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The effects of ball milling on microstructures of graphene/Ni composites and their catalytic activity for hydrogen evolution reaction

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ABSTRACT

The effects of the ball milling on microstructures of the graphene/Ni composites and subsequent hydrogen evolution reaction in acidic solution were investigated. Ni nanoparticles with average grain size of 4 nm were uniformly dispersed on the graphene surface after short time ball milling. While amorphous characteristic was observed due to long time ball milling. The graphene/Ni composites with amorphous structure exhibited higher electrocatalytic performance than the graphene/Ni composites with nanocrystalline structure. The Volmer-Heyrovsky mechanism was found for the graphene/Ni composites with nanocrystalline structure, while the graphene/Ni composites with amorphous structure showed evident Heyrovsky mechanism. The excellent hydrogen evolution reaction and stability of the graphene/Ni composites could be attributed to superior interfacial contact, amorphous Ni, and synergistic effect between amorphous Ni and high conductive graphene.

1. Introduction

Hydrogen could be a kind of desired chemical fuel for fuel requirement in future, considering its clean and without generating greenhouse gases emission [1]. Water electrolysis technique could obtain a large amount of hydrogen [2]. The chemical reaction mechanism of hydrogen evolution reaction (HER) during the water electrolysis involves Volmer reaction, Heyrovsky reaction, and/or Tafel reaction [3]. The electrode materials with highly active and low over-potential had been concerned. Optimized electrode material for water electrolysis should have some characteristics, such as, high specific surface area [4] excellent electrical conductance and the corrosion resistance in working environment [5]. Platinum and other noble metals [6] are the most effective catalysts for HER, however, high price and scarce reserves in nature severely inhibit their large-scale application [7]. Recently, it was found that pure Ni [8] and its alloys [9] with low price exhibited good electrocatalytic activity for HER in alkaline environment. Comparing with polycrystalline Ni obtained with electrodeposition technique, nanocrystalline Ni obtained by dc magnetron sputtering deposition method exhibited higher catalytic activity for the HER in the alkaline electrolyte solution due to increased intercrystalline volume fraction [10]. It was found that the electrocatalytic activity of the Ni nanostructure was three times higher than 2D Ni microstructure in NaOH solution [11]. The optimized electrodeposition process for HER was found for Ni-Fe alloy [12]. Cardoso et al. [13] suggested that the performance of the Ni-based electrodes could decay after life-time service. Recently, it was found that embedded carbon content in Fe-Ni electrodes significantly improved the electrocatalytic property [14]. Graphene has unique two-dimensional structure and excellent physicochemical properties due to their high electrical conductivity and large surface area [15]. The Ni nanoparticles decorated uniformly on graphene sheets by electrophoretic deposition method enhanced the HER performance in alkaline solution [16]. Badrayyana et al. [17] found that the Fe-Ni-Graphene composite coating obtained by room temperature electrodeposition exhibited nearly 3 times higher activity for hydrogen production than Fe-Ni alloy due to increased active surface area.

In this study, the ball milling was employed to prepare the graphene/Ni composite electrode. The effects of ball milling time on microstructures of the graphene/Ni and electrocatalytic activities for HER were investigated.

2. Experimental

The graphene and Ni power (weight ratio 1:1) were loaded into a vacuum ball milling tank with stainless steel balls. The ratio of mixed powder to stainless steel ball is 1–100. The ball milling pro-

