Journal of Power Sources 400 (2018) 232–241

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

$Co_{0.85}Se$ hollow nanospheres anchored on N-doped graphene nanosheets as highly efficient, nonprecious electrocatalyst for hydrogen evolution reaction in both acid and alkaline media

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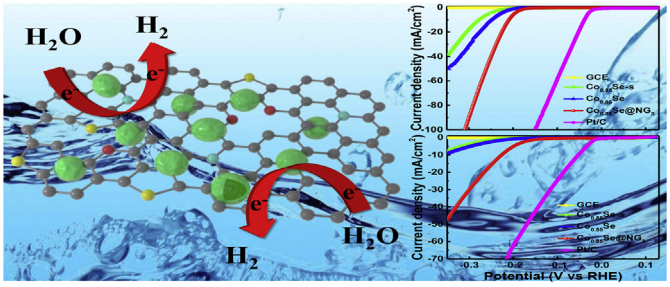
HIGHLIGHTS

- $Co_{0.85}Se$ hollow nanospheres on N-doped graphene (NG) nanosheets are synthesized.
- $Co_{0.85}Se$@NG is synthesized by a facile and cost-effective hydrothermal approach.
- $Co_{0.85}Se$@NG delivers superior HER performance in both acid and alkaline media.
- Excellent HER performance of $Co_{0.85}Se$@NG is due to the unique nanoarchitecture.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
$Co_{0.85}Se$
Hollow nanospheres
Nitrogen-doped graphene
Hydrogen evolution reaction
Electrocatalyst

ABSTRACT

Developing nonprecious electrocatalysts with high efficiency in both acid and alkaline electrolytes is extremely important for realizing scalable water-splitting technology. Herein, for the first time, we present a facile and cost-effective hydrothermal approach to synthesize a novel hybrid electrocatalyst of $Co_{0.85}Se$/nitrogen-doped graphene, where $Co_{0.85}Se$ hollow nanospheres are homogenously anchored on nitrogen-doped reduced graphene oxide nanosheets. This hybrid electrocatalyst delivers outstanding hydrogen evolution reaction performance with very low onset potentials of −159 and −111 mV, low overpotentials of −209 and −227 mV at 10 mA cm^{-2}, and small Tafel slopes of 36.1 and 76.5 mV dec^{-1} in acid and alkaline electrolytes, respectively. Furthermore, it shows superior durability even after 1500 cycles. The excellent electrocatalytic performance of the $Co_{0.85}Se$/nitrogen-doped graphene can be attributed to its well-designed nanoarchitecture. By anchoring $Co_{0.85}Se$ hollow nanospheres on highly conductive graphene nanosheets, the aggregation of $Co_{0.85}Se$ nanospheres is well suppressed, thus increasing the specific surface area and producing abundant exposed active sites. In addition, the charge transfer is greatly facilitated. The remarkable catalytic activity, long-term cycling stability and low-cost synthesis make $Co_{0.85}Se$/nitrogen-doped graphene a desirable non-precious electrocatalyst for hydrogen evolution in both acid and alkaline electrolytes.

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https://doi.org/10.1016/j.jpowsour.2018.08.027
Received 8 June 2018; Received in revised form 1 August 2018; Accepted 9 August 2018
0378-7753/

1. Introduction

With the rapid increase of the severe global energy crisis and environmental contamination as a result of the growing world populations and over-consumption of fossil fuels, it is urgent to search for green, renewable and inexpensive energy to replace conventional energy resources [1–3]. Hydrogen, obtained from electrochemical water splitting, has long been recognized as a promising alternative for energy supply in the future [4–7]. As a pollution-free and high-efficiency method for obtaining hydrogen gas, hydrogen evolution reaction (HER) has received wide attentions [8,9]. As universally known, the conventional catalysts based on noble metals such as Pt possess outstanding HER properties with almost-zero onset potential [10,11]. Moreover, Pt-based catalyst is active in both acid and alkaline media. However, the scarcity and high cost have considerably limited its industrial application [12]. Consequently, development of inexpensive and abundant electrocatalysts with high activity and high stability in both acid and alkaline media is of great importance for industrial application.

Motivated by these challenges, enormous efforts have been devoted and remarkable progress has been made. The inexpensive transition metal compounds, such as phosphides [13–16], carbides [17,18], sulfides [19–21], selenides [22–27] and nitrides [28,29] have been reported to be used as HER electrocatalysts. Among them, cobalt selenides are expected to serve as an ideal candidate for HER due to their intrinsic conductivity and good electrocatalytic activity [30–33]. As a significant part of cobalt selenide family, $Co_{0.85}Se$ shows superior performance for HER because it possesses distinctive electronic configuration, massive unsaturated atoms and high catalytic activity [34–40]. However, the reported catalytic property of $Co_{0.85}Se$ was still lower, compared with the precious Pt-based electrocatalysts, therefore, searching for efficient ways to enhance its HER performance remains necessary.

