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

Abstract

Highly uniform Co₃O₄ nanorods decorated on reduced graphene oxide (rGO) were prepared by a one-pot hydrothermal procedure. During the hydrothermal process, Co²⁺ ions were crystallized to Co₃O₄ nanorods and simultaneously GO was reduced to rGO to form the Co₃O₄/rGO hybrid. The Co₃O₄/rGO hybrid was characterized by scanning electron micrographs, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. The obtained Co₃O₄/rGO hybrid exhibits excellent electrocatalytic performance for oxygen reduction reaction.

Keywords

co₃o₄, nanorods, electrolyte, reaction, alkaline, decorated, reduced, composite, graphene, reduction, oxide, oxygen

Disciplines

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

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1 **Abstract**

2 Highly uniform Co₃O₄ nanorods decorated on reduced graphene oxide (rGO) were
3 prepared by a one-pot hydrothermal procedure. During the hydrothermal process,
4 Co²⁺ ions were crystallized to Co₃O₄ nanorods and simultaneously GO was reduced to
5 rGO to form the Co₃O₄/rGO hybrid. The Co₃O₄/rGO hybrid was characterized by
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8 electrocatalytic performance for oxygen reduction reaction.

9 **Keywords:** Co₃O₄ nanorods; reduced graphene oxide; oxygen reduction reaction

10

1 **1. Introduction**

2 The cathodic oxygen reduction reaction (ORR) is one of the key challenges in
3 developing alkaline-based fuel cells and metal-air batteries [1]. Recently, transition
4 metal oxides [2-5].as promising cathodic materials, have received considerable
5 attention due to their high catalytic activity, low cost and environmental friendliness.
6 However, these materials also suffer from some disadvantages, such as relatively poor
7 electrical conductivity and lower electron transfer rate, which limited their
8 applications in real devices. It is well known that graphene exhibits notable electronic
9 conductivity and high surface area, which could be an attractive support for metal
10 oxides to form a new class of nanocomposites for ORR. [6-8] Dai's group [9-11]
11 reported a series of nanocomposites consisting of Co_3O_4 , Mn_3O_4 , MnCo_2O_4
12 nanocrystals deposited on rGO templates as excellent catalysts for ORR. However, it
13 is still a challenge to develop a simple facile deposition approach to prepare quality
14 metal oxide/rGO catalysts for ORR with stable performance. To the best of our
15 knowledge, the fabrication of Co_3O_4 nanorods decorated on rGO supports for ORR
16 has not yet been reported.

17 In this work, we report a facile route to prepare a Co_3O_4 nanorods decorated rGO
18 hybrid through a one-pot hydrothermal approach showing an efficient pathway for
19 charge transfer. The as-prepared $\text{Co}_3\text{O}_4/\text{rGO}$ exhibits a significant enhancement in
20 electrocatalytic ORR performance in alkaline media, compared with unsupported
21 Co_3O_4 or pure reduced graphene oxide.

2. Experimental

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

Graphene oxide (GO) was synthesized by the modified Hummers method [12]. The Co_3O_4 modified rGO was synthesized as the following procedures. Firstly, 2 mmol $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and 2 mmol $\text{CO}(\text{NH}_2)_2$ 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 $\text{Co}_3\text{O}_4/\text{rGO}$ powders were achieved via vacuum-dry in a vacuum oven at 60 °C for 5 h. For comparison pure Co_3O_4 powder without rGO and rGO without Co_3O_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, 20mA, Cu $\text{K}\alpha$ radiation) and scanning electron microscopy (SEM, JEOL, JSM6700F). The atomic composition of $\text{Co}_3\text{O}_4/\text{rGO}$ was detected by X-ray photoelectron spectroscopy (XPS, Perkin Elmer, Al $\text{K}\alpha$ 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 $80 \mu\text{g cm}^{-2}$ for all the electrochemical testing.

3. Results and Discussion

The fabrication process is illustrated in Figure 1a. Firstly, Co^{2+} ion was easily coordinated with negatively charged oxygen-containing functional groups on GO sheets. Followed by the hydrothermal process, Co^{2+} was oxidized into Co^{3+} by the oxygen-containing functional groups on the GO surface. The oxidized Co^{3+} and Co^{2+} coprecipitated into Co_3O_4 , the resultant Co_3O_4 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 $\text{Co}_3\text{O}_4/\text{rGO}$ samples as shown in Figure 1b. It has been clearly shown that the Co_3O_4 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)

1 analysis given in Figure 1c indicates the existence of Co, O and C. The atomic ratio
2 of Co to O is 3:4 which is in complete accord with the stoichiometry of Co_3O_4 . Si
3 signal aroused from the Si substrate.

