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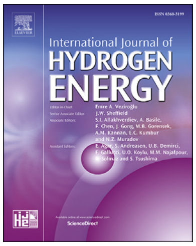

Hierarchical nitrogen-enriched porous carbon materials derived from Schiff-base networks supported $FeCo_2O_4$ nanoparticles for efficient water oxidation

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ABSTRACT

Abundant metal oxides and their composites have attracted great interest in the application of electrochemical energy conversion and storage. In this work, we obtain a hybrid material of $FeCo_2O_4$ nanoparticles anchored on hierarchical nitrogen-enriched porous carbon material (denoted as $FeCo_2O_4$@NPC-450 °C) and study its activity for oxygen evolution reaction (OER). NPC-450 °C is prepared by carbonizing a Schiff-base network (SNW) and SNW is melamine-based material own high nitrogen content and rigid molecular backbone. Compared with $FeCo_2O_4$ and NPC-450 °C, $FeCo_2O_4$@NPC-450 °C hybrid exhibits remarkable OER performance with a small over potential of mere 330 mv at a current density of 10 mA cm^{-2} and a small Tafel slope of 50 mV dec^{-1}. Electrochemical measurements also show that $FeCo_2O_4$@NPC-450 °C present stability for at least 25 h in alkaline solutions. $FeCo_2O_4$@NPC-450 °C shows good performance for OER raises the possibility for cheap and easily prepared catalyst to replace precious metal catalysts.

Introduction

Increasing energy demands and global climate changes have stimulated great concerns about the sustainable energy sources and storage systems [1]. Sustainable energies such as wind and sunlight are comparatively concentrated distribution, so the conversion of sources by water splitting is considered one of the hot research areas of chemistry [2]. However, the sluggish kinetics of oxygen evolution reaction (OER) caused by a complex four-electron oxidation process greatly hinders the large scale production of H_2 fuel from water splitting [3]. Catalysts are critical in the process. To date, commercial OER catalysts still rely on precious metals (e.g., ruthenium and iridium oxides) [4,5]. Large scale industrial application is limited by their high cost. Therefore,

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developing cheap, robust, and efficient OER catalysts are highly and urgent required and have been considered as a huge challenge [6,7].

To alternate these precious and precious-based catalysts, nonprecious metal catalysts have been actively pursued [8–12]. Among them, perovskite metal oxides and first row spinel were widely studied to catalyze OER [13,14]. Many works have been done on a spinel-type structure such as Co_3O_4 [15,16], $NiCo_2O_4$ [17], $NiMn_2O_4$ [18], $CoFe_2O_4$ [19,20], $ZnCo_2O_4$ [21,22], $MnCo_2O_4$ [23], $CuCo_2O_4$ [24], $CaMn_2O_4$ [25] and $MnFe_2O_4$ [26], have been achieved the activity for OER in alkaline media. As we know, the poor electronic conductivity of the spinel oxides hinders the electron transport, therefore carbon materials are usually introduced to the catalyst, $CoFe_2O_4$/graphene [27], $FeCo_2O_4$/graphene [28], Co_3O_4/graphene [29], Co_3O_4/N-graphene [30], Co_2SnO_4/C [31], $MnCo_2O_4$/N-graphene [32], $CoFe_2O_4$/CNTs [33], Mn_3O_4/N-graphene [34], $NiCo_2O_4$/CNTs [35], $NiCo_2O_4$/N-graphene [36], $CoMn_2O_4$/graphene [37] and $CoFe_2O_4$/graphene [27] have been studied to catalyze OER. However, there are few reports about designing of carbon material as conductive support to improve the catalytic performance.

Porous organic polymers have attracted tremendous attention mainly because of highly designable monomers and the synthetic diversity. General methods for the synthesis often use nitrogen related precursors like pyrrole [38], aniline [39], salon [40], and acrylonitrile [41]. Among those available molecular monomer, triazines, especially melamines (MA) [42,43], 66% N by mass, is a good candidate to be employed in the areas of N-rich materials as raw material. Surprisingly, a new catalyst-free method toward the synthesis of high performance porous polymer networks by condensation of MA with terephthalaldehyde in dimethyl sulfoxide (DMSO) has been reported. Such a Schiff-base network (SNW) material has many advantages over conventional nitrogen-rich precursors due to its rigid molecular backbone and high nitrogen content, and it does not need expensive transition-metal catalysts for preparation [44].

