_4$ modified rGO was synthesized as the following procedures. Firstly, 24 mmol $\text{Co(Ac)}_2\cdot4\text{H}_2\text{O}$ and 2 mmol $\text{CO(NH}_2)_2$ as a stabilizer were dissolved into 30 mL distilled water. Then, GO powders (with various mass weights) were added into the above solution and sonicated for 1 h, followed with an addition of 1 mL 6% hydrogen peroxide as an oxidizer and magnetically stirred for 6 h at room temperature. The as-prepared solution was then transferred into a Teflon liner, which was sealed in a steel autoclave. The autoclave was maintained at 190 °C for 5 h and then was allowed to cool down to room temperature by a cool-water system. The resulting precipitate was separated by filtration, and washed with distilled water and absolute ethanol for 5 times. Final black-color $\text{Co}_3\text{O}_4/r\text{GO}$ powders were achieved via vacuum-dry in a vacuum oven at 60 °C for 5 h. For comparison pure $\text{Co}_3\text{O}_4$ powder without rGO and rGO without $\text{Co}_3\text{O}_4$ were also prepared under identical conditions.

2.2 Physical characterization

The crystalline properties and morphologies of the as-prepared materials were characterized by powder X-ray diffraction (XRD, D8-advanced, Bruker, 40 kV, 20 mA, Cu K$\alpha$ radiation) and scanning electron microscopy (SEM, JEOL, JSM6700F). The atomic composition of $\text{Co}_3\text{O}_4/r\text{GO}$ was detected by X-ray photoelectron spectroscopy (XPS, Perkin Elmer, Al K$\alpha$ radiation). Raman spectroscopy was performed using a Jobin-Yvon Lab Ram HR800 system.
2.3 Electrochemical measurement

Electrochemical measurements were performed using a glassy carbon rotating ring disk electrode (RRDE, Pine Research Instrumentation), connected to a CHI 720c potentiostat in a standard three-electrode cell with a platinum wire as the counter electrode and a 3 M KCl saturated Ag/AgCl electrode as the reference electrode. Electrochemical impedance spectroscopy (EIS) measurement was carried out at open circuit potential with an ac perturbation of 5 mV in the frequency range from 0.01 Hz to 100 kHz using a Solartron SI1260 Impedance Analyzer. The catalyst loading on the electrode was maintained as 80 μg cm⁻² for all the electrochemical testing.

3. Results and Discussion

The fabrication process is illustrated in Figure 1a. Firstly, Co²⁺ ion was easily coordinated with negatively charged oxygen-containing functional groups on GO sheets. Followed by the hydrothermal process, Co²⁺ was oxidized into Co³⁺ by the oxygen-containing functional groups on the GO surface. The oxidized Co³⁺ and Co²⁺ coprecipitated into Co₃O₄, the resultant Co₃O₄ nanorods were in-situ grown on the rGO (in-situ thermal reduced from GO as support templates), similar to the formation of rGO sheets decorated with nanoparticles, as reported previously [7, 13]. Scanning electron microscopy (SEM) was employed to investigate the morphologies of Co₃O₄/rGO samples as shown in Figure 1b. It has been clearly shown that the Co₃O₄ nanorods were uniformly deposited onto the rGO substrate with an average length of ~200 nm and a diameter around 20 nm. Energy dispersive spectroscopy (EDS)
analysis given in Figure 1c indicates the existence of Co, O and C. The atomic ratio of Co to O is 3:4 which is in complete accord with the stoichiometry of Co$_3$O$_4$. Si signal aroused from the Si substrate.

