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Novel one-step synthesis of wool-ball-like Ni-carbon nanotubes composite cathodes with favorable electrocatalytic activity for hydrogen evolution reaction in alkaline solution

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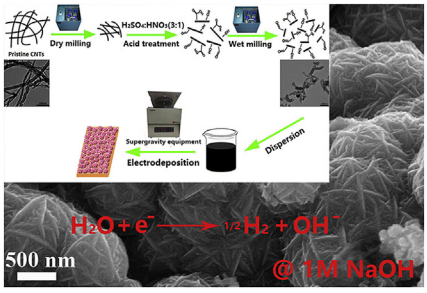
HIGHLIGHTS

- Wool-ball-like Ni-CNTs cathodes were synthesized by a one-step electrodeposition.
- Supergravity field was utilized to prepare non-noble metal cathode for HER.
- The composite cathodes with significantly enhanced HER activity were reported.
- Cathodes with finer grain size and homogeneous distribution of CNTs were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, supergravity fields are performed to prepare Ni-CNTs composite cathodes with wool-ball-like morphology from the Watts bath containing well-distributed functionalized CNTs. The prepared Ni-CNTs composite cathodes are used as noble metal-free electrocatalyst with favorable electrocatalytic activity for hydrogen evolution reaction (HER) in alkaline solutions. The crystal structure and morphology of the composite cathodes are characterized by XRD and SEM measurements. The electrochemical activities of the cathodes are characterized through Tafel polarization measurement, electrochemical impedance spectroscopy and cyclic voltammetric study in 1.0 M NaOH solution. The results indicate that catalytic activities of the Ni-CNTs cathodes prepared under supergravity fields are enhanced significantly, and the sample prepared at rotating speed 3000 rpm from the bath containing 1 g dm^{-3} CNTs exhibits the highest HER activity with smallest Tafel slope and largest exchange current density of 823.9 μA cm^{-2}. Furthermore, the effects of both the CNTs concentrations and the intensities of supergravity fields on the properties of the Ni-CNTs cathodes are investigated.

1. Introduction

The aggravated energy crisis and increased environmental concerns have given rise to a vigorous exploration of clean and renewable alternative energy. Hydrogen as a promising alternative chemical fuel for traditional fossil fuels is an ideal energy carrier

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that holds great potential in the field of clean and sustainable energy technology [1]. Among various technologies for hydrogen evolution reaction (HER), water electrolysis is considered to be one of the most ideal pathways for hydrogen production due to high purity, no pollution and plenty of sources [2]. However, this technology is restrained because of the high energy consumption caused by the large overvoltage for HER [3]. In this case, plenty of researches have been devoted to the search of electrode materials with high electrocatalytic activity to reduce HER overpotential in the past decades [3].

Up to now, Pt or Pt-based materials with negligible overpotentials have been considered as the most effective catalytic materials for HER [4,5]. However, the high cost and limited supply largely hinder their industrialized application. Accordingly, numerous efforts have turned to the development of non-noble-metal based HER catalysts. Among the non-noble metals, nickel is identified as the most excellent candidate due to its relatively high catalytic activity and low cost [6]. So far two major approaches have been carried out to improve the electrocatalytic activity of bare Ni: (i) enlarging the real surface area by preparation of the Ni-based Raney-type materials with porous morphology characteristics [7–9] or (ii) enhancing the intrinsic catalytic activity by combination of Ni with other metals or non-metals such as Ni-Mo [10–13], Ni-Co [14–16], Ni–W [17–19], Ni–S [20–22].

Recently, it has been reported that active solid particles modified Ni-based composite materials prepared by various methods also exhibit a good catalytic activity for HER and attract more and more attention, such as Ni–MoO_3, Ni–MoO_2 [23,24], Ni-based-CeO_2 [25–27], Ni-rare earth (RE) compounds [28] and Ni-polyaniline [29] composite electrodes. The incorporated active particles in the Ni matrix can improve the HER activity by contributing to the formation of nanocrystalline, increasing the surface area of cathode and enhancing the intrinsic activity of materials. Carbon nanotube (CNT) as a superior candidate has attracted tremendous interests owing to the extraordinary chemical and physical properties. Particularly, Ni-CNT composite coatings have exhibited many promising features for further applications in recent researches, such as improved hardness, increased wear resistance, protection against corrosion and enhanced catalytic performance [30–33]. In addition, numerous researchers have been devoted to studying the application of CNTs in hydrogen production [34–38]. Nevertheless, to the best of our knowledge, few studies on the electrocatalytic activity of Ni-CNT composite cathode for HER in alkaline solution have been reported before.

