



Surfactant-Free Nonaqueous Route for Preparation of Metallic Nickel Nanoparticles

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Abstract: In this study, we report a simple nonaqueous technique for preparation of metallic nickel nanoparticles (MNN). Organic alcohols were used as solvent whereas Nickel acetyl acetonate [Ni(acac)₂] was applied as nickel precursor. The product was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that MNN exhibits good distribution and weak agglomeration specially when hexanol was utilized as solvent.

Keywords: Nonaqueous; Free-surfactant; Nickel; Nanoparticles

Introduction

Powder synthesis with size, shape and size-distribution control has been a major part of colloid chemistry for decades and nanoscience research has so far been mostly pertained to development and synthesis of nanopowders and nanostructures [1]. Metal nanoparticles have attracted much attention during the last two decades due to their unique properties and wide varieties of potential applications in various areas [2]. Among them, MNN has recently engrossed practitioners due to its potential applications in magnetic sensors, memory devices, conducting materials and catalysis [3]. Although some techniques such as laser ablation and evaporation have been applied to fabrication of metallic nanoparticles, however expensive instrument costs, complicated vacuum operation and low fabrication rate associated with the vacuum-based techniques are still major concerns [2]. Therefore, a number of different solution based chemical methods have been developed to prepare metal nanoparticles [3]. Some methods such as thermal decomposition [4, 5], supercritical alcohol [2], gelatin induced reduction [6], thermolytic reduction [3] and electroless deposition [8] have also successfully applied for MNN production. In many of them a surfactant has been used as capping agent for controlling the size of nanoparticles. Niederberger introduced a general method for synthesis of inorganic nanomaterials using organic chemistry in many reports [1, 7, 9, 10, 11]. This method called nonaqueous or nonhydrolytic pathway has some advantages in contrast to aqueous routes. This may be included surfactant-free fabrication, high crystallinity of product, exclusion of water and its dual role as solvent and ligand (mainly in metal oxide synthesis which causes some complexities), and introducing a size and shape-controlled technique for nanoparticles fabrication [1, 7]. Surfactant-assisted approaches undoubtedly show outstanding control over the growth of nanoparticles [12] by capping their surface providing several advantages such as low agglomeration, good dispersibility in organic

solvents, and the potential to tailor the surface properties [7]. However, toxicity of the nanoparticles resulted from surfactants bound to the nanoparticle surface and reduction in accessibility of particle surface are major problems specially in gas sensing and catalysis applications [7]. In nonaqueous synthesis, organic solvent other than its solvent role could act as a surfactant due to the fact that organic structure could cap the particles [1, 9, 11]. Indeed, this property minimizes the amount of surfactant. Moreover, nonaqueous synthesis could fabricate final product by direct reaction (for example omitting calcination step in metal oxide preparation which is generally could increase the particle size). In mentioned reports, metal oxides were mainly produced. Here, we describe a novel nonaqueous method for fabrication of MNN. The importance of the present work is that upon such chemistry, production of nickel oxide is more probable.

Experimental

The synthesis of the Ni nanoparticles was carried out using commercially available reagents of Merck company products. Ni(acac)₂ was selected as the Ni precursor. Benzyl alcohol, 1-hexanol and ethylene glycol were utilized as solvents. All chemicals were used as purchased without any further purification. The morphology and particle size of the as-synthesized Ni nanoparticles were investigated using scanning electron microscopy (SEM, Vega, SE detector, operated at 15 kV). The crystalline phase of the Ni nanoparticles was characterized using wide-angle X-ray diffraction (XRD, Philips, PW3710, λ (CuK α) = 1.54 Å). Table 1 summarizes the experimental details for each one of the prepared samples. In a typical procedure (e.g. sample S2 of Table 1) a pre-determined weight of Ni(acac)₂ was dissolved in desired amounts of solvent (benzyl alcohol:hexanol, 1:1). After stirring at 70°C for about 1h, a homogenous green solution was made. Then, the homogenous solution placed in Teflon lined stainless steel autoclave which was

filled up to 75% of the total volume, sealed carefully and placed in a furnace which was preheated to 190°C. The autoclave was kept in the furnace for about 24h at 190°C. During this step, a black precipitate was appeared indicating the presence of metallic nickel. After that, autoclave was pulled out of the furnace and cooled down naturally in air. Finally, the black precipitate was filtered and rinsed 5 times with absolute ethanol and dried in oven at 50°C for 24h.