XRD was performed to investigate the phase structure of GO, pristine Co$_3$O$_4$ and Co$_3$O$_4$/rGO. The as-synthesized GO displayed a typical characteristic (002) peak at 10.1° (Figure 2a). Then after the hydrothermal process, the as-prepared rGO showed a broad (002) peak at 2θ of 24.2°, corresponding to the d-spacing of 0.36 nm, and the strong (002) peak centred at 10.1° disappeared, indicating that GO has been reduced to rGO. [14]. The diffraction peaks of the pristine Co$_3$O$_4$ are in good agreement with the standard Co$_3$O$_4$ (JCPDS card: 42-1467) [15]. The major diffraction peaks of Co$_3$O$_4$/rGO were well indexed with those of Co$_3$O$_4$ except for the broad (002) peak at approximately 25°, which can be attributed to disordered stacked graphitic sheets [16].

This clearly demonstrates that the original GO has been reduced to rGO during the hydrothermal process. The phases of Co$_3$O$_4$ and rGO were further confirmed by Raman spectroscopy. The typical Raman spectra of GO, rGO and Co$_3$O$_4$/rGO are shown in Figure 2b, where the peaks of Raman spectrum of Co$_3$O$_4$/rGO at 193, 470, 520, 615 and 680 cm$^{-1}$, can be attributed to the E$_{g}$, F$_{2g}$ and A$_{1g}$ modes of Co$_3$O$_4$[16]. It is noted that GO exhibits a G band at 1606 cm$^{-1}$, while the corresponding G bands of rGO and Co$_3$O$_4$/rGO are 1586 and 1589 cm$^{-1}$, respectively. The red shifts of G band of rGO and Co$_3$O$_4$/rGO can be attributed to the high ability for recovery of the hexagonal network of carbon [17], which is consistent with the decrease of the D/G ratio.
Figure 2c-f shows the XPS survey of the Co$_3$O$_4$/rGO. The sharp peaks in Figure 2c correspond to the characteristic peaks of C1s, O1s and Co2p, indicating the existence of carbon, oxygen and cobalt elements in the sample. The XPS spectrum for Co2p shown in Figure 2d exhibits two major peaks with binding energies at 780.1 and 797.1 eV, corresponding to Co2p$_{3/2}$ and Co2p$_{1/2}$, respectively, with a spin-energy separation of 17 eV, which is the characteristic of a Co$_3$O$_4$ phase [18]. The C1s XPS spectrum of GO (Figure 2e) could be deconvoluted into four peaks arising from C-C/C=C (284.6 eV) in the aromatic rings, C-O (286.4 eV) of epoxy and alkoxy, C=O (287.8 eV) and O-C=O (289.3 eV) groups, respectively [19]. For Co$_3$O$_4$/rGO (Figure 2f), the intensity of the oxygenated groups decreases significantly, indicating that GO was reduced to rGO during the hydrothermal process [13]. This result is in a good agreement with the results of Raman spectroscopy.

To evaluate the electrocatalytic performance of the as-prepared Co$_3$O$_4$/rGO nanocomposite toward ORR, linear sweeping voltammetry (LSV) was investigated in a 0.1M KOH. As shown in Figure 3a, independent Co$_3$O$_4$ or rGO exhibited relatively poor ORR activity, while the Co$_3$O$_4$/rGO showed a significant improvement of catalytic ORR performance with a positive shift of onset potential, which is much close to that of commercial Pt/C (20 wt% E-TEK). This performance is in good agreement with previous reports [20]. EIS (Figure 3b) was used to probe the electron transfer kinetics at the Co$_3$O$_4$, rGO and Co$_3$O$_4$/rGO electrodes. A semicircle and a linear portion corresponding to a charge transfer and mass transfer process are quite visible at the high frequency and the low frequency range, respectively. Obviously, the
diameter of the semicircle for Co$_3$O$_4$/rGO is significantly smaller than that of Co$_3$O$_4$
and almost similar to that of rGO. This indicates that rGO supporting materials
significantly enhance the electron transfer in Co$_3$O$_4$/rGO, which could promote the
catalytic ORR much easier and more efficiently than Co$_3$O$_4$ without rGO supports.