Composite electrodeposition is an effective technology for the synthesis of Ni-based composite coatings by dispersing the active solid particles into electrolyte. In this case, uniform dispersion of CNTs in the bath is the major factor for the fabrication of coatings with homogeneous CNTs distribution. Herein, to obtain well-dispersed CNTs with proper aspect ratio, pristine CNTs were cut off and oxygen-functionalized by a three-step treatment to improve their dispersion and suspension stabilities. Besides, our previous studies indicated that the mass transfer process during electrodeposition could be significantly enhanced under supergravity field [39,40]. Meanwhile, our recent study has shown that by taking advantage of the supergravity field, superior improvement of electrocatalytic activity for HER on the Ni–CeO_2 composite cathode has been observed [41]. Based on the results, Ni-CNTs cathodes for HER were first synthesized using composite electrodeposition under supergravity field in this paper. The effect of the supergravity field and the CNTs concentration on the morphology, microstructure and electrochemical activity of the composite cathodes were systematically studied.

2. Experimental

2.1. Treatment of CNTs

Pristine multi-walled carbon nanotubes (MWCNTs) of 20–30 nm in outer diameter and 10–30 μm in length were pretreated by three steps before adding into electrodeposition solution. Firstly, as the length to diameter ratio is a critical factor in the homogeneous dispersion of CNTs in electrolyte solution, the pristine MWCNTs were dry milled with ZrO_2 balls for 8 h in a planetary ball mill machine at a rotating speed of 240 rpm. Ball to powder ratio was kept at 50:1. Afterwards, the CNTs were functionalized by subjecting to an acid treatment in a mixture of nitric acid and sulfuric acid (1–3 vol proportion) under high power sonication for 12 h to generate oxygen containing functional groups on the surface of CNTs. The treated CNTs were subsequently washed with distilled water followed by sedimentation, until an approximatively neutral suspension was obtained as measured by a pH meter. After that, the resultant was dried at 80 °C for 12 h. The collected CNTs were finally wet milled with electrodeposition solution including 0.2 g L^{-1} sodium dodecyl sulfate (SDS) for 6 h to acquire a homogeneous covering of surfactant molecules around the CNTs and further cut off the CNTs which haven't been thoroughly exfoliated during dry-milled step. After this three-step treatment the well dispersive CNTs coupled with the bath were directly added into the main electrodeposition solution for composite electrodeposition.

2.2. Synthesis of Ni-MWCNT composite cathodes

The fabrication of Ni-CNTs composite electrodes were carried out in the supergravity equipment which has been described detailedly in our previous paper [39]. A ∅ 10 cm × 2 cm copper foil circular ring was used as substrate for composite electrodeposition and a pure nickel pipe was used as anode. The Ni-CNTs composite cathodes were electrodeposited under various supergravity fields from a conventional Watts bath containing 260 g L^{-1} $NiSO_4 \cdot 6H_2O$, 45 g L^{-1} $NiCl_2 \cdot 6H_2O$, 20 g L^{-1} H_3BO_3 and 0.2 g L^{-1} SDS with 0–2.0 g L^{-1} treated CNTs. The composite electrodeposition was performed under various intensities of supergravity fields by adjusting the value of rotating speed N at a current density of 3 A dm^{-2} for 1 h at 318 K. Prior to each electrodeposition, the electrolyte was subjected to the ultrasonic field to get the CNTs fully disperse and suspend.

2.3. Characterizations

The morphologies of the CNTs were investigated using Hitachi HT 7700 transmission electronic microscope (TEM) operated at 100 kV. The X-ray diffraction (XRD) patterns of the samples were recorded on a RigakuSmart Lab diffractometer with Cu Kα irradiation (λ = 1.5418 Å). The scanning electron microscopy (SEM) measurement was performed to characterize the morphologies of the composite materials on a Zeiss Supra 55 type field emission scanning electron microscope at an accelerating voltage of 20 kV. The chemical compositional analysis of the composite electrodes was carried out using an energy dispersive spectrometer (EDS) attached to the SEM.

2.4. Electrochemical measurements

All electrochemical measurements were performed at 298 K in a standard three-electrode cell with 1 M NaOH solution by the CHI 660E electrochemical workstation. The cell consisted of a platinum foil as the counter electrode, an Hg/HgO electrode in 1 M NaOH (0.097 V vs. standard hydrogen electrode (SHE)) as the reference