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$NiCo_2O_4$ spinel/ordered mesoporous carbons as noble-metal free electrocatalysts for oxygen reduction reaction and the influence of structure of catalyst support on the electrochemical activity of $NiCo_2O_4$

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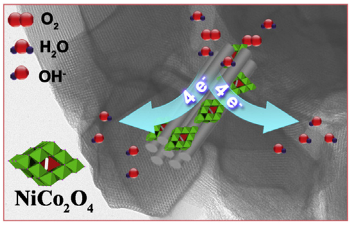
HIGHLIGHTS

- High electrical conductivity of $NiCo_2O_4$ supported on ordered mesoporous carbons.
- Increase of electrocatalytic activity of $NiCo_2O_4$ by ordered mesoporous carbons.
- Dependence of activity of $NiCo_2O_4$ on structure of carbon support.

GRAPHICAL ABSTRACT



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ABSTRACT

Three ordered mesoporous carbons (OMCs) with different structures are used as catalyst supports for growth of $NiCo_2O_4$ spinel. The high surface area of OMCs provides more active sites to adsorb metal precursors. The porous structure confines the growth of $NiCo_2O_4$ and supplies more efficient transport passage for reactant molecules to access the active sites. Due to the structural characteristics of OMCs and catalytic properties of $NiCo_2O_4$, $NiCo_2O_4$/OMCs composites are highly active, cheap, and selective noble metal-free electrocatalysts for the oxygen reduction reaction (ORR) in alkaline solution. The electrochemical activity of $NiCo_2O_4$ supported on three OMCs with different structures, surface areas, pore sizes, pore volumes, and defective sites is studied. $NiCo_2O_4$/OMCs composites may be further used as efficient and inexpensive noble metal-free ORR catalysts in alkaline solution.

1. Introduction

The oxygen reduction reaction (ORR) at the cathode is an important reaction in energy converting systems such as fuel cells. In proton exchange membrane (PEM) fuel cells, the ORR kinetics are very slow at the cathode. In order to accelerate the ORR kinetics to reach a practical usable level in a fuel cell, a cathodic ORR catalyst is needed. Generally, the ORR activity is effectively promoted by Pt-based electrocatalysts, which can generate high cathodic current densities. However, the rarity and high cost of Pt catalysts hinders the large-scale commercialization of fuel cells. In addition, the poor durability of Pt-based catalysts is another key challenge to widespread application. The loss of electrochemical surface area of Pt electrocatalysts contributes to the instability of Pt-based catalysts and thus a decrease of catalytic activity in the overall fuel cells. With the aim of accelerating the application of fuel cells and

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alleviate the cost, extensive research over the past several decades has focused on developing alternative non-precious metal catalysts [1,2]. These electrocatalysts include heteroatoms-doped carbon materials [3,4], transition metal macrocyclic compounds [5], transition metal oxides [6], transition metal chalcogenides [7], and transition metal carbides [8]. In order to increase the activity and durability of transition metal-based catalysts, carbon nanomaterials, such as carbon black [5,9], carbon nanotubes [10,11] and graphene [12], are widely used as supports for dispersion of transition metal-based catalysts. Although much progress has been achieved by using graphene as a catalyst support, the irreversible aggregation of graphene layers and low surface area of graphene limit the performance of supported catalysts. Due to the irreversible agglomeration, catalysts supported on graphene layers are easily sandwiched between aggregated graphene sheets or secluded inside the stacked layers and therefore not available for ORR catalysis. As for carbon nanotubes and carbon black, the catalysts supported on their external surface easily peel off from the surface of carbon nanotubes or carbon black due to the low interaction between the catalysts and carbon supports. So, dispersion of ORR catalysts on carbon materials with high surface area and porous structure is an effective way to increase the ORR activity of catalysts.

Ordered mesoporous carbons (OMCs), different from carbon nanotubes and graphene, not only retain good electronic characteristics and chemical stability, but also show many unique properties, such as ordered porous structure, narrow pore size distribution, and high surface area [13]. The ordered porous structure provides a favorable path for mass transport, while the high surface area and a large number of mesopores of OMCs facilitate the accommodation of catalysts. OMCs doped with nitrogen [14–17], boron [18], sulfur [19], and phosphorus [20] have been used as high-performance catalysts for ORR with long-term stability and high tolerance to methanol. Due to a synergetic effect arising from nitrogen and sulfur co-doping, the sulfur and nitrogen co-doped OMCs showed a superb ORR performance without crossover effect and with a high catalytic activity in alkaline medium [21]. To increase the activity of nitrogen-doped OMCs, some researchers have investigated the addition of transition metal (Fe or Co) into nitrogen-doped OMCs, and a significantly enhanced performance has been obtained [22,23]. These novel OMCs-based ORR catalysts showed high activity for ORR process. The general methods for preparation of heteroatoms-doped carbon involve treatment of carbon with ammonia gas [24], hydrogen sulfide [25], halogen gas [26] or using heteroatom-containing organic compound as precursors during pyrolysis [15,16,20,21,27]. However, due to the evaporation of organic compounds at high temperatures under a flowing atmosphere of inert gas, the toxic nitrogen-containing gas, produced by the decomposition of organic compounds, is emitted into atmosphere and is harmful to environment and human health. Therefore, it is very important to find an environment-friendly method for preparation of OMCs-based noble metal-free catalysts for ORR without the use of toxic heteroatom-containing organic compounds or toxic gases.

