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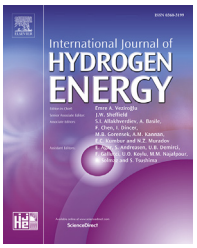

Highly efficient and durable phosphine reduced iron-doped tungsten oxide/reduced graphene oxide nanocomposites for the hydrogen evolution reaction

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ABSTRACT

The design and development of inexpensive and highly efficient electrocatalysts for hydrogen production from water splitting are highly crucial for green energy and the hydrogen economy. Herein, we report phosphine reduced an iron-doped tungsten oxide nanoplate/reduced graphene oxide nanocomposite (Fe-WOxP/rGO) as an excellent electrocatalyst for the hydrogen evolution reaction. This electrocatalyst was synthesized using a hydrothermal method, followed by reduction with phosphine (PH_3), which was generated from sodium hypophosphite. The catalyst onset potential, Tafel slope, and stability were investigated. Accordingly, Fe-WOxP/rGO exhibited impressively high electrocatalytic activity with a low overpotential of 54.60 mV, which is required to achieve a current density of 10 $mAcm^{-2}$. The Tafel slope of 41.99 mV $dec^{-1}$and the linear sweep voltammetry curve is almost the same as 2000 cycles and electrolysis under static overpotential (54.60 mV) is remain for more than 24 h in 0.5 M H_2SO_4. The catalytic activity and conductivity of Fe-WOxP/rGO were higher than WO_xP, Fe-WOxP and WOxP/rGO. Such an outstanding performance of the Fe-WOxP/rGO nanocomposite is attributed to the coupled synergic effect between high oxygen vacancies formation on tungsten oxide in the nanoplate-like structure of Fe-WOxP and rGO nanosheet, making it as an excellent electrocatalyst for hydrogen evolution reaction.

Introduction

Because of increasing environmental pollution and the growing energy crisis, the demands to overcome fossil fuels with green and sustainable energy are increasing [1,2]. Hydrogen molecule H_2 (g) is one of the most attractive and promising new fuels because of its high energy density and nonpolluting behaviors [3,4]. Therefore, various methods such

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as the photoelectrochemical (PEC) [5] and electrochemical [6] redox reaction of water and the steam reforming of hydrocarbons with hot water and oxygen (water gas shift reaction) [7] have been used to produce hydrogen. Among electrochemical methods, splitting water is attractive to support the economy of hydrogen in the future because it is highly efficient and environmentally friendly [8,9].

Platinum (Pt) is one of the most active catalysts for the (HER) hydrogen evolution reaction, but it is precious and rare in the earth's crust and expensive for large-scale applications [10,11]. Therefore, in order to efficiently split water into hydrogen fuel economically, it is critical to developing non-precious catalysts that are highly active, cheap, abundant, and electrochemically stable [12,13]. To replace Pt as the HER electrocatalyst in solutions of acid, numerous tungsten based catalyst have been recently explored because of their Pt-like catalytic behaviors. These include: tungsten phosphide (WP) [14,15], tungsten disulfide (WS_2) [16,17], phosphorus modified tungsten nitride reduced tungsten oxide (P-WN/rGO) [18,19], $WO_{2.9}$ [20], tungsten carbide (WC) [21–23], tungsten oxynitride (WON) [24], molybdenum tungsten phosphide (MoWP) [25], tungsten-doped nickel phosphide (W-NiP) [26], and tungsten dioxide (WO_2) [27]. However, tungsten-based materials still require improved material design and a different approach to efficiently catalyze the HER in acidic media. Therefore, to further enhance the HER and other catalytic activities of different tungsten based materials, they have been anchored onto conductive supports, such as reduced graphene oxide [28], carbon cloth [15,25], graphite felt [29] carbon nanofiber [30], tungsten metal [27], and nitrogen-doped carbon cloth [24]. These conductive support materials not only prevent aggregation but also increase the dispersion of active sites and the conductivity [31]. Among conductive supports, reduced graphene oxide attracts much attention because of its high conductivity and stability [32,33].

