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Effects of PVP on the preparation and growth mechanism of monodispersed Ni nanoparticles

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Abstract

Monodispersed Ni nanoparticles were successfully prepared by chemical reduction with hydrazine hydrate in ethylene glycol. The effect of the amount of polyvinylpyrrolidone (PVP-K30) on the preparation of Ni nanoparticles was investigated. X-ray diffraction (XRD), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM) were employed to characterize the nickel powders. The average nickel particle size can be controlled from 103 nm to 46 nm with increasing the mass ratio of PVP to $NiCl_2 \cdot 6H_2O$. The particles are spherical in shape and are not agglomerated. A possible extensive mechanism of nickel nanoparticle formation has been suggested.

Keywords: Ni nanoparticles; nucleation mechanism; chemical reduction; PVP

1. Introduction

In recent years, the preparation, characterization, and applications of nanosized metals have received increasing attention in various fields, for example, chemistry, physics, biology, and the corresponding engineering [1-6]. These applications require nonagglomerated and uniform particles with a controlled mean size and a narrow size distribution [7-9]. Therefore, the synthesis of controlled shapes and sizes of nanoparticles can be potentially important for these applications.

Ultrafine and nanometer nickel powders have attracted a great deal of attention over the past decade owing to their specific properties such as magnetism, thermal resistance, chemical activity, and the corresponding technological applications including conducting paints, rechargeable batteries, chemical catalysts, hard alloys, optoelectronics, magnetic recording media, etc [10-11]. Until now, several routes of preparing nickel nanoparticles, such as electrodeposition [12], thermal reduction [13], hydrothermal reduction technique [14], sol-gel process [15], sonochemical [16], microemulsion technique [17-18], microwave irradiation method [19], chemical reduction process [20-22], and polyol process [23-25] have been reported. Among these methods, the chemical reduction process is often applied to prepare monodispersed Ni nanoparticles owing to its quick reaction rate, simple procedure, inexpensive cost, and suitability for scaling up [26]. However, the agglomeration of the as-prepared particles using this approach is often serious and the particles size distribution is generally wide. As for the polyol process, it is also a versatile method of preparing ultrafine or nano nickel particles, which can obtain uniform and well-dispersed metal particles; however, it requires a higher reaction temperature and a longer reaction time versus chemical reduction. Egde *et al.* [24] prepared monodispersed 135-nm nickel particles according to the polyol process using PVP as a protective agent. Smaller size monodispersed nickel particles (30 nm) were also made from $Ni(OH)_2$ in ethylene glycol and PVP using Pd or Pt as nucleating agents. Park *et al.* [27] produced nickel particles from the reduction of nickel hydrazine complexes in aqueous solution. The average particles size could be controlled from 150 to 380 nm by adjusting the reaction molar ratio and temperature.

To investigate the physical and chemical properties of metal nanoparticles, especially the size-dependent properties, precise control of the particle size is essentially required. However, the efforts on this issue are not enough. Therefore,

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in this study, nickel nanoparticles were prepared by reduction of a nickel salt with hydrazine hydrate in ethylene glycol. The method preserves the respective advantages of the polyol process and the chemical reduction method in aqueous solution. PVP was employed as surfactant to prevent agglomeration of particles and controlled the particle size from 46 nm to 103 nm with varying the amount used. A new scheme of the reaction mechanism was also promoted in this research.

2. Experimental

2.1. Materials

Nickel chloride ($NiCl_2 \cdot 6H_2O$, A. R.); polyvinylpyrrolidone (PVP K30, A. R, average molecular weight 40000); Sodium hydroxide (NaOH, A. R.); ethylene glycol (EG, A. R.) were purchased from Beijing Chemical Reagent Company, China. All regents were used as received without further purification.

