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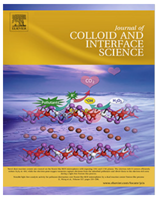

Regular Article

In-situ developed carbon spheres function as promising support for enhanced activity of cobalt oxide in oxygen evolution reaction

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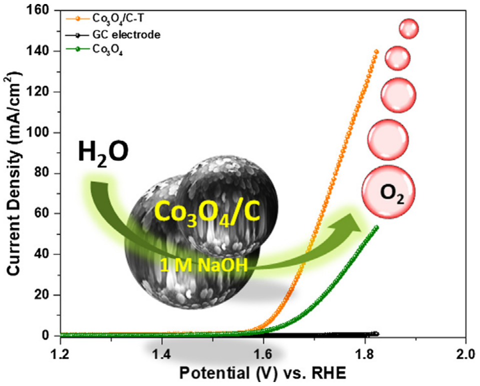
GRAPHICAL ABSTRACT



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ABSTRACT

Highly active, stable electrocatalyst for oxygen evolution reaction (OER) is sincerely required for the practical application of water splitting to get rid from the sluggish reaction kinetics and the stability issue. Here, Co_3O_4 is studied as OER catalyst and to improve the electrocatalytic activity, carbon is chosen as the conducting support. A simple and cost-effective synthetic route is developed for the synthesis of Co_3O_4 on carbon support following hydrothermal route using various hydrolyzing agents. The heterostructure 'Co_3O_4/C' perform well in OER as a non-precious metal catalyst. The best Co_3O_4/C electrocatalyst can generate 10 and 30 mA/cm^2 current densities upon application of 1.623 V and 1.678 V vs. RHE whereas, bare Co_3O_4 can generate current density of 10 and 30 mA/cm^2 upon application of 1.677 and 1.754 V vs. RHE. Carbon in the heterostructure helps to improve the conductivity and at the same time enhances the charge transfer ability which further leads to increase current density and stability to the catalyst. Co_3O_4/C can generate unaltered current density up to 1000 cycles.

1. Introduction

Continuous and uprising demand for energy inspired to develop an efficient process to generate fuel from renewable sources of energy. Water splitting reaction is an economical and promising process to generate highly pure hydrogen [1]. Electrocatalytic water splitting is considered as greener approach compared to other process like coal gasification, partial oxidation etc., because it does not emit any pollutant to environment [2]. Water splitting reaction composed of two half reactions. Hydrogen evolution reaction occurs in cathode. Pt and Pt-based compounds are considered as the best and efficient electrocatalysts for hydrogen evolution reaction [3,4]. On the other hand, in anode oxygen evolution reaction (OER) takes place and the kinetics of OER reaction is sluggish with

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large over potential. RuO_2 and IrO_2 have established themselves as efficient electrocatalysts in OER reaction [5,6]. However, availability, cost, and stability of RuO_2 and IrO_2 electrocatalysts restrict them for their practical applications. So, it is highly demanding to introduce an efficient and stable OER catalyst for the improvement of water splitting efficiency. Considerable attention has already been devoted for the development of efficient electrocatalyst as alternative of RuO_2, IrO_2 for OER with high durability.

A large number of catalysts are already discovered which include metal, metal and carbon based materials [7]. Oxides, alloys, hydroxides, layer double hydroxides, sulfides, selenides, phosphides of Fe, Co, Ni and Mo have already established themselves as efficient catalysts for OER [8–18]. Scientists are dedicatedly trying to improve the catalytic activity of these developed materials. To improve the electrocatalytic activity, doping with hetero atom is also an important approach [19–21]. Different carbon based materials like graphene, CNT, conductive carbon is also developed to function as a support for the synthesis of a wide variety of metal based materials [22–25]. In the last few years it is observed that CoO_x received a potential consideration in OER due to the presence of mixed valence state ($Co^{2+/3+/4+}$) [7,26,27]. Co_3O_4 undergoes phase transformation in the OER condition to generate hydroxides and oxy-hydroxides which play a crucial role. Chen et al., have reported activity of Co_3O_4 largely dependent on the crystal structure and they have synthesized single crystal Co_3O_4 nanocube underlay with a CoO layer which exhibits stable, continuous OER for 1000 h. In situ generated oxyhydroxide layer protects the underlying electrocatalyst [28]. The role of oxygen vacancy in the catalytic activity has been discussed by Xu et al. Following plasma engraving strategy Co_3O_4 was synthesized with high surface area, more oxygen vacancy, and certainly more amount of Co^{2+}. Specific activity of this plasma engraved Co_3O_4 is 10 times higher than that of pristine Co_3O_4 [29]. Activity of Co_3O_4 is largely dependent on the surface area, morphology, oxidation state and also on active charge transportation. Wang et al., discussed that Co_3O_4 nanowire helps in higher charge transportation leads to enhanced electrocatalytic activity towards OER [30]. Therefore, charge transportation is an important parameter to regulate the electrocatalytic activity.

