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ScienceDirect
Applied Surface Science 252 (2006) 8067–8072
applied surface science
www.elsevier.com/locate/apsusc

Modifying effects of polyethylene glycols and sodium dodecyl sulfate on synthesis of Ni nanocrystals in 1,2-propanediol

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Received 19 August 2005; received in revised form 8 October 2005; accepted 9 October 2005
Available online 9 November 2005

Abstract

Morphology-controlled synthesis of nickel (Ni) nanocrystals has been carried out from nickel acetate tetrahydrate with 1,2-propanediol as both solvent and reductant in the presence of modifiers. The as-prepared nanostructured Ni samples have been characterized by powder X-ray diffraction (XRD), transmission electron micrographs (TEM), selected area electron diffraction (SAED) and Fourier transform infrared (FTIR). The presence of modifiers plays an important role in morphology-controlled synthesis of Ni nanocrystals. The modifying and stabilizing effects of single modifiers such as polyethylene glycols (PEGs) and sodium dodecyl sulfate (SDS), and their composites have been investigated.

PACS: 81.20.Ka; 82.80.Ej

Keywords: Ni nanocrystals; Polyol reduction synthesis; Polyethylene glycols; Sodium dodecyl sulfate; Crystal morphology

1. Introduction

Nanostructured nickel (Ni) has been attracting increasing attention in multidisciplinary researches during the recent years because of its novel properties and potential applications in catalyst, magnetic material, electroconductive slurry, battery, surface coating material, solid lubricant and so on [1]. It is well known that nanomaterial properties, such as size- and shape-dependent catalytic activities, novel mechanical behavior, unique magnetic phenomena, crystal shape-dependent thermodynamics and quantum confinement phenomena, closely relate to their size, structure and interaction between nanoparticles. Therefore, it is crucial to control their size, size distribution, external shape and internal structure of nanostructured Ni [2,3].

Recently, many preparation methods have been developed to prepare spherical Ni nanoparticles, such as laser deposition [4], electron beam irradiation [5], aqueous chemical reduction [6], inverse microemulsion [7], γ-radiation-hydrothermal [8], hydrothermal decomposition [9] and ion exchange [10]. Among these methods, chemical reduction method is most extensively used not only owing to its short process and low investment but also to its convenience for controlling the size and shape of nanostructured materials. However, there are few reports on morphology-controlled synthesis of nanostructured Ni with dodecahedron, triangular nanoprism, octahedron and rod-like shapes.

On account of the deficiency of surface ligand of nanostructured Ni nanoparticles, it is easy for them to congregate and oxidize during the synthetic process. Hence organics like glutin [11], polyvinylpyrrolidone [12], polyacrylic acid, polyvinyl alcohol, dithiodialkyl phosphate [13], cetyltrimethyl ammonium bromide [14] are usually used as modifiers to control the growth of nanocrystals and to coat the nanoparticles so as to prevent them from further oxidation and aggregation. By the way, the templating effect of organic modifiers on metal nanoparticles has attracted researcher's interest recently [15,16].

In the present work, we reported the morphology-controlled synthesis of nanostructured Ni from nickel acetate tetrahydrate

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doi:10.1016/j.apsusc.2005.10.010

Table 1
Experimental conditions of Ni nanocrystals

Sample	Precursor amount (mol)	Reductant amount (ml)	Modifier amount
R1	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	PEG-200: 5 ml
R2	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	PEG-600: 5 ml
R3	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	PEG-2000: 5 ml
R4	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	PEG-6000: 5 ml
R5	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	SDS: 5.7780 g
R6	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	SDS + PEG-200: 2.889 g + 2.5 ml
R7	$Ni(Ac)_2{\cdot}4H_2O$: 0.01	1,2-Propanediol: 50	SDS + PEG-2000: 2.889 g + 2.5 ml

in 1,2-propanediol with ecofriendly polyethylene glycols (PEGs) or sodium dodecyl sulfate (SDS) or both as modifiers. The interaction between organic modifiers and the resultant nanostructured Ni was also investigated.