The spinel is a class of minerals of general formulation AB_2O_4. The spinel has been widely used in supercapacitors [28], lithium-ion batteries [29] and electrocatalysts [30]. As noble metal-free ORR catalysts, the spinel exhibited good ORR performance with better fuel crossover resistance and long-term durability in alkaline medium [9,11,30,31]. The spinel is attractive candidate for low cost, earth-abundant electrocatalysts for ORR catalysis. However, owing to their insulating nature, their widespread application and activity has been limited. Carbon materials, with high electrical conductivity, were used as catalyst to supplement the insufficient conductivity of spinel. The combination of spinel and nanostructured carbon materials leads to the formation of composites that can take full advantages of each kind of material and increase the ORR activity of spinel [10,11,32–36]. Herein, $NiCo_2O_4$ was selected as a model spinel to investigate its ORR activity and the effect of structure of carbon supports on ORR activity. Three OMCs (FDU-15, CMK-8, and CMK-3) with different structural parameters were selected as catalyst supports for growth of $NiCo_2O_4$ spinel. As mentioned above, the electrochemical performance of spinel is seriously hindered by its low conductivity. The spinel and OMCs exhibit different physical and chemical properties, which are complementary to each other. Therefore, the combination of spinel and OMCs into hierarchical structure is a promising method to integrate their distinguishing properties together. The accumulation of nickel in the environment may represent a serious hazard to human health [37]. However, compared with heteroatom-containing compounds, for preparation of ORR catalysts, the toxicity of nickel is lower. So, the synthesis of the $NiCo_2O_4$/OMCs is a relatively economical method with little gas emission and little environmental harmfulness in terms of environmental implications. The electrochemical activity of $NiCo_2O_4$ supported on three OMCs with different structures, surface areas, pore volumes, pore sizes, and defective sites was studied. Although ordered mesoporous $NiCo_2O_4$ prepared by using ordered mesoporous SiO_2 as template have been applied as active catalysts for the ORR [38], our methodology is special because: (1) The high electrical conductivity of OMCs can effectively supplement the insufficient conductivity of $NiCo_2O_4$ spinel and increase the ORR activity; (2) The mesopores of OMCs act as confined space, greatly restricting the growth of $NiCo_2O_4$ spinel. Compared with $NiCo_2O_4$ and OMCs, $NiCo_2O_4$/OMCs catalysts show high electrochemical performance for ORR in alkaline solution.

2. Experimental

2.1. Materials

20 wt.% Pt/C commercial electrocatalysts were purchased from Johnson Matthey. Nafion (5 wt.%) was purchased from Sigma–Aldrich. $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and hexamethylenetetramine were purchased from Aladdin Reagent Company.

2.2. Preparation of OMCs and $NiCo_2O_4$/OMCs

Three OMCs (CMK-3, CMK-8, and FDU-15) were synthesized according to literature [39–41]. 1 g of mesoporous silica SBA-15 was added to 5 mL of water containing 1.25 g of sucrose and 0.14 g of H_2SO_4. The mixture was placed in a drying oven at 100 °C and 160 °C for 6 h, respectively. The impregnation of 0.8 g sucrose and 0.09 g of H_2SO_4 and the drying procedure were repeated. The product was pyrolyzed in flowing nitrogen at a temperature of 900 °C. CMK-3 was obtained after the removal of SBA-15 with 5 wt.% hydrofluoric acid at room temperature. The preparation of CMK-8 is same as CMK-3 using KIT-6 as silica template. FDU-15 was prepared using triblock copolymer F127 as soft template. 1.0 g of F127 was dissolved in 20.0 g of ethanol. Then, 5.0 g of 20 wt.% resol in ethanol was added into the mixture. After stirring for 10 min, the solution was then poured into a dish to evaporate the ethanol at room temperature. The dish was placed in an oven of 100 °C for 24 h to induce further polymerization. The resol/F127 composites were then pyrolyzed in nitrogen at 350 °C for 2 h at a heating rate of 1 $°C\ min^{-1}$ to remove the F127, and at 5 $°C\ min^{-1}$ to 900 °C for 4 h for further carbonization. For the preparation of $NiCo_2O_4$/OMCs, 50.0 mg of CMK-3 were dispersed in 50 mL of water. Then, 5.0 mg of $Ni(NO_3)_2 \cdot 6H_2O$ and 10.0 mg of $Co(NO_3)_2 \cdot 6H_2O$ were added to the suspension. After ultrasonication for 2 h, and stirring for 6 h at