Chemical Physics Letters 703 (2018) 56–62

Contents lists available at ScienceDirect

Chemical Physics Letters

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

A high performance p-type nickel oxide/cuprous oxide nanocomposite with heterojunction as the photocathodic catalyst for water splitting to produce hydrogen

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ARTICLE INFO

Article history:
Received 29 January 2018
In final form 9 May 2018
Available online 16 May 2018

Keywords:
NiO/Cu_2O nanocomposite
Heterojunction
Photocathode
Hydrogen production

ABSTRACT

An efficient and robust p-type NiO/Cu_2O nanocomposite was developed as photocathodic catalyst of a photoelectrochemical cell. The nanocomposite with heterojunction demonstrates enhanced photoelectrochemical (PEC) properties and considerable photocatalytic hydrogen generation ability. When ca. 6 wt.% Cu_2O was loaded on the surface of NiO, the sample exhibited the highest photocatalytic activity. The amount of hydrogen evolved from the cathodic chamber of the PEC cell up to 17.6 μmol under 2 h simulated sunlight irradiation with −0.0455 V vs. RHE (reversible hydrogen electrode) bias.

1. Introduction

It is well known that hydrogen is an economic and environmentally friendly energy source [1]. Photoelectrochemical (PEC) water splitting to produce hydrogen is one of the most attractive and challenging tasks for a sustainable society [2,3]. In a PEC water splitting system, the photocathode for hydrogen evolution should be made of a p-type semiconductor, such as CuI, SnS, InP, $ZnFe_2O_4$ and NiO etc [4–8]. Among these semiconductors, nickel oxide is a nonstoichiometric p-type semiconductor with good thermal and chemical stability [9], which makes NiO one of the most appropriate semiconductor substrates for water splitting to produce hydrogen. However, pristine NiO has some intrinsic weakness, such as the large overpotential for hydrogen evolution and low photocatalytic activity [10,11], hindering its practical applications. Modifying NiO with quantum dots is an effective method to improve the photocatalytic properties of the semiconductor [12].

Recently, p-type Cu_2O has been widely reported as a typical photocatalyst because of its low production cost and excellent photovoltaic properties [13]. Besides, its appropriate direct band gap (2.2 eV) enables efficient visible light absorption and its high conduction band level (−0.28 V vs. RHE) is beneficial to the reduction of the protons in the aqueous solution [14]. However, the photocatalytic system consisting of single Cu_2O is less efficient for water splitting to produce hydrogen because of some of its intrinsic defects [15].

In this paper, we report a novel and robust p-type composite semiconductor consisting of NiO and Cu_2O. The composite with heterojunction was prepared by deposition copper precursor on the surface of NiO nanoparticles followed by a low temperature solid reaction. The composite photocathode fabricated by immobilizing composite on the surface of fluorine-doped tin oxide glass demonstrated excellent photocatalytic activity. This work provides a new approach to prepare effective and cost-effective semiconductor catalysts with heterojunction for photocatalytic water splitting to produce hydrogen in a tandem cell.

2. Experimental

2.1. Materials

Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), sodium hydroxide (NaOH), copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), sodium sulfate anhydrous (Na_2SO_4), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$) and ethanol (C_2H_5OH) were purchased in analytical grades from Sinopharm Chemical Reagent Company

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https://doi.org/10.1016/j.cplett.2018.05.020
0009-2614/

(Shanghai, China). All reagents were used without further purification.

2.2. Sample preparation

NiO nanoparticles were synthesized by a modified method reported in previous research [16]. In a typical synthesis, 10 mL of NaOH solution (8 mol L^{-1}) was added dropwise into 20 mL of $NiCl_2$ solution (0.2 mol L^{-1}) under magnetic stirring. The light green NiO precursor can be seen in the process. The mixture was heated to 80 °C and maintained at that temperature for 3 h. The suspension was naturally cooled down to room temperature, and NiO solid was isolated by centrifugation. The product was washed with deionized water and ethanol three times, and then was dried at 60 °C for 12 h. The obtained solid was calcined at 400 °C in air for 2 h, obtaining desired NiO sample.

NiO/Cu_2O nanocomposite was prepared by a low temperature solid reaction method [17,18]. In a typical experiment, the NiO nanoparticles were dispersed in 10 mL of anhydrous ethanol and stirred at room temperature for 1 h. Then, the calculated amount of $Cu(NO_3)_2$ ethanol solution (0.04 mol L^{-1}) was added into the NiO suspension under vigorous stirring. The mixture was stirred at room temperature for 2 h. The solvent was removed by vacuum evaporation. The solid was dried at 80 °C for 6 h and then was calcined in air at 350 °C for 2 h, resulting in Cu_2O modified NiO nanocomposite. The samples were labeled NiO/Cu_2O-x, where x stands for the weight percent of Cu_2O in the sample.

