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The effect of graphene for the hydrogen evolution reaction in alkaline medium



You-guo Huang^a, Hai-lin Fan^a, Zhao-kai Chen^a, Ci-bing Gu^a,
Ming-xue Sun^a, Hong-qiang Wang^{a,c,**}, Qing-yu Li^{b,*}

^a School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, China

^b Guangxi Key Laboratory of Low Carbon Energy Materials, Guilin 541004, China

^c College of Chemical Engineering, Huanggang Normal University, Huanggang 438000, China

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ABSTRACT

In this work, Ni-graphene (Ni-G) composites were prepared on the surface of 304 stainless steel (304 SS) by using a simple, economical and effective electrodeposition technique in a Ni based bath with deposition time from 1 min to 30 min. The effect of graphene for hydrogen evolution reaction (HER) was researched. Graphene content in the Ni-G composite coatings with deposition time of 1 min, 5 min and 30 min was 0.42 at%, 1.47 at% and 2.82 at%, respectively. With the increase of graphene content in the Ni-G composite coatings, the onset overpotential was decreased and exchange current density was enhanced during the HER. The minimum onset overpotential and maximum exchange current density of Ni-G/304 SS for the HER was 75 mV and 1.43 mA cm² in 0.1 mol L⁻¹ KOH solution at 298.15 K. The best Ni-G/304 SS exhibited a maximum current density of 9.50 mA cm⁻² at 1.3 V, which was approximately 7.4 times higher than that of Ni/304 SS, indicating the best activity for hydrogen production. Comparing with the HER of Ni/304 SS and 304 SS, the maximum current density on the Ni-G/304 SS was 18.6 times higher than that on the Ni/304 SS and 12.3 times higher than that on the 304 SS, after starting HER for 60 min. High catalytic activity was attributed to the structural advantages of Ni-G/304 SS, including high specific surface areas and excellent electrical conductivity.

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Introduction

Due to the environmental issues and fossil energy crisis, hydrogen energy, as a sustainable and non-polluting energy, has attracted increasing interest in renewable energy research [1,2]. There are three main pathways for hydrogen production

industrially, that is, steam methane reforming, coal gasification and water electrolysis [3]. Currently, hydrogen production from steam methane reforming ($\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$) and coal gasification ($\text{C} + 2\text{H}_2\text{O} = 2\text{H}_2 + \text{CO}_2$) will result indirectly in CO₂ emissions, whereas water electrolysis uses water as a raw material to only provide hydrogen and oxygen. It means that water electrolysis is a promising way to produce hydrogen in a

* Corresponding author. Fax: +86 0773 585 8562.

** Corresponding author. School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, No. 15 Yucai Road, Guilin, 541004, China.

Fax: +86 0773 585 8562.

E-mail addresses: whq74@gxnu.edu.cn (H.-q. Wang), liqingyu62@126.com (Q.-y. Li).

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sustainable way [3]. However, due to the high overpotential for the HER or oxygen evolution reaction (OER), hydrogen prepared by water electrolysis will lead to high energy consumption. Therefore, it is a necessary to reduce overpotential for the HER or OER [4,5]. Currently, Pt-based and Pd-based catalyst have a low overpotential for the HER, whereas their commercialization is largely hindered by the high cost and limited supply of Pt or Pd [6,7]. Earth-abundant transition metals such as, Fe, Co, Ni have lower prices, while their overpotential for the HER is much higher than precious metals, which can be attributed to low exchange current density and slow transport kinetics in the HER process. Low exchange current density mainly originates from low active surface area, poor electrical conductivity, low electrocatalytic activity, etc. Therefore, cheap hydrogen evolution electrode with large active surface area, good electrical conductivity and high electrocatalytic activity will replace Pt-based or Pd-based catalysts for the HER and it will be widely used in water electrolysis industry.

Graphene, as a two-dimensional carbon material, has an excellent strength, high specific surface area and super conductivity [8–11]. In recent years, researchers used the advantages of graphene to prepare graphene-based composite in order to increase the electrical conductivity and specific surface area, which was widely used in water electrolysis. Y. Li et al. [12] prepared MoS₂/RGO (MoS₂ nanoparticles grown on reduced graphene oxide) by a selective solvothermal synthesis and found that its tafel slope was ~41 mV dec⁻¹ in 0.5 mol L⁻¹ H₂SO₄ solution. TD. Vaden's research group [13] prepared MoO₂/Graphene by co-reduction of ammonium tetrathiomolybdate and graphite oxide using focused solar radiation and found that MoO₂/graphene exhibited highly catalytic activity with a Tafel slope of 47 mV dec⁻¹ and low onset overpotential (340 mV) in 0.5 mol L⁻¹ H₂SO₄ solution. Although, graphene-based composite prepared by these methods have high hydrogen evolution activity, the preparation and usage of these catalysts are complicated, which need to loaded onto carbon rod or other electrode to use.