In this paper, we show that $FeCo_2O_4$ grown on nitrogen-enriched porous carbon (NPC-450 °C) exhibits good performance on OER in alkaline solutions. $FeCo_2O_4$@NPC-450 °C hybrid is synthesized in solution by a general three-step method. (i) We use MA and terephthalaldehyde to obtain SNW under mild conditions. (ii) The SNW is carbonized under a nitrogen flow to prepare nitrogen-enriched porous carbon (NPC-450 °C). (iii) A novel and simple method used to prepare monodisperse $FeCo_2O_4$ NPs on NPC ($FeCo_2O_4$@NPC-450 °C). The synthesis of the procedure is illustrated in Scheme 1. The as-synthesized $FeCo_2O_4$@NPC-450 °C demonstrates enhanced electro catalytic activity towards OER with long-term stability in alkaline solution. The covalent coupling between $FeCo_2O_4$ and NPC-450 °C in $FeCo_2O_4$@NPC-450 °C hybrid renders an efficient electronic conduction, which benefit the reaction kinetics of OER and the utilization of $FeCo_2O_4$. Besides, the coupling between $FeCo_2O_4$ and NPC-450 °C in $FeCo_2O_4$@NPC-450 °C hybrid could prevent the aggregation of $FeCo_2O_4$ nanoparticles, which would further improve the stability of $FeCo_2O_4$ toward OER.

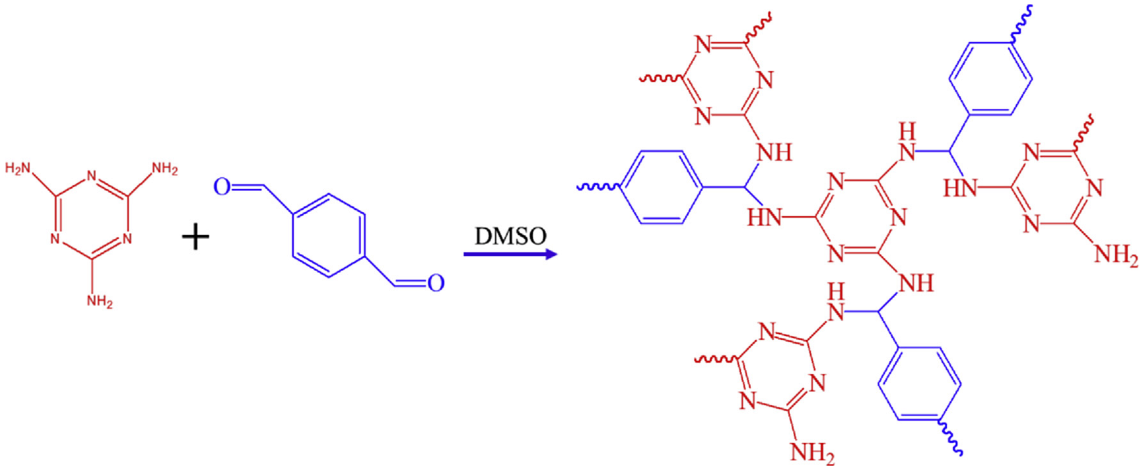
Experimental

Materials

Cobalt (II) nitrate hexahydrate ($CoN_2O_6 \cdot 6H_2O$, ≥99% w/w) and Iron (III) nitrate nonahydrate ($FeN_3O_9 \cdot 9H_2O$, ≥99% w/w) were from Aladdin Corp., melamine, terephthalaldehyde, dimethyl sulfoxide and other chemicals were from Shanghai Chemical Corp. All chemicals were of analytical grade and were used as received without further purification. Deionized water (18.2 MΩ cm) was used in all experiments.

Synthesis of SNW

SNW was prepared as described previously with some modification [45–47]. Melamine (313 mg) and terephthalaldehyde (500 mg) were dissolved in 20 mL dimethyl sulfoxide in a 25 mL glass vial and ultrasonicated for 1 h to form a clear solution. The mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 10 h. The precipitates were collected by a centrifugation and washed repeatedly with acetone, dichloromethane, and deionized water. SNW was vacuum-dried at 60 °C for 24 h. The synthetic route was



Scheme 1 – The synthesis route used to prepare SNW.