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Morphology-controlled synthesis of Ni-B nanoparticles by addition of hydrogen peroxide

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ABSTRACT

In this paper, H_2O_2 was used to control the morphology of Ni-B nanoparticles prepared by chemical reduction of nickel ethylenediamine complex. With increasing H_2O_2 concentration, Ni-B nanoparticle morphology progressed from pompon-like to sea urchin-like and finally to a flower-like shape. The controlled morphology was the result of dynamic equilibrium between the reduction of nickel ions by KBH_4 and oxidation dissolution of Ni-B nanoparticles due to etching by H_2O_2. Additionally, the Ni-B catalyst nanoparticles had large BET areas and more uniform Ni active centers on the surface. However, excess H_2O_2 could disrupt the dynamic equilibrium, allowing the production of various structures of Ni-B nanoparticles. The catalyst composition with a molar ratio of 1:1 Ni ion to H_2O_2 showed the best activity toward electrocatalytic oxidation of ethanol.

1. Introduction

Over the past few years, Ni-B amorphous alloys have been widely used in the fields of catalytic hydrogen generation reactions [1–4], corrosion-resistant materials [5–7], and especially, electrocatalytic materials [8–10]. The most popular method for preparation of Ni-B catalyst is direct chemical reduction, due to the considerably high yield, relatively simple procedure, and potential for large-scale production [11–13].In the field, many efforts have been made to improve the efficiency of Ni-B catalytic activity [14–19], such as optimization of preparation conditions and addition of a metal dopant or organic ligands. However, these methods have previously focused on reducing the spherical particle size, improving dispersion of the particles, and making the surface properties homogeneous. Few studies have investigated the effect of nanostructure changes on catalytic activity, such as nickel-boron tubes [20].

Numerous studies on morphology regulation of noble metals via replacement reactions [21], photochemical processes [22] and ligand-assisted chemical reductions [23] have shown that the morphology of nanoparticles has an important effect on catalytic performance. Zhang [24] found that dynamic control of the morphology of silver nanoparticles could be realized by the addition of H_2O_2 and some reducing agents.

In the present work, distinct morphology of Ni-B amorphous nanoparticles, controlled by H_2O_2, were synthesized. The electrocatalytic activity to ethanol of as-prepared Ni-B nanoparticles catalysts was evaluated in alkaline medium.

2. Experimental

2.1. Catalyst preparation

In a typical process, 200 μL of a 0.5 M $NiCl_2$ aqueous solution, 20 μL of ethylenediamine (ethane-1,2-diamine,en), and a certain amount of hydrogen peroxide (H_2O_2) were dissolved in 5 mL deionized water and vigorously stirred at room temperature. Potassium borohydride (KBH_4, 1 M, 2 mL, pH = 12) was injected into this mixture drop wise while the mixture was kept in an ice bath. The molar ratios of Ni ion to H_2O_2 were 2:1, 1:1 and 1:2. The products obtained were marked as Ni-B-1, Ni-B-2 and Ni-B-3, respectively. Oxygen-free deionized water was used to wash the black precipitate many times until a pH of 7 was achieved. For comparison, a sample without H_2O_2 was prepared using the same procedure described above. This sample will be referenced here as Ni-B-0.

2.2. Catalyst characterization

The morphology of Ni-B nanoparticles was characterized using a transmission electron microscope (TEM, JEOL, JEM-2100). The structure analyses of the catalysts were carried out by X-ray