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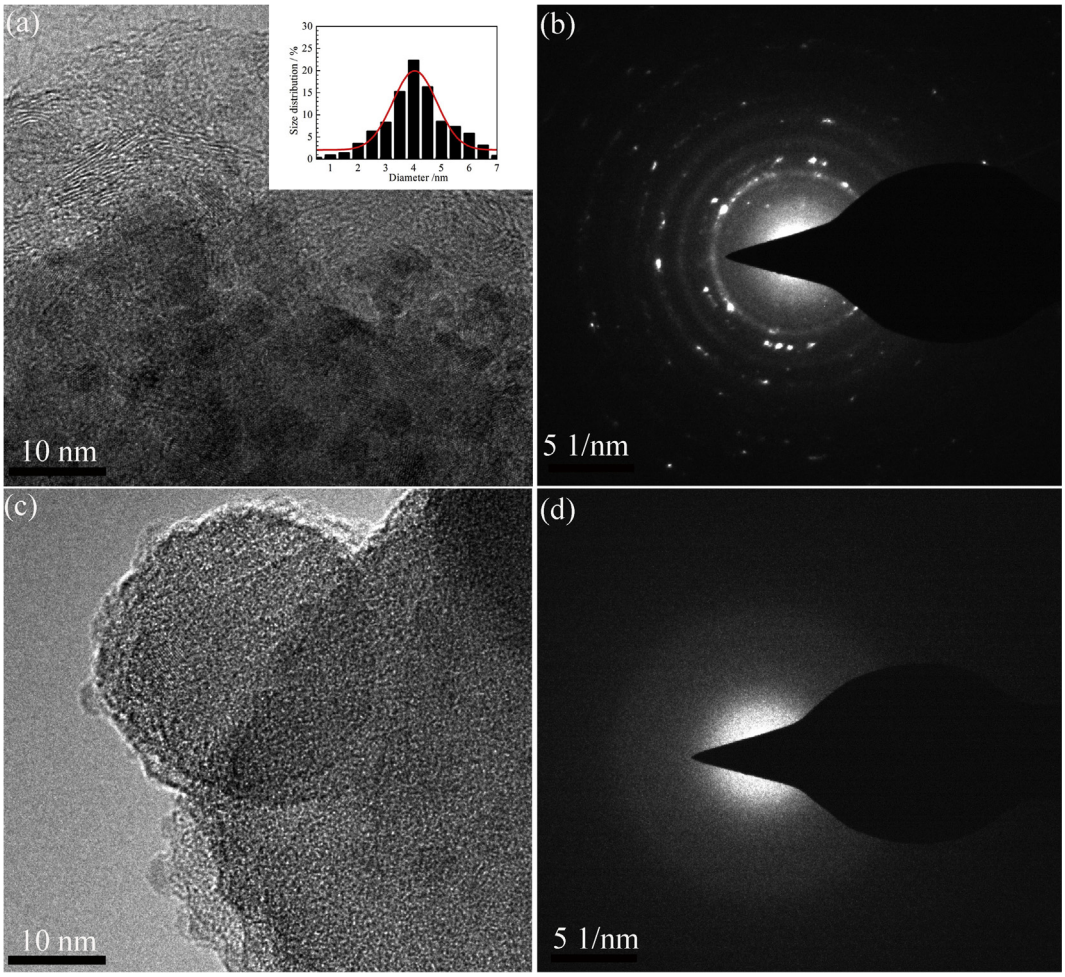

Fig. 1. (a, c) TEM images and (b, d) corresponding SAED patterns of (a, b) graphene/Ni-150 and (c, d) graphene/Ni-300, respectively.

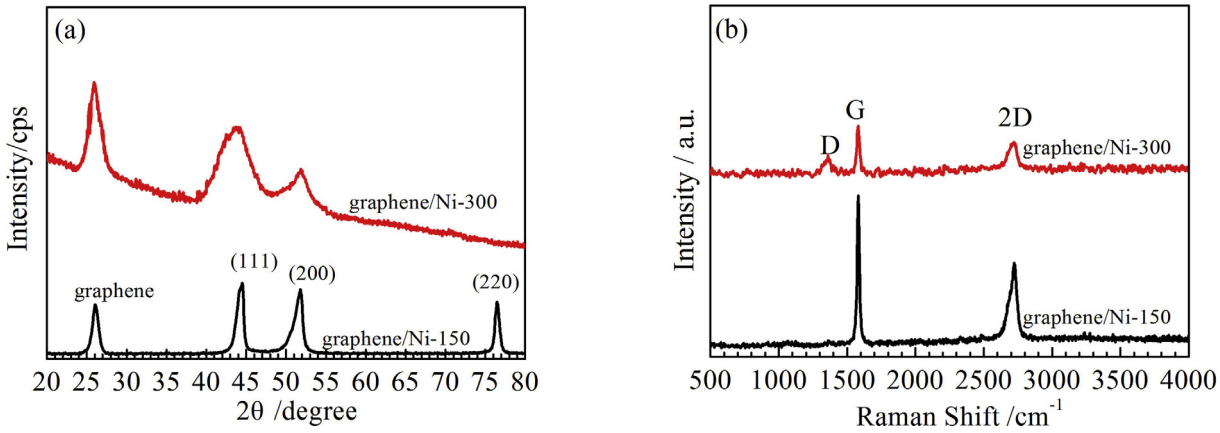

Fig. 2. (a) XRD patterns and (b) Raman spectra of the graphene/Ni composites, respectively.

cess was performed at a rotational speed of 300 rpm in sealed argon atmosphere. Milling experiments were extended to 150 h and 300 h, respectively. Products obtained after ball milling for 150 h and 300 h were nominated graphene/Ni-150 and graphene/Ni-300, respectively. The ball milling process was periodically interrupted for half an hour every 2 h to avoid excessive heating of the vials.

The morphologies and crystallographic structures of as-prepared products were analyzed by transmission electron microscope (TEM, JEOL JEM-2100F), X-ray diffractometer (XRD, Rigaku Ultima IV X-ray diffractometer) and Raman spectroscopy (JASCO NRS-5100, 532 nm). The N_2 adsorption–desorption values were determined by Brunauer–Emmett–Teller (BET) measurements using an ASAP-2010 surface area analyzer.