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Electrohydrodynamic atomization (EHDA) assisted wet chemical synthesis of nickel nanoparticles

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ABSTRACT

In this study nickel nanoparticles were prepared via chemical reduction of nickel acetate using sodium borohydride using electrohydrodynamic atomization (EHDA) technique. This technique was used to spray a finely dispersed aerosol of nickel precursor solution into the reductive bath. Obtained particles were characterized by means of X-ray diffraction (XRD), UV–Visible spectroscopy, and transmission electron microscopy (TEM). Results confirmed the formation of nickel nanoparticles and showed that applying EHDA technique to chemical reduction method results in producing smaller particles with narrower size distribution in comparison with conventional reductive precipitation method.

1. Introduction

In recent years, transition metal nanoparticles have attracted much interest due to their unique electrical, optical, chemical, and magnetic properties which makes them useful in various fields such as microelectronics, optoelectronics, catalysis, and magnetic information storages [1,2]. Due to high dependence of physical and chemical properties of metal nanoparticles on their shape and size distribution [3–5], extensive studies have been done on controlling these parameters in various synthesis methods. However, achieving nanoparticles with smaller size and narrow size distribution is still a challenging issue. Among transition metal nanoparticles, nickel nanoparticles have attracted considerable attention which is mostly due to their magnetic and catalytic properties [4,6–8]. Nickel nanoparticles have a wide range of applications such as in rechargeable batteries [5], chemical catalysts [9], and multilayer capacitors [9,10]. Various chemical methods have been developed for the preparation of Ni nanoparticles such as chemical vapor deposition [11], electroless plating [12], polyol process [13], hydrothermal method [14], wet chemical reduction [15], and microemulsion method [16]. In comparison, chemical reduction method has many advantages. It is a simple, inexpensive and the most versatile method for preparing metallic nanoparticles. In chemical reduction method, metal ions in metal salt solution are reduced to metal particles by a reducing agent. Due to high tendency of transition metal nanoparticles to oxidation and agglomeration, using appropriate surfactants or capping agents are inevitable [17,18]. However, oxidation of metal nanoparticles during their synthesis cannot be completely avoided [19]. Shape and size distribution of particles in chemical reduction method can be easily controlled by adjusting synthesis parameters, e.g. solvent composition, reactants concentration, reaction temperature, surfactant type and concentration [20–23]. One of the most effective parameters on particle size in this synthesis method is the size of reactant droplets. The droplets with smaller size contain fewer reactant ions which lead to generation of smaller nanoparticles in reductive bath. However, decreasing droplet size by simple pouring or dripping of solutions in conventional chemical reduction method is limited due to technological reasons. Recently the advanced technique of electrospray has introduced new routes to nanotechnology. Electrospraying, which is also referred as electrohydrodynamic atomization (EHDA), is a technique which uses strong electric fields for dispersing liquids into fine droplets. In this technique, the liquid flows out of a highly charged capillary nozzle and is forced to be dispersed into fine droplets by electric field. Due to repulsive forces between charged droplets, they are self dispersing in space which prevents droplets coagulation. Electrospray droplets have narrow size distribution and depending on electric field magnitude, their size can range from hundreds of micrometers down to several tens of nanometer [24,25]. EHDA technique can be easily applied to chemical reduction method. By electrospraying the metal precursor solution into reductive bath, very fine nanoparticles with narrow size distribution can be obtained. Recently, Valvo et al. reported the synthesis of tin nanoparticles and Sn–Co compound for Li-ion batteries via electrospraying [26,27]. The precursor droplets size, their velocity and dispersion can be controlled by adjusting EHDA parameters such as voltage magnitude and the flow rate of the liquid [24–27].

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In this paper, we present a novel wet chemical reduction method with the assistance of electrospraying technique to produce fine nickel nanoparticles with narrow size distribution. We also investigated the effects of electrospraying on decreasing the size of obtained Ni nanoparticles.

2. Experimental

2.1. Materials

Nickel acetate ($Ni(Ac)_2{\cdot}4H_2O$), sodium borohydride ($NaBH_4$), cetyltrimethylammonium bromide (CTAB), methanol and butanol were purchased from Merck and used without further purification.

