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Enhanced electrocatalytic performance of NiO_x@MnO_x@graphene for oxygen reduction and evolution reactions

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ABSTRACT

Oxygen electrodes for oxygen evolution reaction and oxygen reduction reaction were intensively investigated due to high overpotential required to drive the four-electron process. A NiO_x@MnO_x@G nanostructure supported homogeneously on graphene nano-sheets through an easy and scalable self-assembly method was studied. The NiO_x@MnO_x@G exhibited a nanostructured NiO_x nanocrystalline with size around 2.3 nm and an amorphous MnO_x with controllable thickness. The 25% NiO_x@MnO_x@G showed remarkable activity for oxygen reduction reaction with a 4-electron process, the half-wave potential was 50 mV, but the stability of 25% NiO_x@MnO_x@G was better than Pt/C-JM. NiO_x@MnO_x@G nanostructure exhibited significantly better activity for oxygen evolution reaction compared with MnO_x, which can demonstrate that NiO_x could tune the activity of surface amorphous MnO_x and dramatically increased oxygen evolution reaction activity. NiO_x@MnO_x@G is demonstrated with superior oxygen catalysts performance for reversible oxygen evolution and oxygen reduction reaction, due to the synergistic effect of NiO_x and amorphous MnO_x.

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Introduction

Oxygen electrochemistry that includes oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is playing an important role in energy conversion and storage equipment, such as reversible fuel cells and metal-air batteries. One of the key issues is to prepare efficient and stable electro-catalysts for ORR and OER due to their high overpotential generating

from the four-electron process. At present, ORR and OER are dependent on precious metals such as Pt, Ru as well as Ir, such as RuO₂/IrO₂ for OER [1] and Pt₃Ni(111) for ORR [2]. Unfortunately, their practical applications are constrained by the expensive price, low availability and poor stability of these precious metals [3–5].

Developing bifunctional catalysts for OER and ORR based on earth-abundant materials are attracting increasing interests worldwide. Non-precious metal oxides such as

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manganese-cobalt oxide nanofibers [6], spinel-type lithium cobalt oxides [7], nanocrystalline $M_xMn_{3-x}O_4$ (M is divalent metals) spinel [8,9], perovskite oxides [10–12], have been developed as OER and ORR bifunctional electrocatalysts. Chemically delithiated lithium cobalt oxide synthesized at 400 °C displayed high activity both for ORR and OER [7]. H.J. Dai group fabricated a Co_3O_4/N -graphene composite that exhibited similar ORR activity but it showed more excellent stability than Pt under alkaline solution and higher activity for OER [13]. Indra et al. reported a solvothermal method to synthesize amorphous and crystalline cobalt iron oxides, amorphous cobalt iron oxide exhibited better catalytic activity than crystalline cobalt iron oxide under photochemical and electrochemical water oxidation conditions [14]. L.M. Dai group developed a nitrogen and phosphorus co-doped mesoporous carbon foam with large surface area through pyrolysis of polyaniline aerogel prepared in the presence of phytic acid, and demonstrated composites exhibited large surface area and good electro-catalytic properties [15].

Among various 3d-metal-based catalysts, manganese oxides are regarded as best non-noble metal catalysts of ORR [16–19], and nickel (Ni) and cobalt (Co) oxides have been demonstrated among the best for OER [20]. Ma and Wang reported α - MnO_2 - $LaNiO_3$ -carbon nanotube (CNT) bifunctional electro-catalysts composites that were prepared by mixing α - MnO_2 nanorods with $LaNiO_3$ nanoparticles and CNTs to improve ORR and OER activity [21]. $MnCo_2O_4$ spinel prepared by sol-gel process followed by calcinations at high temperature exhibited promising activity for OER and ORR [22]. Manganese-cobalt oxide nanofibers prepared by electrospinning method exhibited high catalytic activity for OER and ORR under alkaline condition [6]. Despite intensive focus on developing oxygen electrocatalysts, the overpotential for reversible OER and ORR was still so high that it is significant to develop high active and durable oxygen electrocatalysts using earth-abundant elements. There are also several methods (sol-gel combustion and sonochemical synthesis) to prepare nano materials that have been reported in different literatures [23–30].

