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Short Communication

In-situ grown of Ni_2P nanoparticles on 2D black phosphorus as a novel hybrid catalyst for hydrogen evolution

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ABSTRACT

Nickel phosphide-based nanomaterials have been acted as efficient catalysts for the hydrogen evolution reaction (HER), however, the design of novel and high performance HER catalyst is still a challenge. Herein, we report a novel 2D material black phosphorus (BP) as support for constructing Ni_2P-based hybrid catalyst by a one-pot thermal decomposition approach. TEM results indicated that the monodispersed Ni_2P nanoparticles with small size and good dispersion supported on the surface of layered BP, which implied that more catalytic active sites may be exposed for HER. The as-synthesized Ni_2P/BP hybrid exhibits high HER electrocatalytic performance with low onset overpotential (70 mV), small Tafel slope (81 mV dec^{-1}), large double-layer capacitance (1.24 mF cm^{-2}), high conductivity and good stability, which can be assigned to the strong synergistic effect between Ni_2P and BP. Therefore, BP may be a suitable support for constructing excellent catalysts in electrocatalysis.

Introduction

Nowadays, the design of novel and high performance catalyst for electrochemical hydrogen evolution reaction (HER) is being more and more important because the demand of hydrogen energy was increased and the current environmental was destroyed by fossil fuel [1]. Pt-based noble metal materials exhibit excellent catalytic performance for the HER but their large-scale industrial applications were limited by the high price and rare reserve [2]. Preparing a kind of catalyst which is high-efficiency and cost-effective has become current development trend.

At present, nickel phosphide has been used as excellent HER electrocatalyst. For example, Wang et al. [3,4] reported a 3D self-supported biphasic Ni_5P_4–Ni_2P nanosheet (NS) array cathode and Ni_2P-nanorods (NRs)/Ni electrode by direct phosphorization of Ni foam using red phosphorus as P

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source, respectively. The Ni_5P_4–Ni_2P NS and Ni_2P–NRs/Ni exhibited high catalytic performance for HER in 0.5 M H_2SO_4 solution with an onset overpotential of 54 and 33 mV, respectively. Based on this, Ma et al. [5] also reported a self-supported porous Ni–Fe–P nanocomposite cathode, which exhibited high HER catalytic performance both in 0.5 M H_2SO_4 and 1.0 M KOH solutions. Additionally, the considerable efforts also have been turned to enhance the catalytic activity by combining 2D materials. For example, we have developed a hybrid catalyst by loading Ni_2P nanoparticles (NPs) on 2D nitrogen-doped graphene, which shows promising activity for HER [6]. Recently, black phosphorus (BP), as a novel 2D layered materials, have received widely attention in lithium-ion batteries [7], thin-film solar cells [8] and photocatalysis [9]. There are three allotropes for phosphorus that is white, red, and black. Among the three allotropes, BP showed the best thermal stability, and it is insoluble in most solvents, practically non-flammable, and chemically the least reactive form [10–12]. Up to now, the application of BP as support in electrocatalysis have not been reported. Inspire by this, we think that the construction of a novel and efficient catalyst using BP as support is desirable to enhance the electrocatalytic performance in practical application. In this work, we for the first time report a novel hybrid (Ni_2P/BP) composed of small size Ni_2P NPs and 2D layered BP materials by a one-pot thermal decomposition approach. As expected, the Ni_2P/BP hybrid exhibits the high catalytic performance for the HER.

Experimental

Synthesis of Ni_2P/BP hybrid catalyst

The Ni_2P/BP hybrid catalyst was synthesized by a facile one-pot thermal decomposition approach. Firstly, 0.256 g nickel acetylacetonate, 10 mL oleylamine and 20 mg BP were mixed and stirred under Ar. The mixture was heated to 120 °C and kept for 1 h. Then 3.5 mL trioctylphosphine was injected into the above solution and kept at 320 °C for 2 h. Finally, the product was washed with hexane and ethanol for several times, dried at 60 °C overnight in a vacuum.

Characterization

The samples were characterized by X-ray diffraction (XRD, PROX-ray diffractometer with Cu Kα source), transmission electron microscope (TEM, FEI Tecnai G2 F20) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific/k-Alpha).

