



Carbon coated nickel - Nickel oxide composites as a highly efficient catalyst for hydrogen evolution reaction in acid medium

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ABSTRACT

Carbon coated nickel - nickel oxide composites (Ni/NiO@C/GR-*t-w*) was synthesized from the direct carbonization of the composites composed of Ni-MOF-74 and graphene oxide (GO). Due to the synergetic effects of Ni, NiO and graphene, Ni/NiO@C/GR-*t-w* all exhibited the electrocatalytic performance to HER in acidic medium. When the GO content was 8% and the carbonization temperature was 900 °C, the composites (Ni/NiO@C/GR-900-8) showed the best electrocatalytic properties with an lower overpotential of 108 mV (vs. RHE) at 10 mA cm⁻², a smaller Tafel slope of 44 mV dec⁻¹ and a good stability in a 0.5 M H₂SO₄ solution. The excellent electrocatalytic performance enabled Ni/NiO@C/GR composites to be a favorable HER catalyst to replace the expensive Pt-based materials in the applications of the hydrogen production.

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1. Introduction

Compared with the traditional energy sources such as petroleum and kerosene, the hydrogen energy has been regarded as an ideal clean energy source because of its efficient, eco-friendly, sustainable and renewable properties [1–5]. Due to the advantages of the wide availability of water resources, the high purity of hydrogen and the feasibility of largescale production, electrochemical water splitting provides a promising method to produce hydrogen via hydrogen evolution reaction (HER). However, the implementation of electrochemical water splitting is impeded by the high HER overpotential, which caused a high energy consumption and low efficiency [6,7]. An effective electrocatalyst is required to reduce the overpotential and expedite the HER reaction. To date, noble metals and their derivatives, especially Pt and Pt-based materials, displayed the excellent electrochemical activity towards HER [8,9]. However, the rarity and high cost restricted the largescale applications of noble metals as HER electrocatalysts.

Therefore, the exploration of a highly efficient electrocatalyst with the inexpensive and abundant non-noble metals is critical for the industrialization of HER.

According to the “volcanic effect” curve, transition metals such as Ni or Co have a high current density and low overpotential due to their unoccupied d orbitals and unpaired d electrons [10,11]. These transition metals and their derivatives have come into prominence as the promising electrocatalysts. In particular, Ni-based materials have attracted an increasing attention with the merits of the extensive source, low price and expected endurance in the working environments [12,13]. Nevertheless, their electrocatalytic activity, such as overpotential and stability, still needs improvement to reach the performance of the noble metal electrocatalysts. In general, there are two strategies to improve the electrochemical properties of the Ni-based materials. One is to enhance the intrinsic electrochemical activity of Ni-based materials by the introduction of other catalytic components such as metal alloy [14], metal oxide or hydroxide [15,16], metal phosphides and chalcogenides [17,18]. The combined catalytic component usually facilitates the adsorption of the H atom or the dissociation of water, which improves the electrocatalytic activity of the composite catalysts. For instance, Xu et al. [19] revealed that Ni/NiO/CoSe₂ composites showed the remarkable electrochemical activity for HER in the acidic solution because of the synergistic effect of Ni cores, NiO shells and CoSe₂

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substrate. The metallic Ni, as a conductor, could reduce the internal resistance and NiO shells could efficiently facilitate the dissociation of water. Yan et al. [20] also reported that Ni/NiO nanosheets exhibited the outstanding HER performance. Here, both Ni and NiO were regarded as the catalytic sites, coordinating with each other. Moreover, NiO easily adsorbed OH^- in the electrolyte solution because of the strong electrostatic affinity and the metal Ni could convert H atom into H_2 , which were beneficial for the HER. The other effective strategy is to increase the specific surface area of the Ni-based catalysts, which is generally implemented by reducing the size of catalyst nanoparticles [21], using the template method to form hollow or porous structures [22,23] or combining with porous materials [24]. For example, Liu et al. [25] found that the doping of metals or metal compounds with graphene was an effective method to enhance electrocatalytic properties. Doped graphene could increase abundant active sites and accelerate charge transfer because of its high surface area and outstanding electrical conductivity. Thus the composite consisting of metal-metal oxides and graphene could display the excellent electrochemical activity toward HER. Raouf et al. [26] used MOF-199 as the precursor for preparing Cu/CuO/Cu₂O/nanoporous carbon composites by the carbonization. The prepared composites retained high surface area and exhibited good electrochemical activity toward HER.