2. Experimental

2.1. Materials

1,2-Propanediol (99%), nickel acetate tetrahydrate (98.5%) and sodium hydroxide (96%) were analytical reagent grade. Acetone (99%), PEG-200, PEG-600, PEG-2000, PEG-6000 and SDS were chemical reagent grade. All of them were used as-received.

2.2. Synthesis of nanostructured Ni

In a typical experiment, 0.01 mol of nickel acetate tetrahydrate was dissolved in 50 ml of 1,2-propanediol in a 250 ml four-neck round bottom flask equipped with a heating mantle, a stirring bar, a constant pressure funnel, a thermometer and a condenser. Certain amount of modifier was added into the flask under stirring at 300 rpm. Then 30 ml of sodium hydroxide solution (1.0 M) was added dropwise into the above-mentioned solution at a dropping rate of 30 drops/min under vigorous stirring. Then the whole mixture was heated at 10 °C/min up to 180 °C and kept at 180 °C for 60 min under reflux. After the reaction suspension was cooled to 45 °C, 30 ml of acetone was added into flask to deposit black nanostructured Ni on flask bottom. The resultant nanostructured Ni was kept in the reaction solution for characterization. The experimental conditions are listed in Table 1.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of samples were obtained on a Rigaku D-max 2200 X-ray diffractometer with graphite monochromized Cu Kα radiation (λ = 1.5406 Å). The samples for XRD analysis were prepared as following. The as-prepared nanostructured Ni samples were washed with acetone and distilled water to remove impurities, and then centrifugated from the solution for XRD analysis. Transmission electron microscopy (TEM) was performed with a Phillips TECNAI-12 microscope at an acceleration voltage of 120 kV to characterize particle size and morphology. Samples for TEM imaging were prepared as following. The as-prepared Ni nanocrystals were washed with acetone and distilled water to remove impurities, and then dispersed in acetone. Multiple drops of the dispersion were cast onto a carbon-coated TEM grid and the acetone was allowed to evaporate at room temperature. Selected area electron diffraction (SAED) was performed to determine the crystalline structure. The number percentages, average particle sizes and particle size distributions of different morphological Ni nanocrystals were calculated from the TEM images by measuring at least 200 particles, a weighted-average method being applied. Fourier transform infrared (FTIR) spectra were performed with KBr wafer technique to analyse the interaction between the modifiers and the resultant nanostructured Ni.

3. Results and discussion

3.1. Chemical structure

Fig. 1 shows the representative X-ray diffraction patterns of Ni samples prepared with different modifiers. Samples R3, R5 and R7 were synthesized with PEG-2000, SDS and SDS + PEG-2000 as modifiers, respectively. All the samples show the major characteristic peaks for pure metallic Ni at 2θ values of 44.507° [Ni-1 1 1], 51.846° [Ni-2 0 0] and 76.370° [Ni-2 2 0], accordingly. Since no other peaks are observed, there are no nickel oxides or other crystalline materials formed under the present experimental conditions. The selected area electron diffraction patterns of the as-prepared samples R3 and

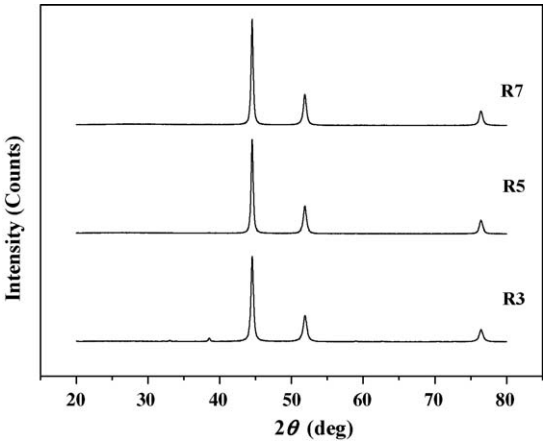

Fig. 1. XRD patterns of representative samples R3, R5 and R7 prepared with PEG-2000, SDS and SDS + PEG-2000 as modifiers, respectively.