Electrochemical test

Electrochemical test was carried out with a 660E electrochemical workstation (CH Instruments) using a three-electrode setup. The working electrode was prepared as follow: 5 mg sample and 1 mL ethanol containing 20 μL 5 wt% Nafion was mixed to form ink solution by ultrasonic. Then 5 μL of ink solution was dropped onto the surface of the glassy carbon electrode (0.1256 cm^2). The preparing process for 20% Pt/C catalyst is same to the as-synthesized catalyst. The loading amount of the catalyst including 20% Pt/C on the electrode was 0.2 mg cm^{-2}. An Ag/AgCl electrode and a Pt wire were used as reference electrode and counter electrode, respectively. In all measurements, the Ag/AgCl reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). In 0.5 M H_2SO_4, E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.222 V + 0.059 pH = E (V vs. Ag/AgCl) + 0.222 V. In pH = 7 PBS electrolyte, E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.222 V + 0.059 pH = E (V vs. Ag/AgCl) + 0.635 V.

Results and discussion

Fig. 1a shows the XRD pattern of the Ni_2P/BP catalyst. The peaks at 40.6°, 44.5°, 47.3°, 54.1° and 72.1° are indexed to (111), (201), (210), (300) and (110) planes of hexagonal Ni_2P (PDF no. 1-089-4864, space group: P-62m, cell parameters: a = 5.859 Å, b = 5.859 Å, c = 3.382 Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$). The others peaks at 16.8°, 26.4°, 34°, 52.3° and 56.7° are indexed to (002), (012), (111), (121) and (123) planes of orthorhombic BP (PDF no. 01-074-1878, space group: Bmab, cell parameters: a = 3.310 Å, b = 4.380 Å, c = 10.50 Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$), which suggested that BP was decorated by Ni_2P NPs successfully.

The chemical bonding structure information was further confirmed by XPS. Fig. 1b–c shows Ni 2p and P 2p spectra of the Ni_2P/BP catalyst. For Ni 2p region, the two peaks are observed at 852.7 and 869.9 eV, which are corresponding to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ in Ni_2P, the peaks at 855.7 and 873.9 eV can be attributed oxidized Ni species and the peaks at 860.4 and 878.1 eV can be assigned to satellites, respectively [13]. For P 2p region, three peaks can be observed at 129.0, 130.3 and 133.1 eV, which can be attributed to the BP [14], P 2p in Ni_2P [13] and oxidized P species [13], respectively. Similar with previous reports [15], we also found from the binding energy of Ni $2p_{3/2}$ and P $2p_{3/2}$ peaks that Ni has a small positive charge and P has a small negative charge in Ni_2P by comparing with Ni and P elementals, which is beneficial for catalyzing HER.

The morphology structure of Ni_2P/BP catalyst was further characterized by TEM. From Fig. 2a–b, a lot of monodispersed Ni_2P NPs with a size of about 7 nm can be observed clearly. The as-synthesized Ni_2P NPs supported on the surface of layered BP with high density and good dispersion, which indicated that more catalytic active sites properly were exposed for HER. Additionally, the lattice fringes with interplanar distances of 0.5296 nm and 0.223 nm can be seen clearly from the high-resolution TEM images (Fig. 2c–d), which can be attributed to the (002) plane of BP and (111) plane of the Ni_2P, respectively. Moreover, the STEM-EDX elemental mapping image (Fig. 2e) confirms the uniform distribution of Ni and P elements throughout the whole layered BP.

Fig. 3a shows the linear sweep voltammogram (LSV) polarization curve with a scan rate of 5 mV s^{-1} of the Ni_2P/BP catalyst in 0.5 M H_2SO_4 solution. For comparison, pure BP and 20% Pt/C catalyst were also tested. The 20% Pt/C catalyst exhibits the highest HER catalytic activity with onset overpotential of zero. Pure BP shows negligible HER catalytic activity with large onset overpotential of 452 mV. It is interesting to find that the catalytic performance can be improved greatly after BP decorated with Ni_2P NPs, the Ni_2P/BP catalyst reveals high HER catalytic activity with onset

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