To date, many approaches have been reported to improve HER properties of catalysts through optimizing their structures, such as hierarchical nanostructure [41,42], hollow microtube [43], hollow spheres [44,45] and nanowires [46]. As generally acknowledged, hollow nanostructure with available interior reaction area and excellent penetrability is generally considered to be important to increase specific surface area and electrocatalytic active sites, and ultimately endows it with much better electrocatalytic performance than solid nanoparticles [43,44,47]. Apart from optimizing the nanostructure of catalysts, various conductive materials such as organic carbon [46,48], reduced graphene oxide [49–51] and carbon nanotubes [52,53] were used as substrate to support electrocatalysts. As an ultrathin two-dimensional material, graphene has been widely employed to grow and support electrocatalysts on account of its superior electric conductivity, large specific surface area as well as outstanding durability [54–56]. In recent years, nitrogen substitutional doping of graphene has been proved to optimize its properties due to the introduction of defect points into a hexagonal carbon lattice and thus modulating the electronic properties [15,57–59]. According to these results, nitrogen-doped graphene (NG) is expected to be used as a support for the synthesis of active materials. However, to our best knowledge, it is still challengeable to synthesize a hybrid of cobalt selenide/carbonaceous nanomaterial, which has rational nanoarchitecture and outstanding HER property in both acid and alkaline electrolytes with a facile approach.

In this work, for the first time, a facile, low-cost one-pot hydrothermal approach is presented to synthesize a hybrid electrocatalyst constructed by $Co_{0.85}Se$ hollow nanospheres homogenously anchored on N-doped graphene nanosheets ($Co_{0.85}Se$@NG). With a combination of unique hollow nanospherical nanoarchitecture, the efficient catalytic activity of $Co_{0.85}Se$ and excellent conductivity of N-doped graphene, $Co_{0.85}Se$@NG shows superior HER activity and remarkable stability in both acid and alkaline conditions.

2. Experimental

2.1. Synthesis of $Co_{0.85}Se$ hollow nanospheres ($Co_{0.85}Se$)

1000 mg of sodium citrate was firstly dissolved into the solution composed of 713 mg of $CoCl_2{\cdot}6H_2O$ and 25 mL of deionized water (DIW). The mixed solution was continuously stirred to form a homogeneous suspension. After this step, 333 mg of SeO_2 and 10 mL of hydrazine hydrate were put into the mixture under stirring. Next, the final black-color mixture was moved into a 50 mL of Teflon-lined autoclave for hydrothermal reaction, which was heated at 180 °C and kept for 15 h in a furnace. After the autoclave cooled down naturally, the acquired powder was washed with absolute ethyl alcohol and DIW for at least three times. The final powder was collected after drying at 60 °C and keeping for 12 h under vacuum. For comparison, $Co_{0.85}Se$ solid nanospheres ($Co_{0.85}Se$-s) catalyst was fabricated by a simple hydrothermal method [60].

2.2. Synthesis of $Co_{0.85}Se$ hollow nanospheres/nitrogen-doped graphene hybrid ($Co_{0.85}Se$@NG)

The graphite oxide (GO) was synthesized from natural graphite powder by Hummers' methods [55]. An appropriate amount of fresh GO powder was dispersed into 25 mL of DIW to form GO aqueous solution. The $Co_{0.85}Se$@NG hybrid was synthesized by the same hydrothermal reaction condition as that for $Co_{0.85}Se$. 25 mL of GO solution was added to the mixture of sodium citrate and $CoCl_2{\cdot}6H_2O$, and all the other steps are the same as the synthesis process of $Co_{0.85}Se$. To optimize the concentration of GO aqueous solution, various GO concentration of 1, 2, 3, 4 and 5 mg mL^{-1} was used for the synthesis of $Co_{0.85}Se$@NG, which are marked as $Co_{0.85}Se@NG_1$, $Co_{0.85}Se@NG_2$, $Co_{0.85}Se@NG_3$, $Co_{0.85}Se@NG_4$ and $Co_{0.85}Se@NG_5$, respectively.

2.3. Materials characterization

The crystalline structures of $Co_{0.85}Se$-s, $Co_{0.85}Se$ and $Co_{0.85}Se@NG_3$ catalysts were investigated by X-ray diffraction (XRD, Rigaku diffractometer, from 10° to 80°). Raman spectroscopy was executed by a Raman microscope (Renishaw) with excitation laser lines of 532 nm. The chemical composition of $Co_{0.85}Se@NG_3$ catalyst was performed by X-ray photoelectron spectroscopy (XPS, Kratos XSAM800 Al Ka radiation). The component ratio of $Co_{0.85}Se@NG_3$ hybrid was determined by thermogravimetric analysis (TA Instruments, TGA-Q50) in the temperature range of 30–800 °C at a heating rate of 10 °C min^{-1} under air atmosphere. In addition, the morphologies and microstructures of the samples were examined by scanning electron microscopy (SEM, JSM 7000F, JEOL), transmission electron microscopy (TEM, Tecnai F20) and high-resolution TEM (HRTEM, Tecnai F20) with an accelerating voltage of 200 kV. The specific surface area and pore-size distribution of as-prepared products were determined by using nitrogen adsorption–desorption isotherms (ASASP2020).

2.4. Measurements of electrocatalytic performance

All the electrochemical performance of as-prepared samples was studied in both acid (0.5 M H_2SO_4) and alkali (1 M KOH) at an electrochemical workstation (CHI660D). In acid electrolyte, a saturated calomel electrode (SCE) and a graphite rod were used as reference electrode and counter electrode, respectively. While in alkaline electrolyte, reference electrode and counter electrode are a Hg/HgO electrode and a platinum (Pt) net, respectively. The glassy carbon electrode (GCE, 3 mm in diam) was used as working electrode. Potentials shown in this paper were all calibrated to reversible hydrogen electrodes (RHE). Therefore, in acid, $E_{RHE} = E_{SCE} + 0.254$ V, while in alkali, $E_{RHE} = E_{(Hg/HgO)} + 0.923$ V. And the potential corresponding to current density of 0.5 mA cm^{-2} was identified as onset potential. For