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GO supported Fe doped Ni(OH)$_2$ hexagonal nanosheets for hydrogen evolution reaction in neutral electrolytes

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Abstract

Exploiting non-noble metals catalysts with excellent performance for hydrogen evolution reaction (HER) has aroused gigantic interest, but still challenges. Herein, we reported the graphene oxide (GO) supported Fe doped Ni(OH)$_2$ hexagonal nanosheets (GO-Fe,Ni HHNs) for HER firstly. SEM and XRD were carried out to investigate the morphology and crystal structure of the GO-Fe,Ni HHNs systematically. The elements and bonding of the sample were measured via using XPS. In addition, we found that the recrystallization treatment could significantly improve the morphology and crystallinity of the nanosheets. Most important, the GO-Fe,Ni HHNs possessed exceptional catalytic performance and stability in PBS solution. The overpotential (10 mA cm$^{-2}$) and Tafel slope were 190 mV and 110 mV dec$^{-1}$, respectively, significantly better than that of other non-noble metal catalysts reported before.

1. Introduction

Hydrogen (H$_2$) is a class of high energy density fuel, and considered as a promising candidate to replace fossil energy, including petroleum, natural gas, and coal [1, 2]. So far, electrocatalytic hydrogen production technology has aroused tremendous research interest in recent years owing to its mild reaction conditions, environment friendly, and high-purity [3–5]. However, the high overpotential for the hydrogen evolution reaction (HER) is an non-assignable bottleneck to realize the application of electrocatalytic technology in practice [6]. Developing high performance catalysts is recognized as the prospective approach to decrease the overpotential of HER [7]. Thus, various efforts have been devoted to the design and synthesis of highly efficient catalysts. Some noble metal, such as Pt, Ir, and Ru, show excellent catalytic activity, but the expensive preparation cost and scarce resources hinder their widespread application in industry [8–10]. Thus, it is urgent eager to explore non-noble metal catalysts with high catalytic performance.

Iron (Fe) and nickel (Ni) are the most common and low-priced metal compare to other transition metal, such as Pt, Ir, Cu, and Co, etc [11]. In recent years, a series of Ni based catalysts, viz. metal nanoparticles, phosphide, sulfide, and hydroxide, have been designed and synthesized for HER from water decomposition [12–14]. In addition, abundant of evidences show that the HER performance of bimetallic synergism catalyst is better than that of single metal catalyst [15, 16]. Although the catalytic performance of bimetallic catalysts has been improved significantly in the strong acid or base electrolyte solution. The intrinsic poor conductivity inhibits the further improvement of its performance [17]. Therefore, the strategy of in situ growth of catalyst on conductive substrate is a satisfactory method to further improve its catalytic performance. In fact, it is also necessary to fabricate high efficiency catalyst in neutral electrolyte solution because the strong acid or base electrolyte not only impact environment, but also corrode the equipment and catalyst [18, 19]. Thus, developing low-cost bimetallic catalyst for HER in neutral electrolyte is a promising way to overcome the bottleneck caused by strong acid or base electrolytes.

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In this work, we designed and synthesized Fe doped Ni(OH)$_2$ hexagonal nanosheets (Fe,Ni HHNs) in situ grown on the conductive graphene oxide (GO) for HER in neutral electrolyte solution. The excellent conductivity of GO could be used to ameliorate the intrinsic poor conductance of hydroxide. In addition, the morphological transformation of Ni(OH)$_2$ from irregular nanosheets to hexagonal nanosheets were realized in the recrystallization process. When the concentration of Fe atoms was 9%, the overpotential ($10 \text{ mA cm}^{-2}$) and Tafel slope of GO-Fe,Ni HHNs for HER in the neutral solution were 190 mV and 110 mV dec$^{-1}$, respectively, which were better than that of other low-cost metal catalysts reported previously. Meanwhile, It also possessed a satisfactory catalysis stability, indicating tremendous application potential in practice.

2. Experimental

2.1. Materials and characterization
Potassium phosphate buffer solution (PBS) and flake graphite and were bought from Alfa-Aesar and Sigma-Aldrich, respectively. (NH$_4$)$_2$S$_2$O$_8$, NiCl$_2$, KMnO$_4$, FeCl$_3$, and Na(OH) were purchased from SAAN Chemical Technology Co. Ltd. H$_2$SO$_4$, NaNO$_3$, and P$_2$O$_5$ were bought from innochem.