2.2. Synthesis

Nickel nanoparticles were synthesized by reduction of Ni^{2+} cations dissolved in the sprayed droplets of nickel precursor solution. Different solvents were tried as precursor/reductive solutions medium in order to achieve suitable solutions for electrospraying and reduction processes. Butanol and methanol were chosen as synthesis media due to their high stability in electrospray. No water is used because it prevents forming a stable electrospray due to its high electrical conductivity and also it causes the formation of nickel hydroxide instead of Ni nanoparticles. As precursor solution, nickel acetate was dissolved in a mixture of methanol/butanol with volume ratio of 1:1. Concentration of solution was 0.12 M. For preparing reductive bath, cationic surfactant CTAB was dissolved in methanol and after stirring, $NaBH_4$ was added to the solution as a reducing agent. Due to the spontaneous reaction of $NaBH_4$ with methanol, about 40 wt% more than calculated stoichiometric amount of $NaBH_4$ was added to the bath to ensure complete reduction of precursor. The precursor solution was injected into the reductive bath through an electrified capillary nozzle with inner diameter of 0.6 mm using a syringe pump at a constant flow rate of 30 ml/h. A ring with diameter of 2 cm made of stainless steel used as a counter electrode. Capillary nozzle was fixed at the center of ring with no distance between the end of the nozzle and ring center. The schematics of the experimental set-up are shown in Fig. 1. In order to achieve EHDA in multi-jet mode, a high voltage of 6.3 kV was applied between the nozzle and ring. Dripping mode obtained by applying no voltage to produce Ni nanoparticles by simple reductive precipitation. The experiments were carried out in air and at room temperature. Images of two different modes of spraying used in this study are shown in Fig. 2. Droplet and jet diameters were estimated to be about 2000 μm (2 mm) and 30–40 μm, respectively. A strong black color was observed immediately after spraying started, which is corresponded to the reduction of nickel ions into metallic nickel. Reduction reaction could be expressed as:

$$\begin{aligned}Ni(CH_3COO)_2 + 2NaBH_4 \rightarrow Ni\downarrow + 2CH_3COONa\downarrow \\ + 2BH_3\uparrow + H_2\uparrow\end{aligned} \quad (1)$$

Precipitates were separated from solution by centrifugation, washed with methanol and acetone several times and dried at 70 °C.

2.3. Characterization

Obtained particles were characterized by X-ray diffraction using a D-5000 X-ray diffractometer with Cu-Kα radiation (k = 0.154178 nm). Particles shape and size were studied by Philips EM208S (100 kV) Transmission Electron Microscopy. UV–Vis

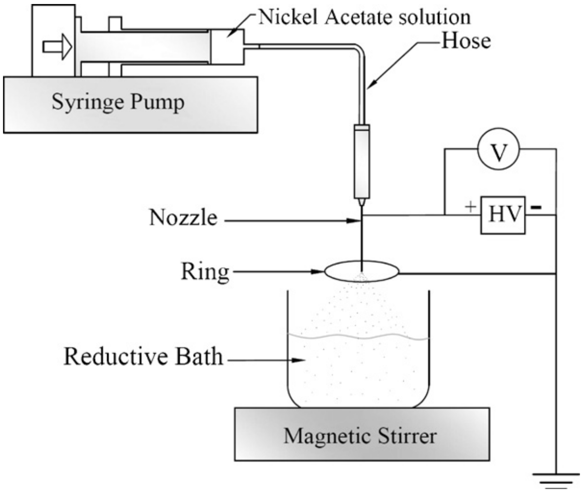

Fig. 1. Schematics of experimental set-up.

