Journal of Power Sources 285 (2015) 169–177

Contents lists available at ScienceDirect

Journal of Power Sources

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

Nanostructured nickel phosphide supported on carbon nanospheres: Synthesis and application as an efficient electrocatalyst for hydrogen evolution

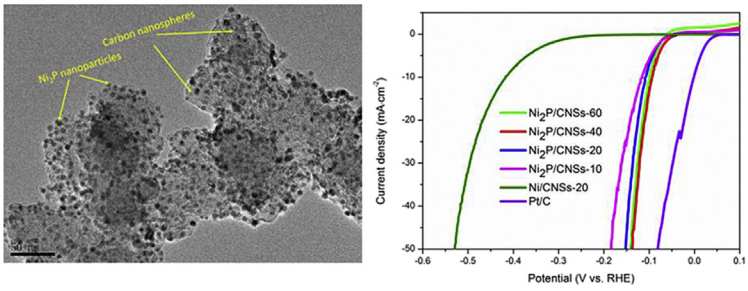
Yuan Pan, Yunqi Liu*, Chenguang Liu*

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China National Petroleum Corporation (CNPC), China University of Petroleum, 66 West Changjiang Road, Qingdao, Shandong 266580, PR China

HIGHLIGHTS

- Nanostructured nickel phosphides supported on carbon nanospheres (CNSs) have been synthesized for the first time.
- The Ni_2P/CNSs-*x* hybrids exhibit excellent activity and stability for the HER.
- The Ni_2P/CNSs-*x* hybrids exhibit higher catalytic activity than the Ni/CNSs hybrid.
- The Ni_2P/CNSs-*x* hybrids can be a promising candidate for substituting noble metal catalyst.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form
11 March 2015
Accepted 15 March 2015
Available online 17 March 2015

Keywords:
Nanostructured
Nickel phosphide
Carbon nanospheres
Electrocatalyst
Hydrogen evolution reaction

ABSTRACT

New electrocatalysts to replace noble metal catalysts for the hydrogen evolution reaction (HER) are highly desired to produce renewable and environmentally-friendly energy. In this work, nanostructured nickel phosphides supported on carbon nanospheres (CNSs) with different carbon content (Ni_2P/CNSs-*x*, $x = 10, 20, 40, 60$) are synthesized by thermal decomposition using nickel acetylacetonate as nickel source and trioctylphosphine as phosphorus source in an oleylamine solution containing CNSs for the first time. The structure and morphology are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and N_2 adsorption-desorption. Then the electrocatalytic properties of as-synthesized Ni_2P/CNSs-*x* for the HER are studied. In addition, the Ni/CNSs-20 hybrid is synthesized and the electrocatalytic properties are studied. The results show that all the Ni_2P/CNSs hybrids exhibit higher catalytic activity than the Ni/CNSs-20 hybrid. The catalytic activity of the as-synthesized Ni_2P/CNSs hybrid can be enhanced by changing the carbon content. The superior catalytic activity is attributed to the coupling effect between the Ni_2P nanoparticles and CNSs, the electronic effect of Ni, the ensemble effect of P, the large surface area, and the high electron conductivity of CNSs. This study paves the way for the design of HER electrocatalysts with high performance and low-cost that can be employed under acid conditions.

1. Introduction

Hydrogen is considered to be an ideal energy carrier that can meet the increasing energy demand and environmental pollution

* Corresponding authors.
E-mail addresses: liuyq@upc.edu.cn (Y. Liu), cgliu1962@sina.com (C. Liu).

http://dx.doi.org/10.1016/j.jpowsour.2015.03.097
0378-7753/

[1] and therefore increasing attention has been paid to the production of hydrogen [2]. The development of efficient and sustainable hydrogen production technologies to satisfy global energy demand in an economical and environmentally friendly manner is required. Nowadays, electrolysis of water is regarded as a clean and renewable method to produce hydrogen [3]. Generally, the electrochemical hydrogen evolution reaction (HER) is catalyzed by Pt-based noble metal catalysts [4] but large scale applications of these noble metal catalysts are limited due to the high price and low abundance [5]. Therefore, the development of efficient, stable and inexpensive non-noble metal electrocatalysts to replace Pt-based noble metal catalysts for the HER is highly desired, although many difficulties are still ahead.

Over the past years, several kinds of Mo-based materials have been used as effective HER catalysts, such as molybdenum sulfide [2], molybdenum boride [6], molybdenum nitride [7], molybdenum selenium [8], and molybdenum carbide [9]. Recently, transition-metal phosphides (TMPs), such as nickel phosphide [10], molybdenum phosphide [11], iron phosphide [12], and cobalt phosphide [13], have emerged as attractive HER electrocatalysts. The electrical conductivity and surface area of electrocatalysts are important factors which influence the electrocatalytic efficiency. Therefore, carbon materials have been adopted as ideal supports to enhance the electrocatalytic activity due to their high electrical conductivity and large surface area [14] and, as a consequence, carbon nanospheres (CNSs) are good candidates due to their excellent physicochemical properties [15]. For example, Bian et al. [16] synthesized an efficient electrocatalyst for hydrogen evolution based on MoS_2 on ordered mesoporous carbon nanospheres. The as-synthesized nanocomposites exhibited high catalytic activity for the HER with a low overpotential and a very high current density. Sun et al. [17] synthesized a nanohybrid electrocatalyst, which consisted of carbon nanospheres decorated with single-crystal Pt nanowires, via a simple chemical route. However, reports are rare on the design and electrocatalytic properties of novel electrocatalysts based on nanostructured nickel phosphide supported on carbon nanospheres.