Herein, we develop a new two-step approach by integrating the hydrothermally grown nanoplate-like structure of iron-doped WO_3 directly on reduced graphene oxide, followed by reduction with PH_3, which was generated in situ from sodium hypophosphite. PH_3 reduces iron-doped tungsten trioxide nanoplates (Fe-WO_3) to iron-doped tungsten oxide phosphate (Fe-WOxP). Here, PH_3 was employed both as a reducing agent and a source of phosphorus precursor which results in Fe-WOxP on reduced graphene oxide (Fe-WOxP/rGO). The catalytic activity and the conductivity of the synthesized material were enhanced because of the synergic effect between the high oxygen vacancies in the nanoplate-like structure of Fe-WOxP and the rGO nanosheets. The Fe-WOxP/rGO nanocomposite shows a Tafel slope and an onset potential at 10 mA cm^{-2}, of 41.99 mV dec^{-1} and 54.60 mV at 10 mA cm^{-2}, respectively. This is among the best values reported for non-precious metal catalysts. Compared with WOxP, Fe-WOxP and WOxP/rGO nanocomposites, and the Fe-WOXP/rGO nanocomposite offer a smaller charge-transfer and ohmic resistance between the electrode/electrolyte interfaces, leading to a much improved electrocatalytic activity. To the best of our knowledge, this is the first report of the electrocatalytic activity of Fe-WOxP/rGO for the hydrogen evolution reaction (HER).

Experimental section

Synthesis of Fe-WOxP/rGO nanocomposite

To prepare the Fe-WOxP/rGO all chemicals used were available commercially analytical grade reagents and were used without further purification. Iron-doped WO_3/rGO nanocomposite (Fe-WO_3/rGO) was prepared by dissolving 1 g of $Na_2WO_4 \cdot 2H_2O$ and 100 mg of $FeCl_3$ in 25 mL of deionized water with constant stirring. Then, 3 M HCl was slowly added drop by drop until the solution pH reached about 1. Subsequently, 1.53 g of anhydrous oxalic acid ($H_2C_2O_4$) was added. The solution was further diluted to 50 mL by adding deionized water. Before transferring the solution into Teflon-lined stainless-steel autoclave for the hydrothermal process, 2 g of $(NH_4)_2SO_4$ added. A 20 mL of graphene oxide was prepared by dissolving 20 mg of GO in 20 mL of deionized water under sonication for 30 min and added to the aforementioned solution. The resulting solution was sonicated for another 30 min. Subsequently, the solution was transferred to a Teflon-lined stainless steel autoclave. The temperature of the oven was maintained at 180 °C for 24 h. The Fe-WO_3/rGO precipitate was filtered and washed three to four times with ethanol and deionized water, then dried overnight in a freeze drier. For comparison, WO_3 and WO_3/rGO were prepared using the same procedure but without the addition of $FeCl_3$. Subsequently, Fe-WOxP/rGO was prepared by chemical vapor deposition (CVD) method, in which 0.10 g of Fe-WO_3/rGO and 1 g of $Na_2HPO_2 \cdot H_2O$ were put together in porcelain boat side by side by maintaining the temperature at 500 °C for 2 h with rate of heating 3 °C per minute; during the process, $Na_2HPO_2 \cdot H2O$ was upside the stream of argon flow. WOxP, Fe-WOxP, and WOxP/rGO were prepared using the same procedure. The schematic of the synthesis of Fe-WOxP/rGO is shown in the supporting information (Scheme S1).

Characterization of materials

XRD with a Cu K α source of radiation (Bruker, D2 Phaser diffractometer) was used to examine the crystal structures of the as-synthesized WOxP, Fe-WOxP, WOxP/rGO and Fe-WOxP/rGO. For Morphology, a field-emission scanning electron microscope (FESEM, JSM 6500F, JEOL) TEM coupled with Energy dispersive X-ray spectroscopy (EDS) were employed to study the elemental mapping. To examine the elemental composition of the catalyst, X-ray photoelectron spectroscopy (XPS) experiments were performed. Raman spectroscopy was used to identify functional groups vibration, stretching, and the defects in rGO.

Electrochemical measurements

All electrochemical measurements were performed with a Solatron electrochemical analyzer (CH Instruments, Inc., Shanghai) at room temperature. The atypical three-electrode system was used with a glassy carbon electrode (GCE) as working electrode, a saturated calomel electrode (SCE) as the reference electrode (E (RHE) = E (SCE) + 0.260 V) after calibration), and a platinum wire and graphite rod as the counter electrode. The ink of the Fe-WOxP/rGO catalyst was prepared

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