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RAPID COMMUNICATION

One-pot synthesis of diiron phosphide/nitrogen-doped graphene nanocomposite for effective hydrogen generation

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Abstract
A nanocomposite comprising diiron phosphide (Fe_2P) nanoparticles and nitrogen-doped graphene (NGr) was synthesized by a facile one-pot reaction. Such a nanocomposite showed efficient electrocatalytic activity in hydrogen evolution reaction (HER) in both acidic and basic solutions. The optimal overpotential required for the current density of 20 mA cm^{-2} (η_{20}) in acidic solution is 164 mV, which is favourably comparable to those of recently reported non-precious electrocatalysts; whereas in basic solution the value of η_{20} is 376 mV. The HER activity of Fe_2P/NGr can be correlated to Fe_2P nanoparticles in the nanocomposite, and NGr is beneficial to the electron transport from electrode to the catalyst. The faradaic efficiency of Fe_2P/NGr nanocomposite in HER is nearly 100% in both acidic and basic solutions. The stability of Fe_2P/NGr nanocomposite during HER has been demonstrated by potentiostatic electrolysis and accelerated degradation experiments. Tafel slope was determined to be 65 mV dec^{-1}, which suggests that the HER processes might proceed along a Volmer–Heyrovsky mechanism. The catalytic activity of Fe_2P/NGr nanocomposite is influenced by synthesis temperature, which may result in the differences in phase purity, particle size and specific surface areas of the composite material. The charged natures of Fe and P in Fe_2P nanoparticle might be responsible for the HER activity of Fe_2P/NGr nanocomposite.

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Introduction

As an alternative energy carrier, hydrogen has a promising application potential in clean and renewable energy technology [1,2]. Hydrogen generation from electrolysis and photoelectrolysis of water is attracting extensive attention. The efficient hydrogen generation from the electrolysis or photoelectrolysis requires effective catalysts to promote the hydrogen evolution reaction (HER). Although platinum-group metals have exhibited superior catalytic activity in the HER, the high cost and low abundance undoubtedly hinder their widespread commercial applications. The exploitation of effective and low-cost HER catalyst is therefore urgently desirable [3-8].

Transition metal chalcogenides (*e.g.*, molybdenum sulfides [5-9], tungsten sulfides [8,10,11], cobalt dichalcogenides [12,13], iron dichalcogenides [12,13], and nickel dichalcogenides [12,13]) and carbides (*e.g.*, molybdenum carbides [14-16], and tungsten carbides [17,18]) have gained increasingly wide attentions in the field of HER catalyst. Recently the exploration of HER catalyst among metal phosphides has been stimulated, and the successful examples include nanostructured Ni_2P [19], $Ni_{12}P_5$ [20], CoP [21-23], Co_2P [24], FeP [25,26], and MoP [27]. Metal and nonmetal components in these metal phosphides have small positive and negative charges, respectively. These charged natures are analogous to those of active sites (*i.e.*, the hydride and proton acceptors) in efficient hydrogenase and its analogues $[(Ni(PS3^*)(CO)]^{1-}$ and $[Ni(PNP)_2]^{2+}$). It is therefore implied that other metal phosphides having similar charged nature might also be the promising candidates as an effective HER catalyst.

In practical application, the process of hydrogen generation includes not only the HER occurring at catalyst/electrolyte interface, but also the electrons transporting in electrode (*i.e.*, the electrons transport from the support of the catalyst to the catalyst, among the catalyst, and finally to the surface of the catalyst). A pathway of electron transport with small electron transport resistance is therefore also essential for an effective hydrogen generation device. Electrocatalysts loaded on conductive carbon materials (*e.g.*, carbon nanotube, graphene, carbon cloth, and so on) have superior catalytic activities to the corresponding pristine electrocatalysts. Although various approaches have been developed to load electrocatalysts onto these conductive supports, a convenient method for the one-pot synthesis of carbon-loaded electrocatalysts remains definitely unexploited.

In this study we report the convenient fabrication of a nanocomposite containing diiron phosphide (Fe_2P) nanoparticles and nitrogen-doped graphene (NGr) and its effective catalytic activity in HER. The Fe_2P/NGr nanocomposite was fabricated cost-efficiently by a one-pot reaction of ferric chloride ($FeCl_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and melamine ($C_3H_6N_6$). The nanocomposite exhibits efficient catalytic activity in HER. The optimal overpotential required for the current density of 20 mA cm^{-2} (η_{20}) is as small as 164 mV. This value is favourably comparable to the most reported values of non-precious HER catalysts. Comparative experiments confirm that Fe_2P nanoparticle is the active component of the nanocomposite in HER, and NGr behaves as a conductive support that enhances the electron transport in electrode. Potentiostatic electrolysis and accelerated degradation experiments show that the Fe_2P/NGr nanocomposite works stably in long-term hydrogen generation in both acidic and basic solutions. Tafel analysis suggests that the HER process follows Volmer–Heyrovsky mechanism. Fe and P in Fe_2P component have slight positive and negative charges, respectively, and the HER activity of Fe_2P component is likely to be correlated with the charged natures of Fe and P. These results not only present a new nanocomposite as an effective HER catalyst, but also introduce a facile method for the one-pot synthesis of electrocatalyst loaded onto conductive support.

Materials and methods

Synthesis

In a typical experiment, $FeCl_3 \cdot 6H_2O$ (0.1 g), $NH_4H_2PO_4$ (0.021 g), $C_3H_6N_6$ (4.0 g), and an appropriate amount of deionized water were mixed in a mortar mixer. The mixture was naturally dried and then loaded in a quartz tube mounted in a tube furnace. The quartz tube was pumped to 20 Pa and filled with high purity nitrogen (99.999%). This procedure was repeated five times prior to heating for removing oxygen in the tube. After that, the temperature was increased to 800 °C (heating rate: 3 °C min^{-1}), and maintained at 800 °C for 30 min. During the heating process, the quartz tube was flowed with high purity nitrogen (flow rate: 100 sccm). After the reaction, the furnace was cooled naturally to room temperature.

Characterization

Transmission electron microscopy (TEM, 200 kV, JEM2100, JEOL) and scanning electron microscopy (SEM, JSM7001F, JEOL) were utilized to investigate the morphology of products. For the TEM investigation, the product was dispersed in ethanol by ultrasonication. The dispersion was dropped onto a carbon-coated copper grid (300-mesh), and the copper grid was then dried at 100 °C for 5 min before the TEM characterization. The high angle annular dark field scanning TEM (HAADF-STEM) and the Energy-dispersive X-ray spectroscopy (EDX) elemental mapping experiments were performed on TECNAI G^2 20 transmission electron microscope (FEI) equipped with a GENESIS 2000 XM 30T system. The EDX spectra were recorded using an Oxford Instruments' INCA system equipped on JSM7001F. Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance diffractometer with graphite-monochromated Cu $K\alpha$ radiation (1.54178 Å). The X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB250Xi System (ThermoFisher) equipped with a monochromatic Al $K\alpha$ (1486.6 eV) source and a concentric hemispherical energy analyzer. The Raman spectrum was obtained from A DXR Raman microscope (ThermoFisher).

Electrochemical measurement

All electrochemical measurements were carried out with an electrochemical workstation (CHI 614D, CH Instrument) in a three-electrode electrochemical cell.