Transition metal (Co, Mn, Fe, Cu, etc.) oxides with mixed valences are reportedly able to serve as donor–acceptor chemisorption sites for the reversible adsorption of oxygen and hence have the potential to replace noble metal based electrocatalysts. However, metal oxides, which are poorly conductive, frequently suffer from dissolution and aggregation during the electrochemical reaction. A suitable strategy for overcoming the above-mentioned problems is to anchor these transition metal oxides onto graphene. Graphene-based transition metal oxide electrocatalysts thus showed remarkable improvements in electrochemical activity, durability and dispersion [31–33]. Here, we developed a $NiO_x@MnO_x$ nanostructure supported on graphene ($NiO_x@MnO_x@G$) using a simple and green self-assembly method, and $NiO_x@MnO_x@G$ exhibited a fine nanocrystalline NiO_x and an amorphous MnO_x homogeneously supported on graphene nanosheets. This structure can meet the advantages of both Mn and Ni by controlling the thickness of amorphous MnO_x , showing bifunctional properties for reversible OER and ORR with remarkable activity and durability due to the synergistic effect compared to their

individual components and even noble Pt/C, Ir black and Pt/C: Ir black (1:1) mixture catalysts.

Experimental

Raw chemicals

As-received graphene ordered from USA (1.6 nm Flakes) was purified that had been mentioned below [34]: 60 mg graphene was immersed in 60 mL 30 wt% HCl before ultrasonication about 1 h. Slurry was dispersed in 50 mL 30 wt% HCl, which was stirred overnight, and then was centrifuged and washed by distilled water for three times. HNO_3 (65%, Fluka), KOH, C_2H_5OH , $C_{10}H_{14}NiO_4$, $KMnO_4$, $C_2H_6O_2$ (EG), C_2H_5OH , and nafion solution (5 wt% in isopropanol as well as distilled water), poly(ethyleneimine) (PEI, MW = 1300) were all purchased from Sigma-Aldrich directly used.

Preparation of $NiO_x@MnO_x$ supported on graphene

Preparation of NiO_x

As previously reported, graphene was functionalized by PEI [35–37]: simply, 60 mg graphene was ultrasonicated in ultrapure water in 0.5 wt% PEI for 2 h, and slurry was mixed for 24 h before filtration, which was washed to exclude PEI. Received solids were dried in oven for 24 h around 80 °C. Products were named as PEI-G.

50 mg PEI-G was ultrasonicated in 100 mL EG for 1 h before adding certain amount of $C_{10}H_{14}NiO_4$ (the loadings were controlled at 25 wt% based on NiO). The dispersion was sonicated for 30 min and then was stirred for 1 h before putting inside microwave oven (1000 W) around 4 min. The dispersion was stirred overnight. The solution was then filtered and washed. As-received catalysts were named as NiO_x .

Preparation of $NiO_x@MnO_x@G$

15 mg NiO_x was ultrasonicated in 40 mL ultrapure water for 30 min before adding approximate amount of $KMnO_4$ solution (1 mg/mL), and the loadings were controlled as 5 wt %, 10 wt % and 25 wt % based on MnO_2 . The slurry was stirred for 30 min before adding 40 mL ethanol. Then mixtures were refluxed around 100 °C for 2 h. Solution was filtered by membrane (0.2 μm), which was washed by ethanol. Prepared materials were noted as $NiO_x@MnO_x@Graphene$, which can be abbreviated as $NiO_x@MnO_x@G$. For comparison, the MnO_x supported on PEI/G were prepared following the same method.

Catalysts characterizations

Thermo gravimetric technique was used to study loadings for NiO_x as well as $NiO_x@MnO_x@G$ in air flow from 100 °C to 800 °C. Powder was identified by X-ray diffractometer (XRD, Bruker D8 Advances) that was operated with Cu K α ($\lambda = 1.5406$ Å) between 20° and 90°. X-ray photoelectron spectroscopy (XPS) was tested by ESCALAB 250Xi instrument from Thermo Fisher. The XPS spectra were referenced by C 1s of substrates with 284.5 eV binding energy. STEM as well as elemental mapping (Titan G2 60–300, FEI) was used to test the distribution of NiO_x as well as $NiO_x@MnO_x@G$.

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