2.3. Photoelectrode preparation

To 5 mL of the solution consisting of ethanol-ethylene glycol-polyvinyl pyrrolidone (4 mL: 1 mL: 1.5 mg), 20 mg of the as-prepared NiO nanoparticles or NiO/Cu_2O composite was added under ultrasonic treatment to form a suspension. The suspension was spin-coated on the surface of a clean fluorine-doped tin-oxide (FTO) substrate. The FTO plate with the deposited sample was dried on a heating plate at 50 °C for 20 min and was then sintered in Ar at 400 °C for 0.5 h.

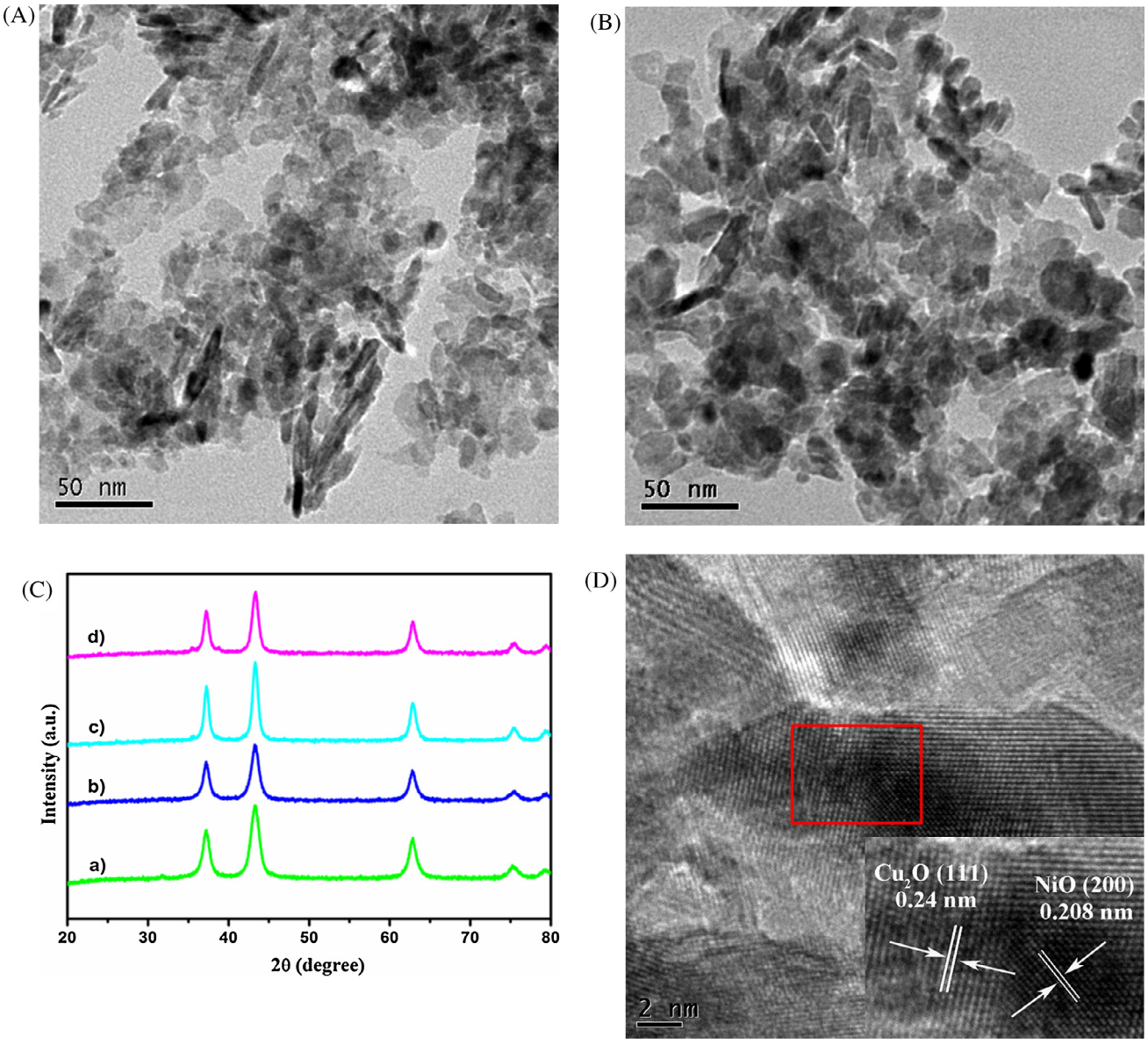

Fig. 1. TEM images of (A) NiO and (B) NiO/Cu_2O-6; (C) XRD patterns of the samples of (a) NiO, (b) NiO/Cu_2O-3, (c) NiO/Cu_2O-6 and (d) NiO/Cu_2O-9; D) HRTEM of NiO/Cu_2O-6. Inset: the magnified image of labeled area.