The morphology of the sample was observed by using transmission electron microscope (TEM, JEM-2200FS) and scanning electron microscope (SEM, S-4800). X-ray photoelectron spectroscopy (XPS, ESCALAB250XI) and powder x-ray diffraction (PXRD, Empyrean) were carried out to investigate the element and crystal structure of samples, respectively. Electrochemical workstation (CHI 760E) was used to the hydrogen evolution reaction (HER) of the sample in the three electrode system (working electrode, reference electrode : Ag/AgCl electrode, and counter electrode : Pt electrode). The linear sweep voltammetric (LSV) curves of the sample was measured under the scan rate of 10 mV s$^{-1}$, and the Tafel slope were calculated according to the equation : $\eta = a + b \log J$. The stability of catalyst was investigated by measuring the chronopotentiometry curves and LSC curves. Finally, all the measured potentials were converted to reversible hydrogen electrode (RHE) according to the equation : $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059pH$.

2.2. Preparation of GO-Fe,Ni HHNs
The graphenoxide (GO) was fabricated according to the modified hummers method reported before [20]. The schematic diagram of the preparation of GO was shown in figure 1. Further, The GO was dispersed in a
mixed solution, including NiCl₂ and FeCl₃. Then, the above solution was strongly stirred on a magnetic stirrer to disperse the GO evenly. After that, the 0.5 M NaOH solution was added to the above mixed solution slowly at 100 rpm. Subsequently, the solution was transferred to the autoclave and sealed to for recrystallization at different temperature (120 °C, 150 °C, and 180 °C). Finally, the GO supported Fe,Ni hydroxide hexagonal nanosheets (GO-Fe,Ni HHNs) were obtained after centrifugation and washing with deionization. Figure 1 also showed the schematic diagram of the preparation of GO-Fe,Ni HHNs.

3. Results and discussion

3.1. Fabrication of GO film

Figure 2(a) shows the XRD pattern of GO film prepared by modified hummers method. Only one characteristic peak appeared at ~10.5°, corresponding to a layer spacing of 0.8 nm, indicates that a high quality GO is obtained [21]. Meanwhile, TEM is carried out to obvious the morphology of GO, as shown in figure 2(b). It shows a thin and clean surface morphology of GO film. Thus, both XRD and TEM confirm that a satisfactory GO film is prepared via the modified hummers method.

3.2. Fabrication of Ni(OH)₂ hexagonal nanosheets

Figure 3 shows the XRD patterns of coprecipitated and recrystallized Ni(OH)₂ nanosheets. The XRD peak position appeared at 19.2°, 32.8°, 38.1°, 51.8°, 58.9°, 62.5°, 69.8°, and 72.6° are attributed to the (001), (100), (101), (102), (110), (200), (103), and (201) plane [22]. According to the shereer equation, the interplanar spacing (D-spacing) at different peak position are 4.63 Å (19.2°), 2.71 Å (32.8°), 2.33 Å (38.1°), 1.76 Å (51.8°), 1.56 Å

![Figure 2](image1.png)

![Figure 3](image2.png)
The characteristic peak of recrystallized Ni(OH)$_2$ is consistent with coprecipitated Ni(OH)$_2$, confirming that the recrystallization process can not alter the crystal structure. As expected, the crystal quality of Ni(OH)$_2$ was significantly improved in the recrystallization process. As can be seen from figure 3, the XRD half peak width of the recrystallized Ni(OH)$_2$ nanosheets are gradually narrowed with the increase of temperature, which indicates the amelioration of crystal quality. Moreover, the morphology of recrystallized Ni(OH)$_2$ has also undergone a subversive improvement, as confirmed by SEM images in figure 4.

Figure 4(a) is the SEM image of coprecipitated Ni(OH)$_2$, which shows the irregular nanosheets. The ultrafast reaction rate between Ni$^{2+}$ and OH$^-$ is unfavorable to grow the regular nanosheets. Figure 4(b) is the SEM image of recrystallized Ni(OH)$_2$, showing the regular hexagonal shape. In the recrystallization process, the Ni(OH)$_2$ nanosheets was dissolved and recrystallized at a lower rate, which was conducive to the formation of regular nanosheets and the improvement of crystallinity. With the increase of temperature, the regular nanosheets is further ameliorated, and remains a satisfactory hexagonal shape after 150 ℃ (figures 4(c) and (d)).