In order to eliminate the catalyst immobilization step and reduce cost, electrodeposition, as a simple, economical and effective technique, was used to prepare graphene-based composite for the HER. S. Chen et al. [14] reported a hybrid electrocatalyst of free-standing N-doped graphene hydrogel films decorated with MoS_x clusters by electrodeposition, which had an overpotential of 140.6 mV at the current density of 10 mA cm⁻², a Tafel slope of 105 mV dec⁻¹ and strong durability in 0.1 mol L⁻¹ H₂SO₄ solution. Z. Pu et al. [15] synthesized graphene-WS₂/Ti through the potentiodynamic deposition and found that graphene-WS₂/Ti exhibited highly catalytic activity with low onset overpotential (180 mV), a small Tafel slope (67 mV dec⁻¹) and good stability in 0.5 mol L⁻¹ H₂SO₄ solution. However, the overpotential of these catalysts was much larger, which could be attributed to poor conductivity of MoS_x or WS₂. Compared with semiconductor materials (e.g. MoS_x or WS₂), pure metals (e.g. Ni or Co) has a good conductivity. L. Liu's research group [16] synthesized Ni-G composite through the electrodeposition on the copper foil and found that Ni-G/Cu had a hardness of 6.85 GPa and an elastic modulus of 252.76 GPa. P. Kumar et al. [17] prepared Ni-G composite on mild steel by the

electrodeposition and found that Ni-G composite had the higher corrosion resistance property than the bare Ni coatings in 3.5% NaCl solution. These reports illustrated that Ni-G composite had high mechanical strength and corrosion resistance. Whereas, they had no reports of Ni-G composite for the HER. S. Badranyana et al. prepared Co–Ni-G [18] and Fe–Ni-G [19] composite electrodes at different current densities on copper substrate and found that the best hydrogen evolution activity was approximately 4 times better than that of binary Co–Ni alloy, 3 times better than that of binary Fe–Ni alloy in 6 mol L⁻¹ KOH solution. What's more, K. Hashimoto et al. [20] reported carbon addition to Ni–Mo alloys would decrease the nanocrystalline grain size and remarkably enhance the activity for hydrogen evolution. However, to the best of our knowledge, there are few reports about effect of graphene content in the Ni-G composite coatings for the HER. Therefore, we developed Ni-G/304 SS to use 304 SS as substrate, graphene as dispersed phase. The effect of graphene for the HER was researched in 0.1 mol L⁻¹ KOH solution.

Experimental

Ni-graphene composite electrodeposition

The Ni-G composite coatings were synthesized by electrodeposition technique from a Ni bath solution containing graphene slurry (Solid content, 5%, Ningbo Institute of Materials Technology and Engineering), the composition and parameters of which were given in Table 1. The substrate for electrodeposition was 304 SS (70 mm × 60 mm × 3 mm). A highly purified (99.99%) nickel sheet with 70 mm × 60 mm × 3 mm was used as the soluble anode. Prior to the electrodeposition, 304 SS was soaked in a alkaline solution of NaOH (25 g L⁻¹), Na₂CO₃ (35 g L⁻¹), Na₃PO₄·12H₂O (35 g L⁻¹) and Triton X-100 (4 g L⁻¹) for 10 min at 363.15 K, then soaked in a acid solution of H₂SO₄ (98%, 100 ml L⁻¹), HNO₃ (68%, 100 ml L⁻¹) and HF (40%, 100 ml L⁻¹) for 30 min at the room temperature. After the completion of each procedure, the samples were cleaned by deionized water. Afterwards, in order to improve the adhesion between Ni-G and 304 SS, pure Ni film of ~2 μm as a transition layer was deposited in a solution of NiCl₂·6H₂O (240 g L⁻¹) and HCl (37%, 80 ml L⁻¹) with a current density of 2 A dm⁻² for

Table 1 – The composition and parameters of Ni composite electrodeposition.

Composition	Parameters
NiSO ₄ ·6H ₂ O	270 g L ⁻¹
NiCl ₂ ·6H ₂ O	45 g L ⁻¹
Saccharin	2 g L ⁻¹
H ₃ BO ₃	40 g L ⁻¹
Sodium dodecyl sulfate	0.1 g L ⁻¹
Cellulose sodium	0.5 g L ⁻¹
Graphene slurry	40 g L ⁻¹
Temperature	338.15 K
pH	4.20
Current density	2 A dm ⁻²
Magnetic stirring	300 r min ⁻¹
Time	1, 5, 30 min

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