Different carbon based materials like graphene, graphene oxide, CNT, C_3N_4, carbon are getting used as conducting supporting material to develop efficient and stable electrocatalyst. Pan et al., have reported that Mo_2C stabilized by a carbon layer on reduced graphene oxide shows improved electrocatalytic activity towards HER reaction due to the close contact of Mo_2C and graphene and the presence of carbon layer on Mo_2C [31]. Yu et al., have synthesized carbon coated porous NiP, where the amorphous carbon improves conductivity by enhancing the charge transfer ability [32]. Yang et al., have generated an amorphous layer of carbon on Co_3O_4 at the time of synthesis on carbon cloth. In situ formed carbon layer helps to enhance the stability in OER catalysis. It can work up to 86.8 h at a constant current density of 100 mA/cm^2 [33]. Zhang et al., reported the efficient electrocatalytic activity of Co_3O_4 particles on highly conductive heteroatom doped carbon support. The heterojunction of Co_3O_4 and carbon support facilitates the electron transfer by avoiding the charge accumulation on Co_3O_4 particles [34]. Therefore, literature reports suggest that the electronic conductivity and the structural stability can be improved when the desired materials are anchored on carbon [35]. Singh et al., have observed that when Co_3O_4 is grafted on N-doped graphene it can function as an efficient catalyst for OER reaction. It can generate current density of 10 mA/cm^2 with a very low over potential of ~280 mV [36].

Being inspired from the previous studies, in the present report amorphous carbon supported Co_3O_4 nanoparticles are synthesized following a simple hydrothermal route. Here, Co_3O_4 is synthesized on carbon support, where, the synthesized metal oxide is anchored in a single step. The structural information has been observed from XRD analysis. Raman, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS) analyses have also been performed to know the synthesized materials in detail. In the hydrothermal process, hydrolyzing agent was varied to change size, shape, and morphology of Co_3O_4. Co_3O_4/C can function as an efficient catalyst for OER reaction in alkaline condition. The most efficient Co_3O_4/C can generate 10 mA/cm^2 current density upon application of 1.62 V vs. RHE. From the point of activity and stability, the catalytic efficiency of Co_3O_4/C is comparable with commercial RuO_2. Co_3O_4/C shows a very small Tafel value of 70 mV/decade and unaltered current density up to 1000 cycles.

2. Experimental section

2.1. Synthesis

For the synthesis of Co_3O_4 on carbon support, $CoCl_2·6H_2O$ was used as the precursor of cobalt. Ammonium hydroxide, sodium hydroxide and triethylene amine (TEA) were used as hydrolyzing agent in different sets. Glucose was used as the carbon source. Following a simple hydrothermal technique Co_3O_4 was decorated on C. The overall synthesis procedure is shown in Scheme 1. In the following hydrothermal condition glucose undergoes dehydration to generate 'C'. Controlled hydrothermal reaction was carried out using glucose as the starting material at 180 °C for 16 h and the developed material was washed and collected for characterization.

2.2. Co_3O_4/C in TEA method

First, 1.0 g glucose was dissolved in 20 mL of DI water and to this 5 mL of 0.1 M aqueous solution of $CoCl_2·6H_2O$ was slowly added and stirred for 15 min. Second, 20 mL of TEA was directly added along with 5 mL of DI water and stirred well to get a clear solution. Finally, hydrothermal reaction was carried out at 180 °C for 16 h. After completion of the reaction, it was cooled down and the black product was thoroughly washed with DI water followed by ethanol for five to six times. Product was dried at 60 °C for 10 h in air oven and kept for further characterization and application. Co_3O_4/C synthesized from TEA method was denoted as Co_3O_4/C-T throughout the MS.

2.3. Co_3O_4/C in NaOH method

Similar methodology was followed for the synthesis of Co_3O_4/C only sodium hydroxide was used as hydrolyzing agent instead of TEA. Throughout the MS, Co_3O_4/C synthesized using NaOH as hydrolyzing method was denoted as Co_3O_4/C-N.

2.4. Co_3O_4/C in NH_3 method

For the synthesis of Co_3O_4/C, ammonium hydroxide was used as hydrolyzing agent keeping unchanged the other conditions. Co_3O_4/C synthesized by using NH_3 was denoted as Co_3O_4/C-A. Different amounts of glucose were used in the reaction to vary the amount of 'C' in Co_3O_4/C. 2.0 g, 0.5 g and 1.0 g of glucose were used in three different sets of reaction keeping other parameters unaltered and the samples were denoted as Co_3O_4/C-A-C1, Co_3O_4/C-A-C2 and Co_3O_4/C-A-C3.

2.5. Pristine Co_3O_4 nanostructure

Bare Co_3O_4 was synthesized using the similar hydrothermal procedure with unaltered reaction parameters, except glucose was avoided.