2.2. Preparation of monodispersed nickel nanoparticles

A typical experiment was performed as follows. A homogeneous solution was formed after dissolving NaOH solution in hydrazine hydrated ($N_2H_4 \cdot H_2O$) (solution A). Another solution was formed after dissolving nickel chloride ($NiCl_2$) in absolute ethylene glycol (EG), which contained PVP polymer for particle protection. The color of the solution was green (solution B). Solution A was added to a 3-necked reaction flask with a capacity of 250 mL and was agitated for 10 min. Then, adding solution B into A, it was agitated continuously at 60°C for 30 min. After a few minutes, the solution turned black in color, which was believed to indicate the formation of nickel particles. After mixing and heating, the solutions became supersaturated and precipitated. The precipitates were separated from the mother liquor by centrifugal separation, and washed repeatedly with distilled water and acetone until the pH was 7. The powder was finally dried in vacuum at 40°C. Grey-black nickel nanoparticles were obtained.

2.3. Characterization

The nickel nanoparticles were characterized by X-ray diffraction using Cu K_α radiation with graphite monochromator. The size and morphology analyses and selected area electron diffraction (SAED) of nickel particles were performed using transmission electron microscopy (TEM, Hitachi H-800 with accelerating voltage of 150 kV) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2010).

3. Results and discussion

3.1. Structural characterization

The formation of nickel nanoparticles is confirmed by XRD studies (Fig. 1(a)). It can be seen that the diffraction peaks at (111), (200), (220), (311), and (400) pertain to the face centered cubic (fcc) lattice of nickel. The value of the lattice constant calculated from the XRD pattern was found to be 3.5220 nm, which is within the error of the reported value with a = 3.5240 nm given by JCPDS file No. 65-2865. The corresponding selected area electron diffraction (SAED) pattern is indicated in Fig. 1(b). Five fringe patterns with plane distances of 0.203, 0.176, 0.125, 0.106, and 0.102 nm from inner to outer can be observed. These correspond to the (111), (200), (220), (311), and (222) diffraction planes of pure fcc nickel. In accordance with the above two analyses, it can be concluded that the particles prepared in this study were pure nickel of fcc structure. The average particle size

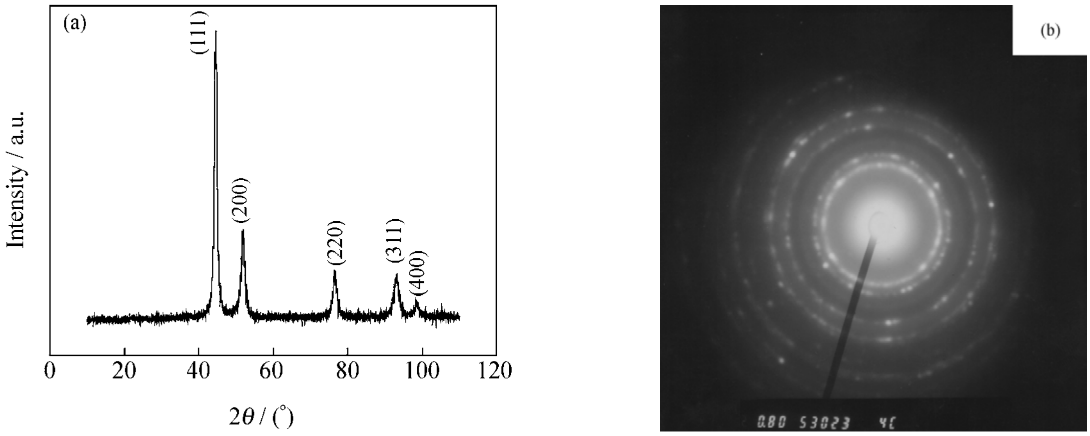

Fig. 1. XRD pattern (a) and electron diffraction pattern (b) of nickel nanoparticles (Ni^{2+} concentration at 0.1 mol/L, the molar ratio of N_2H_4 to Ni^{2+} at 8.0, the molar ratio of NaOH to Ni^{2+} at 1.0, the mass ratio of PVP to $NiCl_2 \cdot 6H_2O$ at 4.0, and the reaction temperature at 60°C).