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Magnetic metal phosphide nanorods as effective hydrogen-evolution electrocatalysts

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ABSTRACT

Efficient and economical hydrogen evolution reaction (HER) from water splitting holds a bright prospect for clean energy. Replacement of expensive Pt-based catalysts with earth-abundant catalysts is beneficial for this field. In this study, nanoscale magnetic metal phosphides including Co₂P, Co_{1.33}Ni_{0.67}P and Ni₂P nanorods are synthesized by a facile solution method. Their HER activities and stabilities on glassy carbon and Ti electrodes are investigated. The Co₂P nanorods deposited on glassy carbon electrodes are found to show higher activity and better reversibility than the Co_{1.33}Ni_{0.67}P and Ni₂P counterparts. Nevertheless, the Co_{1.33}Ni_{0.67}P and Ni₂P samples on Ti electrodes gain a significant activity promotion after annealing in H₂/Ar atmosphere. Investigation of the Tafel curves shows that the Co₂P nanorods on glassy carbon have the lowest Tafel slope while their exchange current density on Ti electrode exhibits a high value which is comparable to that of Pt electrode. Furthermore, the cyclic voltammetric tests show that the reversibility of annealed Co₂P on Ti electrode is the best, which emphasizes the superiority of Co species in catalyzing HER reaction. Finally, the three magnetic metal phosphide catalysts are found to exhibit good stabilities in acidic conditions according to the galvanostatic testing results. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is regarded as a clean and efficient fuel for internal combustion engines and electrochemical fuel cells [1–4]. At present hydrogen gas is commercially produced by steam-reforming of hydrocarbons, a process which generates CO₂

as a waste product. Therefore there is currently great interest in improving the alternative processes such as photocatalysis or electrolysis which split the water molecule directly. Electrolysis via the hydrogen evolution reaction (HER) is convenient for producing small quantities of H₂ but, if electrical efficiency is required, the HER must be promoted using a noble metal catalyst such as Pt [5]. Such catalysts have a high

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electrocatalytic activity and good electrochemical stability. Unfortunately, large-scale industrial applications of this technology are limited by the high cost and scarcity of the noble metals. As a result, there has been considerable interest in replacing Pt-based catalysts for HER with catalysts based on earth-abundant metals or metal compounds. Considerable efforts have been made toward the development of advanced catalysts with high HER efficiency but low cost. A variety of inorganic catalysts have been developed so far such as MoS₂ [6–8], MoS_x [9,10] MoB [11], Mo₂C [11], MoSe₂ [12], WO₃ [13], Ni–Mo–N [14], and Ni–Mo [15–17]. Generally performance is adequate in alkaline electrolytes but there is more commercial interest in finding an efficient way to obtain the HER in acidic electrolytes [17]. Unfortunately, most of the alternative electrocatalysts are not stable in acidic solution. Here we consider whether magnetic metal phosphides have the potential to be relatively low-cost, high-performance HER catalysts with adequate stability in acidic solution.

Magnetic metal phosphides are already known to be excellent catalysts for hydrodesulfurization (HDS) [18,19], photocatalysis [20] and water-gas shift [21]. Recently, Popczun et al. reported that Ni₂P nanospheres on Ti foil exhibited very high HER catalytic activity in acidic solution [22]. Liu et al. performed density functional theory calculations and found that the Ni₂P (001) surfaces had exposed Ni and P sites that could facilitate the catalysis of HER [23]. There are, however, still many interesting issues that have not been considered yet, including for example, the HER catalytic activity of non-spherical magnetic metal phosphide nanocrystals, the influence of their surface status on their catalytic performance and whether alloying with Co would be advantageous. As an important class of magnetic metal phosphides, cobalt phosphides have been investigated for their special magnetic [24,25] and catalytic properties [26,27]. Recently, studies on the electrochemical performance of cobalt phosphide nanomaterials have indicated that they can be used as anode materials for potential applications in lithium ion batteries [28,29]. In comparison, reports on the electrocatalytic HER performance of nanoscale cobalt phosphides are very rare.