The transferred electron number was studied using rotating-disk electrode (RDE)
measurements (Figure 3c) according to the following Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{0.62nFC_0D^{2/3}v^{-1/6}\omega^{1/2}} + \frac{1}{nFkC_0}$$

where $\omega$ is the angular velocity, $n$ is the number of electrons transferred, F is
Faraday’s constant, $C_0$ is the concentration of dissolved oxygen (1.2×10$^{-6}$ mol cm$^{-3}$),
$D$ is the diffusion coefficient of oxygen (1.9×10$^{-5}$ cm$^2$ s$^{-1}$), $v$ is the kinetic viscosity of
solution and $k$ is the apparent electron transfer rate constant.

The parallel fitting lines of the Koutecky-Levich plots (insert of Figure 3c) at
different potentials suggest first-order reaction kinetics toward the concentration of
dissolved oxygen and similar electron transfer numbers for ORR [21]. The number of
electrons transferred in ORR was calculated to be 3.50, indicating that Co$_3$O$_4$/rGO
favors a 4 electron oxygen reduction process. In other words, O$_2$ can be dominantly
reduced to the final hydroxyl ion at these potentials. The almost same $n$ value (3.52) is
derived from the result of the RRDE test carried out at 1600 rpm. The measured H$_2$O$_2$
yields for Co$_3$O$_4$/rGO catalyst are below 25% over the potential range of -0.3 to -0.6V,
suggesting the high efficiency of the ORR on Co$_3$O$_4$/rGO [21]. Furthermore, the
chronoamperometric curves for catalytic ORR were recorded to study the durability of
the Co$_3$O$_4$/rGO at -0.55 V. The Co$_3$O$_4$/rGO catalyst shows stable ORR performance
after 6000 s of operation. While commercial Pt/C reveals a slight degradation after 2000 s of operation. This again confirms that the Co$_3$O$_4$/rGO nanocomposite has a superior activity and stability for catalytic oxygen reduction in the 0.1M KOH. Through the preliminary study of the mass ratios of Co$_3$O$_4$ to rGO, it demonstrated that the best catalytic performance was achieved from Co$_3$O$_4$/rGO with a mass ratio of 2.6.

4. Conclusion

Heterogeneous Co$_3$O$_4$/rGO was synthesized by a simple one pot hydrothermal method. This method leads to a uniform distribution of Co$_3$O$_4$ nanorods on rGO sheets. The Co$_3$O$_4$/rGO hybrid exhibits higher catalytic activity and durability for ORR than the unsupported Co$_3$O$_4$, which present this material an efficient, low cost cathodic catalyst for alkaline-based fuel cells and metal-air batteries.

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References

**Figures captions**

Figure 1. A schematic for preparation of Co$_3$O$_4$/rGO hybrid (a); SEM image (b) and EDS spectrum (c) of the Co$_3$O$_4$/rGO.

Figure 2. (a) XRD patterns of GO, rGO, Co$_3$O$_4$ and Co$_3$O$_4$/rGO. (b) Raman spectra of GO, rGO and Co$_3$O$_4$/rGO. (c) XPS survey spectra of Co$_3$O$_4$/rGO. (d) Co2p XPS of Co$_3$O$_4$/rGO (insert: O1s), (e, f) C1s XPS for GO and Co$_3$O$_4$/rGO.

Figure 3. (a) LSV curves of Co$_3$O$_4$, rGO, Co$_3$O$_4$/rGO and Pt/C in 0.1 M KOH O$_2$ saturated solution with rotation speed at 400 rpm (dashed line: LSV curve of Co$_3$O$_4$/rGO in 0.1 M KOH N$_2$ saturated solution). (b) Nyquist plots of Co$_3$O$_4$, rGO and Co$_3$O$_4$/rGO at open potential. (c) LSV curves for Co$_3$O$_4$/rGO at various rotation speed. Insert: Koutecky-Levich plots (according to Fig 3c) at different electrode potentials. (d) Chronoamperometric curves for O$_2$ reduction on the Co$_3$O$_4$, rGO and Co$_3$O$_4$/rGO at the potential of -0.55 V.
Figure 1
Figure 2
Figure 3