Cobalt nanoparticle decorated graphene aerogel for efficient oxygen reduction reaction electrocatalysis

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ABSTRACT

Transition metals have attracted particular research interest for sustainable ORR electrocatalysis but zero-valent ones have been often ignored. In this work metallic cobalt nanoparticle decorated graphene aerogel (CoNPs/rGO aerogel) was synthesized via a facile hydrothermal reaction, followed by thermal annealing in reducing H_2 atmosphere. As-prepared CoNPs/rGO aerogel demonstrates commercial Pt/C-comparable ORR activity through a predominant four-electron pathway, as well as excellent durability and methanol tolerance superior to Pt/C in alkaline medium. This work suggests that metallic cobalt nanoparticle is highly efficient to boost the ORR activity of neighboring carbon besides various cobalt compounds.

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Introduction

Electrochemical oxygen reduction reaction (ORR) is the bottleneck step controlling the ultimate performance of various energy conversion and storage devices such as low-temperature fuel cells and metal—air batteries [1,2]. This kinetically sluggish cathodic half-reaction results in high over-potential and efficiency loss of the energy devices. Pt is the most active ORR catalyst, but its high cost, limited resource and poor durability hinder its wide commercial applications [3,4]. Many efforts have been devoted to exploring sustainable ORR catalysts to replace precious Pt-based electrocatalysts. In this regard, non-precious metal and metal-free ORR electrocatalysts have been the focus of extensive research for several decades [5—13].

Transition metals (Fe, Mn, and Co) have attracted particular interest since the pioneer work by R. Jasinski [14]. Inspired by this work, various transition metal species including oxides, chelate compounds, chalcogenides, carbide, nitride, oxynitride, and oxyhydroxides were synthesized and loaded on supporting carbon such as graphene nanosheets for ORR electrocatalysis [15—23]. Although the exact mechanism by which the metal species boosts the ORR activity of neighboring carbons still remains as an open question, recent studies reveal that there is a charge transfer process across the graphene-metal interface, depending on the graphene-metal spacing and the Fermi level difference between the graphene and metal [24]. Such a process changes the work function and electronic structure of the carbon atoms and is believed to be responsible to the enhanced ORR activity observed on graphene-supported transition metal species, as

demonstrated by the impressive ORR activity of graphene-Co_3O_4, graphene-Fe_3O_4, graphene-$MnCo_2O_4$, etc., [19,25−30].

Compared to oxides, carbide, nitride, oxynitride, and oxy-hydroxides, etc., zero-valent transition metal has been often ignored for ORR catalysis. In very limited literature, zero-valent transition metal nanoparticles are encapsulated by graphitic layer [31−37]. At the same time, nitrogen-doped carbon was generally used to support/encapsulate those metallic nanoparticles as it is believed the N atom offers better coordination to the metal than C atom, and in turn better ORR activity [31−36,38]. The interfacial charge transfer between metal and N-doped carbon may lead to improvement of the catalytic performance of transition metal on N-doped carbon [39]. Interestingly, a recent work unveils that the N-metal coordination is not necessary for high ORR activity [40].

Herein, we report a highly efficient ORR catalyst consisting of metallic Co nanoparticles grown on graphene hydrogel. It is synthesized via a simple hydrothermal reaction and subsequent thermal annealing in reducing H_2 atmosphere. Electrochemical evaluation exhibits that as-prepared cobalt nanoparticle decorated reduced graphene (CoNPs/rGO) aerogel displays high limiting current density, excellent methanol tolerant ability and long-term durability superior to that of commercial Pt/C catalysts in alkaline medium. Both the half-wave potential and four-electron reduction selectivity are very close to that of Pt/C. Present work suggests that zero-valent cobalt is also highly efficient to boost the ORR activity of neighboring carbon even though there is no nitrogen dopant in the carbon.