In this study, we synthesize one-dimensional magnetic metal phosphide nanocrystals including Ni₂P, Co_{1.33}Ni_{0.67}P and Co₂P nanorods by using a facile injection method. The HER activities and stabilities are investigated on the as-prepared nanorods after they had been deposited onto electrodes of Ti and glassy carbon. The results obtained demonstrate that the Co₂P nanorods on glassy carbon have the lowest Tafel slope of the samples tested. The exchange current density of Co₂P on the Ti electrode exhibits a high value which is comparable to that of a Pt electrode. We also observed that the HER activities of Ni₂P and Co_{1.33}Ni_{0.67}P nanorods on Ti electrodes can be greatly improved by annealing in an Ar/H₂ atmosphere. To the best of our knowledge, the HER electrocatalytic properties of one-dimensional magnetic metal phosphide nanocrystals have not been reported so far. The excellent electrocatalytic performances observed in this study suggest that the magnetic metal phosphide nanocrystals are promising as a lower cost, non-Pt substitute catalyst for H₂ production via electrolysis of water.

Material and methods

Chemicals and materials

Cobalt acetylacetonate (Co(acac)₂, 98%, Acros), nickel acetylacetonate (Ni(acac)₂, 96%, J&K), oleylamine (OAm, 80–90%, Acros), trioctylamine (TOA, >90%, TCI), trioctylphosphine (TOP, 97%, Strem), oleic acid (OA, 85%, Aladdin), and titanium foil (99.9%, 3 mm thickness) were used as received.

Synthesis of Ni₂P nanorods

The synthetic method employed is based on our previous study on the synthesis of one-dimensional magnetic metal phosphide nanomaterials [30,31]. In a typical synthesis, a stock solution containing 1 mmol of Ni(acac)₂, 1.2 mmol of OA and 10 mL of TOA was prepared at 120 °C for 20 min and cooled to room temperature. Then, the stock solution was slowly injected (0.05 mL/min) using a syringe pump into a stirred mixture containing 5 mL of TOA and 2.4 mmol of TOP heated at 300 °C. The resulting solution was maintained at 300 °C until the stock solution was completely delivered.

Synthesis of Co_{1.33}Ni_{0.67}P nanorods

A stock solution containing 0.125 mmol of Ni(acac)₂, 0.375 mmol of Co(acac)₂, 3 mmol of TOP and 10 mL of OAm was prepared at 120 °C for 20 min and cooled to room temperature. The stock solution was then delivered to stirred mixture containing 5 mL of OAm and 5 mmol of TOP heated at 315 °C via 4 processes. In each process, the injection rate was kept at 0.125 mL/min, and the solution was heated at 315 °C for 10 min.

Synthesis of Co₂P nanorods

A stock solution containing 0.5 mmol of Co(acac)₂, 1.2 mmol of OA and 10 mL of OAm was prepared at 120 °C for 20 min and cooled to room temperature. The stock solution was then delivered to stirred mixture containing 5 mL of OAm and 5 mmol of TOP heated at 330 °C for 4 processes. In each process, the injection rate was kept at 0.125 mL/min, and the solution was heated at 330 °C for 10 min.

All the above reactions were carried out under the protection of high-purity argon gas. After cooling to room temperature, the obtained products were washed using the mixture of hexane and ethanol, separated by centrifugation, and dried in vacuum.

Preparation of working electrodes

A stock hexane solution containing the as-prepared nanorods (5 mg/mL) was prepared by ultrasonically dispersing the sample powders for 20 min. Then 20 μL of the nanorod solution was deposited onto the polished Ti or glassy carbon electrode of 5 mm in diameter whose Teflon-coating is detachable, followed by drying under ambient conditions. To investigate the influence of annealing treatment, some of the deposited

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