3.3. Fabrication of Fe doped Ni(OH)$_2$ hexagonal nanosheets (Fe,Ni HHNs)

To fabricate the low-cost bimetallic catalyst and improve its catalytic performance, Fe atoms were used to dope into the Ni(OH)$_2$ hexagonal nanosheets. Figure 5 show the SEM images of Fe doped Ni(OH)$_2$ hexagonal nanosheets with different concentration. With the increase of Fe atoms concentration from 3% to 9%, a hexagonal shape of Fe,Ni HHNs is remained (figures 5(a)–(c)). However, when the concentration of Fe atoms exceeds 12%, the Fe,Ni HHNs began to damage, which may result their catalytic performance degradation (figure 5(d)).

Figure 6 shows the XRD pattern of Fe,Ni HHNs with different Fe atoms doped concentration. The XRD characteristic peak located at 10.5°, 22°, 35°, 41°, and 60° are divided into (003), (006), (012), (015), and (110) crystal face of Fe,Ni hydroxide nanosheets [23]. The corresponding D-spacing of different characteristic peak are 8.36 Å (10.5°), 4.06 Å (22°), 2.58 Å (35°), 2.18 Å (41°), and 1.46 Å (60°), respectively. It indicates that Fe atoms are doped into the Ni(OH)$_2$ hexagonal nanosheets successfully. In addition, The crystallinity of Fe,Ni HHNs with the doped concentration of 12% Fe atoms is significantly lower than that of Fe,Ni HHNs with low doped concentration. This result is consistent with figure 5.
Figure 7(a) shows the linear sweep voltammetric (LSV) curves of Fe,Ni HHNs with different Fe doped concentration in PBS solution. The overpotential of Fe,Ni HHNs with 3%, 6%, 9%, and 12% Fe atoms doped concentration are 300 eV, 280 eV, 240 eV, and 310 eV, respectively. It indicates that the catalytic performance of bimetallic catalyst is gradually improved with the increase of Fe concentration. However, the catalytic performance of Fe,Ni HHNs decays rapidly as its structure is destroyed (figures 5(d) and 7(a)). The Tafel slope of Fe,Ni HHNs with 9% Fe doped concentration (160 mV dec⁻¹) is also lower that of other concentration.
3.4. Fabrication of GO-Fe,Ni HHNs

In order to further increase of the conductivity and catalytic performance of the Fe,Ni HHNs, the GO as a conductive carrier was used to support Fe,Ni HHNs. Figure 8(a) shows the SEM image of large area GO-Fe,Ni HHNs, and a partial magnified SEM image is shown in figure 8(b). It is obvious that the Fe,Ni HHNs can be uniformly loaded on the GO surface. Further, the SEM mapping image also confirm that all elements, viz. Fe, Ni, O, and C, are distributed homogeneously (figures 8(c)–(f)).

Figure 9(a) shows the XPS survey spectra of GO-Fe,Ni HHNs. The essential elements, viz. C, Ni, Fe, and O, are appeared on the XPS survey spectrum. The C1s XPS spectrum of GO-Fe,Ni HHNs is shown in figure 9(b), the binding energy located at 284.5 eV, 285.2 eV, 186.6, and 288.1 eV can be divided into C-C, C=O, C1s, respectively [24–26]. It confirm that abundant of hydroxyl and carboxyl groups are generated in the preparation process of GO film. Figure 9(c) is the Ni 2p XPS spectrum, which shows that two binding energy peaks appeared at 873.6 eV and 856.1 eV, are corresponded to Ni 2p₁/₂ and Ni 2p₃/₂, respectively [27]. In addition, the two satellite peaks are emerged at 861.2 and 879.7 eV. Figure 9(d) is the Fe 2p XPS spectrum, the binding energy appeared at 712 eV and 725 eV are attributed to Fe 2p₁/₂ and Fe 2p₃/₂, respectively [27]. Therefore, all measurements confirm that the Fe atoms are doped into Ni(OH)₂ hexagonal nanosheets.
3.5. Catalytic performance measurement of GO-Fe,Ni HHNs