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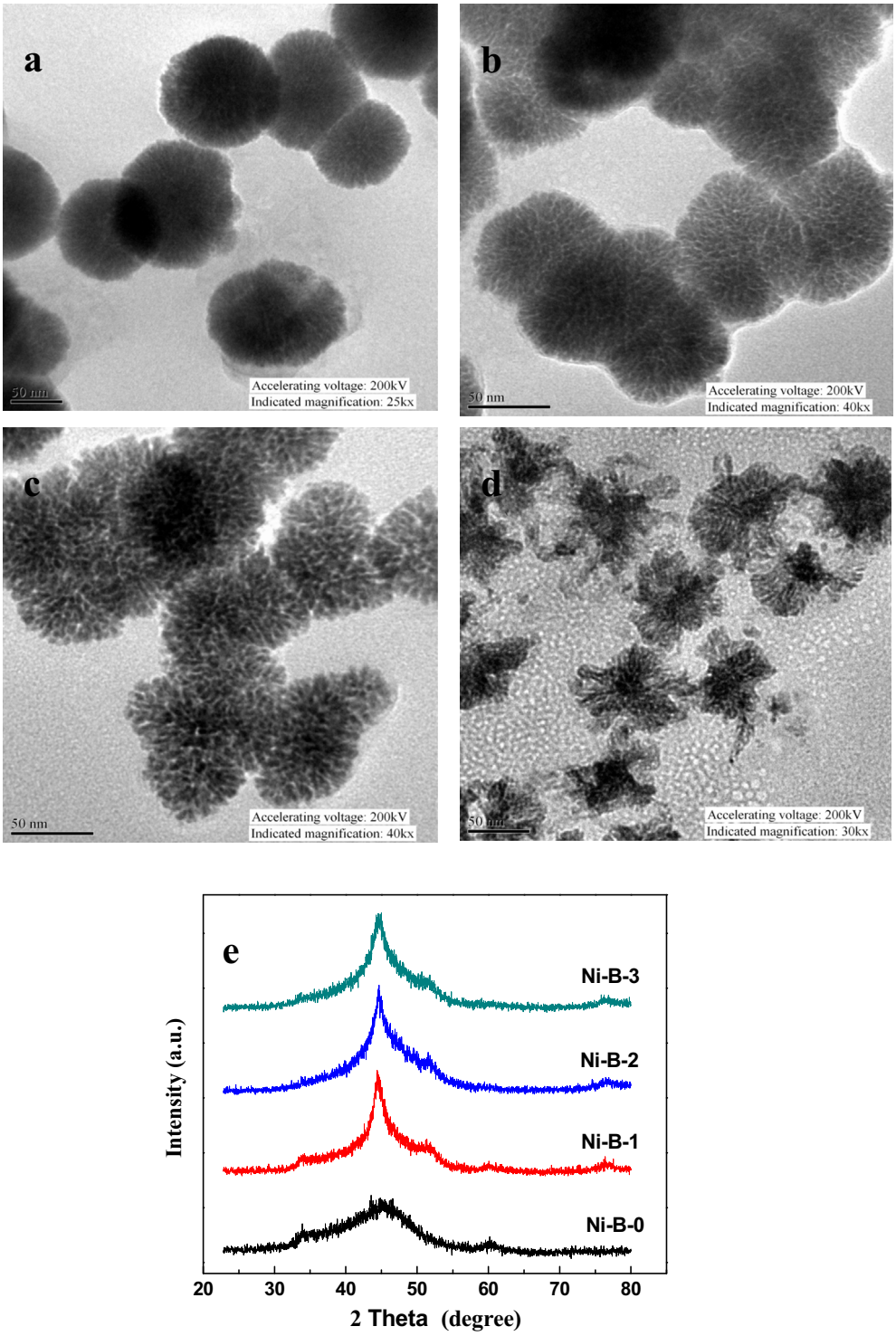

Fig. 1. TEM images of (a) Ni-B-0, (b) Ni-B-1, (c) Ni-B-2 and (d) Ni-B-3, (e) XRD patterns of the four Ni-B nanoparticles.

diffraction (XRD, Rigaku, D/max 2500PC) with Cu Kα radiation (γ = 1.5418 Å). H_2-TPD was performed by using a TP-5076 instrument (Tianjin Xianquan instrument Co. Ltd, P.R. China). The BET surface area was measured using a surface area analyzer (Quantachrome Instruments, Autosord-IQ).

2.3. Activity measurement

The electrochemical measurements were performed using an LK98B electrochemical analyzer (Tianjin Lan Like Chemical and Electron High Technology Co. Ltd, P.R. China). A standard three-electrode cell was used and controlled at (25 °C ± 0.1 °C) using water bath during the experiment. A platinum foil (0.16 cm^2) and Hg/HgO (1.0 M NaOH) were used as counter and reference electrode. The working electrode was a modified glassy carbon electrode (GCE) with surface area of 0.07 cm^2. 5 mg Ni-B nanoparticles were dispersed in 10 mL ethanol with 10 μL of 5% Nafion, under continuous sonication, to obtain a homogenous suspension. 5-μL suspension was then dropped onto the surface of the GCE. The electrode was then allowed to air-dry at room temperature. The