Inspired by the above analysis, we developed a facile method to prepare a hybrid electrocatalyst (Ni/NiO@C/GR-*t-w*) containing Ni/NiO, graphene and porous carbons, which was derived from the carbonization of the composites composed of Ni-MOF-74 and graphene oxide (GO), as shown in Schematic 1. Here, MOFs were employed as a precursor to prepare Ni/NiO nanoparticles and also as a template to make Ni/NiO nanoparticles distribute well over the porous carbon matrix. In addition, GO can be thermally reduced to graphene which possesses the large surface area, the excellent electrical conductivity and mechanical strength at a high temperature [27,28]. Benefiting from these outstanding properties, the incorporation of graphene not only conduces to enlarge the surface areas and enhances the electrical conductivity of the prepared composite catalyst, but also facilitates the dispersion and stability of the catalyst in the aqueous solution [29,30]. Thanking to the merits of metallic Ni, NiO and graphene, the resulting Ni-based composite exhibited an excellent electrocatalytic performance to HER in the acidic medium with a lower overpotential and a smaller Tafel slope.

2. Experimental

2.1. Materials

2,5-Dihydroxyterephthalic acid (DOBDC, 98%) was acquired from Aldrich. Flaked graphite was obtained from Nanjing Xianfeng Nano Co. (Nanjing, China). Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), N,N-dimethylformamide (DMF), methanol and

ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents used in this work were of analytical grade and used without further purification.

2.2. Synthesis of Ni-MOF-74, Ni-MOF-GO(*w*%) and Ni/NiO@C/GR-*t-w*

GO was synthesized according to the previous publication [31].

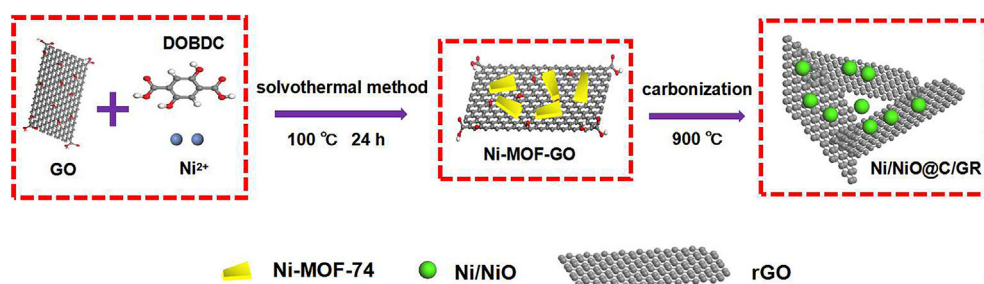
Ni-MOF-74 was prepared by the reported solvothermal method [32]. In a typical preparation, DOBDC (0.3615 g) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.7835 g) were dissolved into a mixed solution of 50 mL DMF, 50 mL water and 50 mL ethanol. The above mixture was transferred into a 200 mL Teflon reactor and heated at 100 °C for 24 h. After cooling to the room temperature, the resulting product was washed with DMF and followed by immersing in methanol for 6 days. During this time, the solvent was replaced by the fresh methanol every day to ensure that DMF were swapped out completely. The final product was dried under vacuum at 80 °C for 12 h. The obtained yellow crystal was Ni-MOF-74.

The synthesis of Ni-MOF-GO(*w*%) composite was similar to that of Ni-MOF-74. A certain amount of GO was added into the solution of DOBDC and $\text{Ni}(\text{NO}_3)_2$ under the magnetic stirring and then the suspension was maintained at 100 °C for 24 h. After cooling to room temperature, the product was washed with DMF and followed by immersing in methanol for 6 days. The synthesized composites were denoted as Ni-MOF-GO(*w*%), where *w*% represented the added GO contents with a weight percentage of 2%, 4%, 8% and 13%, respectively.

Carbon coated nickel - nickel oxide nanocomposites were prepared by the carbonization. The obtained Ni-MOF-GO(*w*%) was placed in the tube furnace. The furnace was heated to a certain temperature (700, 800 or 900 °C) with a rate of 5 °C min⁻¹ and kept the final temperature for 5 h. The whole process of carbonization was carried out in the atmosphere of N_2 . The final products were denoted as Ni/NiO@C/GR-*t-w*, where *t* was the carbonization temperature (700, 800 or 900 °C) and *w* was the added GO contents (2%, 4%, 8% or 13%).

2.3. Characterization

X-ray diffraction (XRD) data were obtained on RU-200B/D/MAX-RB diffractometer (Rigaku, Japan) using Cu-K α radiation ($\lambda = 1.5418$) in the 2θ range of 5–80°. X-ray photoelectron spectra (XPS) were conducted using a VG Multilab 2000 spectrometer (Thermo VG Scientific, USA). Scanning electron microscopy (SEM) patterns of all samples were recorded by a JSM-5610LV scanning electron microscope (JEOL, Japan). Raman spectra were taken on an INVIA Raman spectrometer (Renishaw, UK).



Scheme 1. Schematic diagram for the synthesis of Ni/NiO@C/GR.

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