Experimental

Synthesis of GO

All chemicals were of analytical grade and used without further purification. GO was synthesized by using the Hummers method with minor modification [6]. Briefly, 1 g of graphite and 0.6 g of $NaNO_3$ were added into a 250 mL flask containing 35 mL of concentrated H_2SO_4. The mixture magnetically stirred for 0.5 h in an ice bath and followed by an ultrasonic bath for 15 min. 4.5 g of $KMnO_4$ was added slowly into the flask with vigorous stirring. After stirring overnight at room temperature, 36 mL of deionized (DI) water was slowly added in the flask and was further stirred at 50 °C for 12 h and 35 °C for 12 h. After that 12 mL of 30 wt% H_2O_2 was added to the mixture and stirred for another 3 h at 35 °C. GO suspension was obtained by ultrasonication after washing the mixture several times with 5 wt% HCl and DI water.

Synthesis of graphene hydrogel and CoNPs/rGO aerogel

In a typical synthesis of graphene hydrogel, 30 mL of GO suspension (3.0 mg mL^{-1}) was placed in a 100 mL beaker for 30 min ultrasonic in an ice bath, then 450 mg ascorbic acid was added with vigorous magnetic stirring to obtain reduced GO (denoted as rGO for comparison) [41]. The mixture was transferred to a 50 mL autoclave, and placed in an electric oven at 180 °C for 12 h. After that, the product (rGO hydrogel) was dried at 60 °C and transferred to another 50 mL autoclave,

to which a cobalt solution preparing by dissolving 582 mg of $Co(NO_3)_2 \cdot 6H_2O$ into 8 mL H_2O and 40 mL ammonium hydroxide was added to drown the hydrogel. The autoclave was sealed and heated at 90 °C for 12 h to form $Co(OH)_x/rGO$ as precursor of CoNPs/rGO. The $Co(OH)_x/rGO$ was freezing-dried, and then heated at 800 °C in H_2 atmosphere to obtain CoNPs/rGO aerogel. The temperature is increased at 5 °C min^{-1} to 800 °C and maintained at 800 °C for 1 h.

Electrochemical measurements

Linear sweep voltammetry (LSV) measurements were carried out with an Autolab potentiostat (PGSTAT302N) system coupled with a Pine rotator (AFMS-LXF). A Hg/HgO electrode and a Pt foil were employed as the reference electrode and the counter electrode, respectively. Freshly prepared 0.1 M KOH solution was used as the electrolyte, which was bubbled with O_2 or N_2 for at least 15 min prior to each experiment. The working electrode was prepared by casting as-prepared catalyst onto the disk electrode of a platinum-glassy carbon rotating ring disk electrode (RRDE) (disk diameter: 5.61 mm; inner diameter of ring 6.25 mm; outer diameter 7.92 mm, from Pine Research Instrumentation). In details, 2.0 mg of catalyst was dispersed in 1.0 mL of ethanol and 50 μL Nafion (5 wt% in isopropanol, Aldrich) to form a slurry with the assistance of sonication. 25 μL of the catalyst slurry was loaded onto the disk electrode and natural drying.

For cyclic voltammetry (CV) experiment, the working electrode was change to a glassy carbon electrode (3 mm diameter), on which the catalyst was loaded by casting 7 μL of the catalyst slurry.

Characterizations

Scanning electron microscopy (SEM) images were performed on a JSM-6510LV (JEOL, Tokyo Japan). X-ray diffraction (XRD) patterns were collected using a powder X-ray diffractometer (RIGAK, D/MAX 2550 VB/PC, Japan). Transmission electron microscopy (TEM) characterization was carried out on a JEM-2100 TEM system (JEOL, Tokyo Japan) at an acceleration voltage of 200 kV. X-ray photoelectron spectrum (XPS) characterization was performed on an ESCALAB 250Xi system from Thermo Fisher.

Results and discussion

The synthetic procedure of CoNPs/rGO aerogel was schematically illustrated in Fig. 1. Reduced graphene oxide (rGO) hydrogel was first prepared by self-assembling GO through a hydrothermal reaction in the presence of ascorbic acid [41]. Subsequently, Co(II) ions were mixed with rGO hydrogel to coordinate and/or adsorb on the surface of rGO owing to the presence of the oxygen-containing groups in the rGO hydrogel, which shows high affinity towards transition metal ions [24]. Upon the changing of the solution pH and/or temperature, the pre-coordinated or adsorbed Co(II) ions was hydrolyzed to form oxyhydroxide or oxide nanoparticles on rGO