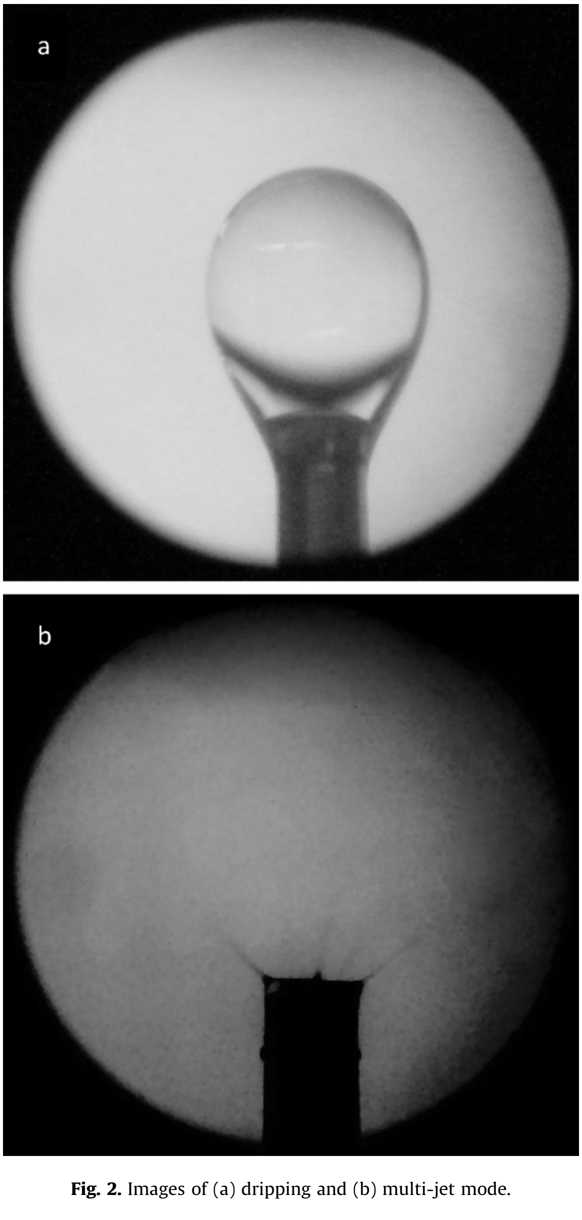

Fig. 2. Images of (a) dripping and (b) multi-jet mode.

spectra of nanoparticles were recorded by double-beam Shimadzu UV-2450 Scan UV–Vis spectrophotometer.

3. Results and discussion

Morphology of synthesized Ni nanoparticles was investigated by TEM and results are shown in Fig. 3. It can be seen that particles produced in multi-jet mode (Fig. 3b) are spherical and have a narrow size distribution with an average size of 2–4 nm. Although particles are agglomerated, they are still discernable and no big particle is observed. Particles produced in dripping mode (Fig. 3a) are larger and less homogeneous in size distribution and shape in comparison with particles produced in multi-jet mode. Size of the particles in dripping mode is in the range of 10–20 nm. As it was expected, the results show that applying electric field to dripping mode clearly affects the morphology of nanoparticles and yields a homogeneous distribution of smaller particles. SAED pattern recorded from these nanoparticles is consistent with fcc structure of crystalline nickel (inset at a).

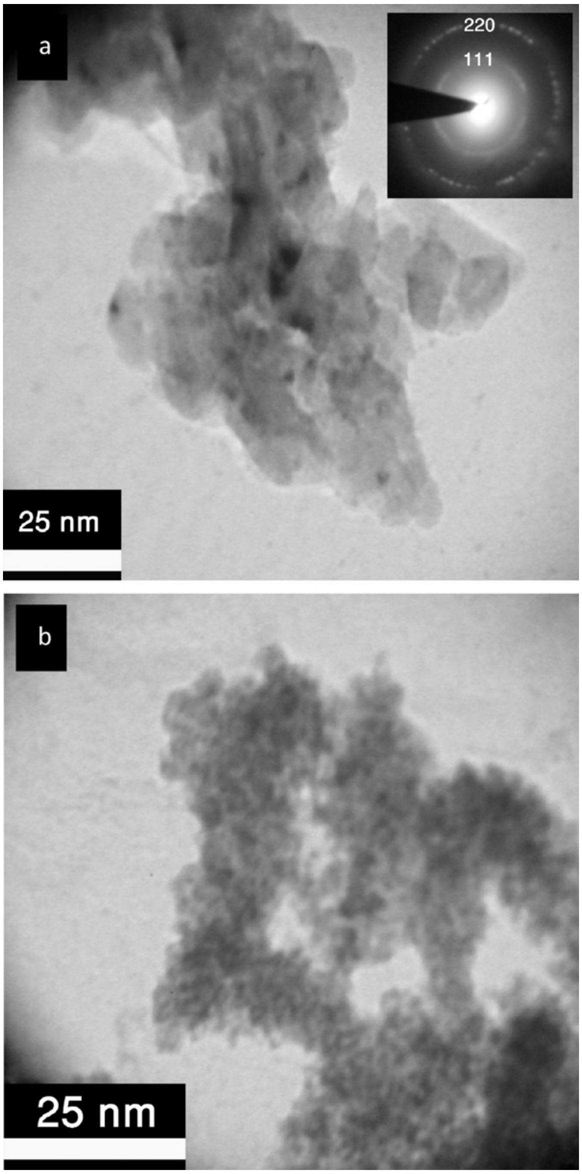

Fig. 3. TEM image of nickel nanoparticles synthesized in (a) dripping and (b) multi-jet mode and SAED pattern of particles (inset at a).