In this work, we report the first synthesis of nanostructured nickel phosphide supported on carbon nanospheres with different carbon content (Ni_2P/CNSs-*x*, x = 10, 20, 40, 60) prepared by thermal decomposition using nickel acetylacetonate [$Ni(acac)_2$] as nickel source and trioctylphosphine (TOP) as phosphorus source in an oleylamine (OAm) solution containing CNSs. The structure and morphology of the as-synthesized Ni_2P/CNSs-*x* were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and N_2 adsorption-desorption. We further studied the electrocatalytic properties of the as-synthesized Ni_2P/CNSs-*x* for the HER. Additionally, a Ni/CNSs-20 hybrid was synthesized and its electrocatalytic properties were studied. The results show that the Ni_2P/CNSs-*x* hybrids exhibit excellent electrocatalytic activity for the HER with a low overpotential, a high current density, a small Tafel slope, and good stability.

2. Experimental

2.1. Materials

Nickel(II) acetylacetonate ($Ni(acac)_2$, 95%), trioctylphosphine (TOP, 90%), oleylamine (OAm, 95%) and carbon nanospheres were obtained from Aladdin Chemistry Co. Ltd. Hexane (≥99.5%), ethanol (≥99.7%), and sulfuric acid (H_2SO_4, 98%) were obtained from Sinopharm Chemical Reagent Co. Ltd.. Nafion solution (5% in a mixture of lower aliphatic alcohols and water) was purchased from Sigma–Aldrich. All chemicals were used as received without further purification. All reactions were carried out under an argon atmosphere using standard air-free techniques.

2.2. Synthesis of Ni_2P/CNSs-*x* hybrids

In a typical synthesis, $Ni(acac)_2$ (0.256 g, 1 mmol), OAm (7 mL, 21.3 mmol) and *x* mg CNSs (x = 10, 20, 40, 60) were placed in a four-neck flask and stirred magnetically under a flow of argon. The mixture was heated to 120 °C with a heating rate of 10 °C min^{-1} and kept at this temperature for 30 min to remove moisture and dissolved oxygen. After TOP (3.4 mL, 7.5 mmol) was quickly injected into the solution, the mixture was rapidly heated to 320 °C and maintained for 2 h. After cooling to room temperature, the black precipitate was washed three times with a mixture of hexane and ethanol by centrifugation (4000 rpm, 10 min). Then the Ni_2P/CNSs-*x* hybrids with different carbon content were obtained by drying in vacuum at 60 °C for 24 h.

2.3. Synthesis of Ni/CNSs-20 hybrid

$Ni(acac)_2$ (0.256 g, 1 mmol), OAm (7 mL, 21.3 mmol) and CNSs (20 mg) were placed in a four-neck flask and stirred magnetically under a flow of argon. The mixture was heated to 120 °C with a heating rate of 10 °C min^{-1} and kept at this temperature for 30 min to remove moisture and dissolved oxygen. After TOP (1 mL, 2.2 mmol) was quickly injected into the solution, the mixture was rapidly heated to 200 °C and maintained for 30 min. After cooling to room temperature, the black precipitate was washed three times with a mixture of hexane and ethanol by centrifugation (4000 rpm, 10 min). The Ni/CNSs-20 hybrid was obtained by drying in vacuum at 60 °C for 24 h.

2.4. Characterization

X-ray diffraction (XRD) was performed on a panalytical X'pert PROX-ray diffractometer with Cu Kα monochromatized radiation (λ = 1.54 Å) and operated at 45 kV and 40 mA. Transmission electron microscopy (TEM) was performed on a JEM-2100 UHR microscope (JEOL, Japan) at an accelerating voltage of 200 kV. An energy dispersive X-ray (EDX) instrument was attached to the TEM system. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALABMK II spectrometer using an Al K_α (1486.6 eV) photon source. N_2 adsorption-desorption experiments were carried out on a ChemBET 3000 (Quantachrome, USA) instrument.

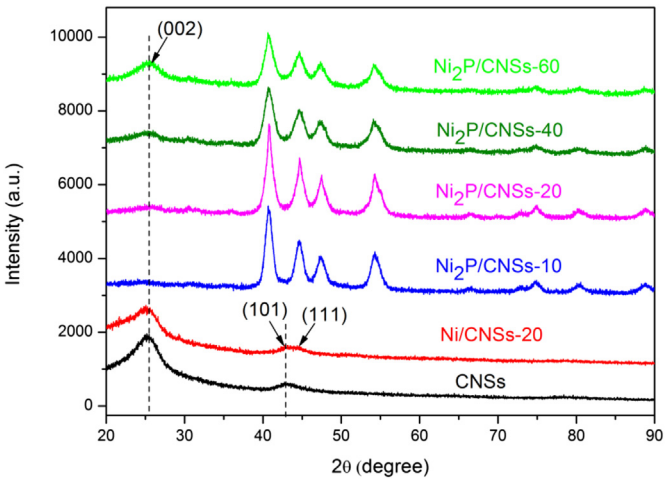


Fig. 1. XRD patterns of the as-synthesized Ni_2P/CNSs-*x* and Ni/CNSs-20 hybrids.