In order to evaluate the catalytic performance of GO-Fe,Ni HHNs, all samples were applied for HER in neutral electrolyte. Figure 10(a) is the LSV curve obtained from Fe(OH)$_3$, Ni(OH)$_2$, Fe,Ni HHNs, GO-Fe,Ni HHNs, and Pt/C. (b) Tafel slope of Fe(OH)$_3$, Ni(OH)$_2$, Fe,Ni HHNs, GO-Fe,Ni HHNs, and Pt/C. (c) Nyquist plots of Fe(OH)$_3$, Ni(OH)$_2$, Fe,Ni HHNs, and GO-Fe,Ni HHNs. (d) LSV curves of GO-Fe,Ni HHNs with different cycles. (e) Chronoamperometric of GO-Fe,Ni HHNs at current density of 10 mA cm$^{-2}$. (f) Overpotential and Tafel slope statistics image of non-noble metal catalysts.

Figure 9. (a) XPS survey spectrum of GO-Fe,Ni HHNs. (b) C1s XPS spectrum of GO-Fe,Ni HHNs. (c) Ni2p XPS spectrum of GO-Fe,Ni HHNs. (d) Fe2p XPS spectrum of GO-Fe,Ni HHNs.
the HER overpotential compare with the single metal hydroxide. Meanwhile, the GO as a conductive carrier can also substantially decrease the charge-transfer resistance $R_{ct}$ (figure 10(c)), table 1 show the solution resistance $R_s$ and charge-transfer resistance $R_{ct}$ of all samples. It is obvious that the $R_{ct}$ of GO-Fe,Ni HHNs is significantly lower that of other samples, which is beneficial to improve the catalytic performance. Figure 10(b) shows the Tafel slope of Fe(OH)$_3$, Ni(OH)$_2$, Fe,Ni HHNs, GO-Fe,Ni HHNs, and Pt/C catalyst. As expected, the Tafel slope of GO-Fe,Ni HHNs (115 mV/dec) possess the lower value compare with single metal hexagonal (Ni(OH)$_2$: 210 mV/dec, Fe(OH)$_3$: 230 mV dec$^{-1}$) and Fe,Ni HHNs (160 mV dec$^{-1}$). This value is also extraordinary close to Pt/C catalyst (110 mV dec$^{-1}$). These results indicate that the GO-Fe,Ni HHNs shows a satisfactory catalytic performance compared to other low cost metal catalyst (figure 10(f)), such as phosphates, nitrides, carbides, sulﬁdes, and hydroxides [5, 12, 13, 25–30].

In addition, the LSV curve is further carried out to assess the stability of GO-Fe,Ni HHNs. As can be seen from figure 10(d), there is no obvious attenuation after 2000 cycles. This result is consistent with the chronoamperometric curves of GO-Fe,Ni HHNs at the current density of 10 mA cm$^{-2}$ (figure 10(e)). A stable chronoamperometric curves can be maintained after 10 h, indicating the satisfactory catalytic stability. Therefore, the GO-Fe,Ni HHNs possess excellent catalytic stability and immense application potential in practice.

### 4. Conclusion

In summary, we reported a Fe doped Ni(OH)$_2$ hexagonal nanosheets as bimetallic catalyst for HER in neutral electrolyte solution. To improve the intrinsic poor conductivity of hydroxide, the GO as an excellent conductive carrier was used to support the bimetallic catalyst. In addition, the recrystallization process was the key technology to realize morphology transformation from irregular nanosheets prepared by coprecipitation method to hexagonal regular nanosheets. For the catalytic performance, the overpotential of GO supported Fe doped Ni(OH)$_2$ hexagonal nanosheets (GO-Fe,Ni HHNs) was 190 mV at the current density of 10 mA cm$^{-2}$, and its Tafel slope is 115 mV dec$^{-1}$. All measurement results confirm that the catalytic capacity of GO-Fe,Ni HHNs is significant better than other low-cost metal catalyst reported before. Thus, it shows conspicuous application potential in practice.

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### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

### Statement

We guarantee that the manuscript is original and unpublished and is not being considered for publication elsewhere.

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| Samples          | $R_s$/Ω | $R_{ct}$/Ω |
|------------------|---------|------------|
| GO-Fe,Ni HHNs    | 3.66    | 12.63      |
| Fe,Ni HHNs       | 3.66    | 23.54      |
| Ni(OH)$_2$       | 1.9     | 45.1       |
| Fe(OH)$_3$       | 1.5     | 61.5       |
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