X-ray diffraction patterns of synthesized nanoparticles are shown in Fig. 4. No crystalline peak is detectable in diffraction patterns of samples which is the typical feature of the amorphous materials. This can be attributed both to the effects of reducing agent and high surface to volume ratio of particles produced with the assistance of electrospraying. As it have been reported earlier [21,28], reduction precipitation of metal nanoparticles by $NaBH_4$ generally leads to generation of weakly ordered particles with small sizes and large surface areas. This is due to the fast reducing nature of $NaBH_4$ which causes instant formation of solid particles. On the other hand, as indicated in TEM images, using EHDA is effective in reducing particles size which results in increasing the contribution of surface atoms and enhancing the surface reactivity. Thus, formation of surface amorphous oxides and residual contaminants are expected during the processing of materials. Similar results have been reported recently by Valvo et al. for tin nanoparticles [26] and Sn–Co compound [27] produced via electrospraying. From these results it can be concluded that using electrospraying in reductive precipitation and $NaBH_4$ as reducing agent result in generating small nanoparticles with increased surface areas which leads to amorphization of collected precipitates.

UV–Visible spectroscopy of collected powders dispersed in methanol was also carried out to confirm the formation of nickel nanoparticles. Fig. 5 shows the UV–Visible absorption spectrum of synthesized Ni nanoparticles produced in multi-jet mode. The

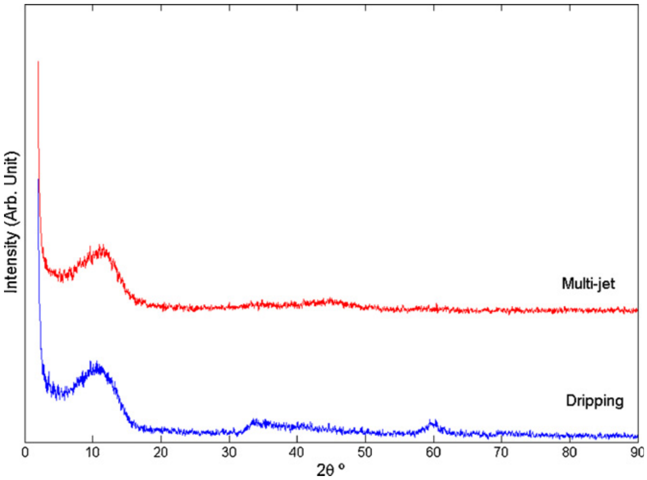

Fig. 4. XRD patterns of nickel nanoparticles synthesized in dripping and multi-jet mode.

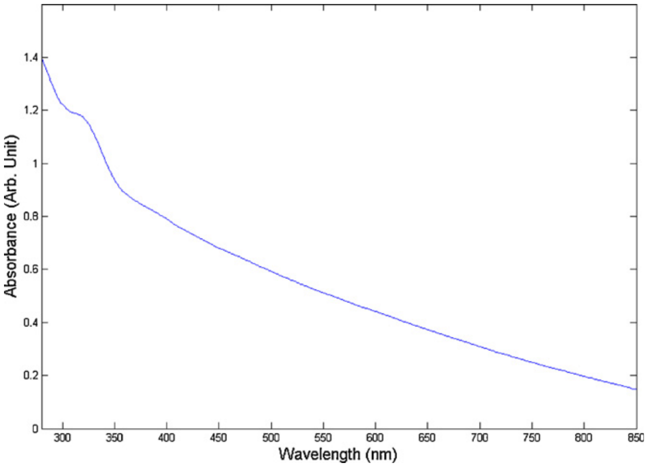

Fig. 5. UV–Visible absorption spectrum of Ni nanoparticles synthesized in multi-jet mode dispersed in methanol.

absorption band of particles produced in dripping mode was similar to Fig. 5. Based on Mie's theory, Creighton and Eadon [29] have reported the calculated optical spectrum of various metal nanoparticles in water and in vacuum and Ni nanoparticles exhibited Surface Plasmon Resonance (SPR) absorption between 300 and 400 nm. It has also been reported that ethanol dispersion of Ni nanoparticles stabilized with dodecylamine and polyvinylpyrrolidone exhibited SPR absorption around 300–350 nm [30], and SPR absorption of Ni nanoparticles in ethylene glycol was 355 nm [31]. As shown in Fig. 5, SPR absorption peak appeared at about 320 nm which according to reports is consistent with the formation of Ni nanoparticles.

4. Conclusions

In this paper, we introduced a novel versatile technique for synthesizing nanoparticles by chemical reduction method, which was successfully used to produce fine nickel nanoparticles. Using electrohydrodynamic atomization we could decrease the size of obtained particles from 10–20 nm down to 2–4 nm and increase the homogeneity of particles size distribution.

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