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Electrospun transition/alkaline earth metal oxide composite nanofibers under mild condition for hydrogen evolution reaction

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ABSTRACT

Transition/alkaline earth metal oxide composite nanofibers (TAMNs) $Ca_3Co_4O_9$ and $MgCo_3O_5$ as a new class of oxide materials for hydrogen evolution were successfully fabricated by electrospinning followed by calcinations under mild condition, and characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), high resolution transmission electron microscope (HR-TEM), Raman spectroscopy, X-ray powder diffraction (XRD) and electrochemical method. The layered $Ca_3Co_4O_9$ and $MgCo_3O_5$ nanofibers (NFs) have promising capabilities as electrocatalyst for hydrogen evolution, exhibit low Tafel slope of 76 and 98 mV/decade for hydrogen evolution reaction (HER). The affordability and electrocatalytic properties have endowed TAMNs as a potential replacement for precious metal in electrocatalytic applications.

Introduction

Since the beginning of the industrial society, the economical development is heavily depending on fossil fuels. But, the gradual decline of fossil fuels reserving along with environmental pollution problems calls for urgent utilization of sustainable energy resources. Hydrogen, as a clean and totally-recyclable resource with a practically unlimited supply, has been increasingly considered as the "fuel of the future" [1-4], hydrogen energy is one of the most promising candidates for replacing petroleum fuels in the future if the greenhouse gas byproducts cannot be produced during its preparation and use.

Two potential technologies, photo- [5-15] and electrocatalytic [16-32] ones have been developed on hydrogen evolution reaction (HER) for several decades. However, there still exist significant challenges to be overcome. For photocatalytic technique, issues such as low productive rate, low photon absorption capability and the separation issue for mixed H_2 and O_2 agents (especially for power of catalysts) need to be overcome. Despite to the advantageous that photoelectrochemical (PEC) cells having no separation issue, the current density generated by the PEC cell is still about 3

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orders of magnitude lower than the electrocatalytic water splitting [33]. Hence, one focus of research in HER is based on electrocatalytic processes that attract much interest worldwide.

Currently, layered misfit oxide structures have garnered much attention and prestige in several applications such as thermoelectric materials and high-temperature superconductors. But, its potentials for important electrochemical applications such as hydrogen evolution and oxygen reduction reactions have not been systematically studied. A recent study found that calcium cobalt complex oxide nanocrystals (NCs) have good performance for hydrogen evolution. The basic idea of material preparation was by a solid state reaction. But the experiment required repeated grinding and high temperature calcinations for more than 140 h, and a Tafel slope of 87 mV/decade for HER was achieved by $Ca_3Co_4O_9$ single crystals [34]. Such a complex preparation process consumes high energy, therefore simple preparation method is urgent to be developed.

Electrospinning is a notably versatile technique to prepare nanofibers (NFs) with various properties depending on polymer precursors. Electrospun nanomaterials have been applied in many research areas owing to its large specific surface area, porous structure, small grain size, and controllable length ranging from several nanometers to several centimeters [35–37].

In this paper, electrospun polyvinyl alcohol (PVA) NFs containing transition/alkaline earth metal nitrate tetrahydrate/acetate tetrahydrate were collected on doped fluoride SnO_2 transparent conductive (FTO) substrate. A mild condition heated in the furnace at 600 °C for only 5 h with a heating rate of 2 °C min^{-1} and then naturally cooled to room temperature was used to prepare transition/alkaline earth metal oxide composite nanofibers (TAMNs). The electrochemical results showed that TAMNs possess excellent electrocatalysis toward hydrogen evolution. The hydrogen evolution property of TAMNs prepared under mild condition is almost equal to that of $Ca_3Co_4O_9$ NCs prepared under above mentioned complex condition.

Experimental section

Materials

All chemicals were analytical grade, or better, and were used as received. PVA and hexaaminoruthenium (III) trichloride were purchased from Sigma-Aldrich. Cobalt (II) acetate tetrahydrate, magnesium nitrate tetrahydrate and Calcium nitrate tetrahydrate were obtained from Sinopharm and J&K Chemical Technology, respectively. Sodium hydroxide, sodium phosphate monobasic, sodium phosphate dibasic, concentrated sulfuric acid, potassium hydroxide, and potassium ferricyanide were supplied by Beijing Chemical Reagent Company. Ultrapure water produced by Millipore Mili-Q purification system was used throughout the experiments.

Calcium cobalt composite oxide synthesis

At first, 2.0 g calcium nitrate tetrahydrate and 3.0 g cobalt (II) acetate tetrahydrate were mixed with 2.0 g PVA and 15 mL distilled water, the mixture was magnetically stirred at 80 °C for 2 h to obtain a homogenous solution and used as electrospinning precursor. The precursor solution was loaded into a 10 mL syringe of the electrospinning set-up with a stainless steel needle, and ejected with a flow rate of 0.28 mL h^{-1}. The FTO slide was pretreated to ensure its cleanness. A positive potential of 21.54 kV was applied between the needle tip and FTO collectors with a distance of 10 cm. In the electric field, the ejected polymer jet was accelerated toward the collector, and NFs were formed on the FTO slide after solvent evaporation. These electrospun NFs were heated in the furnace at 600 °C for 5 h with a heating rate of 2 °C min^{-1} and then natural cooling to room temperature.

Characterization

X-ray powder diffraction (XRD) pattern was obtained on RINT2000 vertical goniometer using K radiation ($\lambda = 1.5418$ Å, 40 kV, 100 mA; scanning rate 4°min^{-1}) in the range of 20-70°. Raman spectroscopy was recorded with Lab RAM ARAMIS (HORIBA Jobin Yvon, France) over the range 200–1800 cm^{-1}. The morphology was investigated using scanning electron microscopy (SEM) with a FEG electron source at a 5 kV electron beam. The microstructure of the NFs was characterized by an FEI Tecnai F-20 field-emission high resolution transmission electron microscope (HR-TEM) (Hillsboro, OR, USA) operating at 200 kV. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 600 °C under nitrogen.

Cyclic and linear sweep voltammetry were carried out with electrochemical analyzer (CHI 852C, Shanghai CH Instrument Company, China) connected to a computer. All voltammetric experiments were performed in a 4 mL electrochemical cell at room temperature using a three-electrode system. An Ag/AgCl electrode was utilized as a reference electrode, while a platinum electrode served as an auxiliary electrode. All electrochemical potentials in this report are stated versus the Ag/AgCl reference electrode, unless otherwise stated.

Results and discussion

SEM characterization

The morphologies of TAMNs were examined by SEM. Fig. 1 shows SEM images of composite NFs before (a) and after (b and c) calcinations at 600 °C for 5 h. From Fig. 1a, it can be seen that the surface of the electrospun PVA/$Ca(NO_3)_2$/$Co(CH_3COO)_2$ NFs is very smooth and almost free of beads or breakages, it indicates the good spinnability of the solution [38]. Fig. 1b represents the composite NFs-modified FTO after calcinations at 600 °C for 5 h. The NFs were still attached to the surface of FTO tightly, which proved that the composite electrode has been successfully fabricated. The diameters of these electrospun NFs before and after calcinations were about 1500 and 500 nm, respectively. After calcination, the diameter of NFs decreased caused by losing PVA during calcination. It can be clearly observed from