4 XRD was performed to investigate the phase structure of GO, pristine Co_3O_4 and
5 $\text{Co}_3\text{O}_4/\text{rGO}$. The as-synthesized GO displayed a typical characteristic (002) peak at
6 10.1° (Figure 2a). Then after the hydrothermal process, the as-prepared rGO showed a
7 broad (002) peak at 2θ of 24.2° , corresponding to the d-spacing of 0.36 nm, and the
8 strong (002) peak centred at 10.1° disappeared, indicating that GO has been reduced
9 to rGO. [14]. The diffraction peaks of the pristine Co_3O_4 are in good agreement with
10 the standard Co_3O_4 (JCPDS card: 42-1467) [15]. The major diffraction peaks of
11 $\text{Co}_3\text{O}_4/\text{rGO}$ were well indexed with those of Co_3O_4 except for the broad (002) peak at
12 approximately 25° , which can be attributed to disordered stacked graphitic sheets [16].
13 This clearly demonstrates that the original GO has been reduced to rGO during the
14 hydrothermal process. The phases of Co_3O_4 and rGO were further confirmed by
15 Raman spectroscopy. The typical Raman spectra of GO, rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ are
16 shown in Figure 2b, where the peaks of Raman spectrum of $\text{Co}_3\text{O}_4/\text{rGO}$ at 193, 470,
17 $520, 615$ and 680 cm^{-1} , can be attributed to the E_g , F_{2g} and A_{1g} modes of Co_3O_4 [16]. It
18 is noted that GO exhibits a G band at 1606 cm^{-1} , while the corresponding G bands of
19 rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ are 1586 and 1589 cm^{-1} , respectively. The red shifts of G band of
20 rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ can be attributed to the high ability for recovery of the
21 hexagonal network of carbon [17], which is consistent with the decrease of the D/G
22 ratio.

Figure 2c-f shows the XPS survey of the $\text{Co}_3\text{O}_4/\text{rGO}$. 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 $\text{Co}2\text{p}_{3/2}$ and $\text{Co}2\text{p}_{1/2}$, respectively, with a spin-energy separation of 17 eV, which is the characteristic of a Co_3O_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 $\text{Co}_3\text{O}_4/\text{rGO}$ (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 $\text{Co}_3\text{O}_4/\text{rGO}$ nanocomposite toward ORR, linear sweeping voltammetry (LSV) was investigated in a 0.1M KOH. As shown in Figure 3a, independent Co_3O_4 or rGO exhibited relatively poor ORR activity, while the $\text{Co}_3\text{O}_4/\text{rGO}$ 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_3O_4 , rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ 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 rang, respectively. Obviously, the

diameter of the semicircle for Co₃O₄/rGO is significantly smaller than that of Co₃O₄ and almost similar to that of rGO. This indicates that rGO supporting materials significantly enhance the electron transfer in Co₃O₄/rGO, which could promote the catalytic ORR much easier and more efficiently than Co₃O₄ without rGO supports.

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

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

where ω 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} cm² s⁻¹), ν 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 Co₃O₄/rGO favors a 4 electron oxygen reduction process. In other words, O₂ 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 H₂O₂ yields for Co₃O₄/rGO catalyst are below 25% over the potential range of -0.3 to -0.6V, suggesting the high efficiency of the ORR on Co₃O₄/rGO [21]. Furthermore, the chronoamperometric curves for catalytic ORR were recorded to study the durability of the Co₃O₄/rGO at -0.55 V. The Co₃O₄/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 Co₃O₄/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 Co₃O₄ to rGO, it demonstrated that the best catalytic performance was achieved from Co₃O₄/rGO with a mass ratio of 2.6.

4. Conclusion

Heterogeneous Co₃O₄/rGO was synthesized by a simple one pot hydrothermal method. This method leads to a uniform distribution of Co₃O₄ nanorods on rGO sheets. The Co₃O₄/rGO hybrid exhibits higher catalytic activity and durability for ORR than the unsupported Co₃O₄, which present this material an efficient, low cost cathodic catalyst for alkaline-based fuel cells and metal-air batteries.

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Figures captions

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

Figure 2. (a) XRD patterns of GO, rGO, Co_3O_4 and $\text{Co}_3\text{O}_4/\text{rGO}$. (b) Raman spectra of GO, rGO and $\text{Co}_3\text{O}_4/\text{rGO}$. (c) XPS survey spectra of $\text{Co}_3\text{O}_4/\text{rGO}$. (d) $\text{Co}2\text{p}$ XPS of $\text{Co}_3\text{O}_4/\text{rGO}$ (insert: $\text{O}1\text{s}$), (e, f) $\text{C}1\text{s}$ XPS for GO and $\text{Co}_3\text{O}_4/\text{rGO}$.

Figure 3. (a) LSV curves of Co_3O_4 , rGO, $\text{Co}_3\text{O}_4/\text{rGO}$ and Pt/C in 0.1 M KOH O_2 saturated solution with rotation speed at 400 rpm (dashed line: LSV curve of $\text{Co}_3\text{O}_4/\text{rGO}$ in 0.1 M KOH N_2 saturated solution). (b) Nyquist plots of Co_3O_4 , rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ at open potential. (c) LSV curves for $\text{Co}_3\text{O}_4/\text{rGO}$ 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_3O_4 , rGO and $\text{Co}_3\text{O}_4/\text{rGO}$ at the potential of -0.55 V.

Figure 1

Figure 2

Figure 3