Table 1. Sample Condition

Sample	Benzyl alcohol	1-Hexanol	Ethylene glycol
S1	only	-	-
S2	1	1	-
S3	1	4	-
S4	-	only	-
S5	-	-	only

Results and Discussion

The XRD patterns of the black precipitate for sample 1 and sample 4 are represented in Fig. 1a and Fig. 1b, respectively. All the diffraction peaks could be indexed to cubic ($a=3.523 \text{ \AA}$) Ni according to standard JCPDS card No.04-0580. From Fig. 1, one could be observed is the high crystallinity of MNN which is in consistent with previous reports [7, 10]. By applying the Debye–Scherrer formula $D= k\lambda/(\beta \cos\theta)$, where D is the main crystallite size, λ is the wavelength of the X-ray radiation (1.54 \AA), k is a constant to be taken as 0.9, β is the full width at half maximum height of the peak (FWHM) and θ is the diffraction angle, resulted in 25 nm crystallite size for S1 and 19nm crystallite size for S4. Therefore nanocrystalline metallic nickel was successfully prepared by organic solvents. The SEM images of all samples are represented in Fig. 2. The effect of benzyl alcohol on MNN could be observed in Fig 2a. It is obvious that benzyl alcohol effectively controlled the size of MNN by capping them. Moreover, it seems that MNN form a spherical morphology in organic solvents such as benzyl alcohol. However, the size of MNN is more than 100nm (and less than 200nm) which is a broad size distribution. Therefore in this case benzyl alcohol shows a good solvent role but it is not a strong surfactant. Fig 2b shows a better control of organic solvent over controlling size of MNN. Most of the particles in Fig. 2b are less than 150nm in size and they exhibit a better distribution. By applying more hexanol to system, control over size and size distribution will enhance. This fact could be understood comparing Fig 2b and Fig 2c. In Fig. 2c the size of all particles are less than 100nm (with an average of 85nm). There is not much difference between Fig 2c and Fig 2d(less than 5nm in average). We could describe such observation as follow. Ni(ac ac)₂ is surrounded by alcohol molecules in the solution. When the temperature increases above 180-190°C, the Ni(ac ac)₂ will brake to its components(Ni and the rest organic ligands) and Ni nucleates formed(which cause changing the colour of

solution to black). In the mean time, organic solvent acts as a surfactant and controls the growing of Ni nucleates by capping them and preventing from agglomeration. Despite the spatial conformation of hexanol, it can act more effective than benzyl alcohol. Both S4 and S5 are effective routs for fabrication of MNN. However it is clear that the length of organic solvent is very important in MNN fabrication. S5 was selected for this study where ethylene glycol is solvent. The size of MNN in Fig. 2e is more than 200nm. This could be related to the short length of ethylene glycol chain. As an extra point, it should be noted that the conditions of experiment are sensitive. For example, in S4, the presence of small amount of aqueous phase could result in totally different result. In such case, nickel hydroxide will produce which after calcination transforms to nickel oxide nanowall as shown in Fig. 3.

Conclusion

In summary, MNN were successfully produced by nonaqueous method assisting organic solvents as surfactant. The XRD pattern showed a high crystallinity of MNN and a main grain size less than 25nm. SEM images of MNN in all five samples introduced a spherical morphology of MNN. The role of hexanol was excellent as size controlling agent. Benzyl alcohol exhibited a middle role while ethylene glycol showed a poor effect over controlling MNN size because of its short length.

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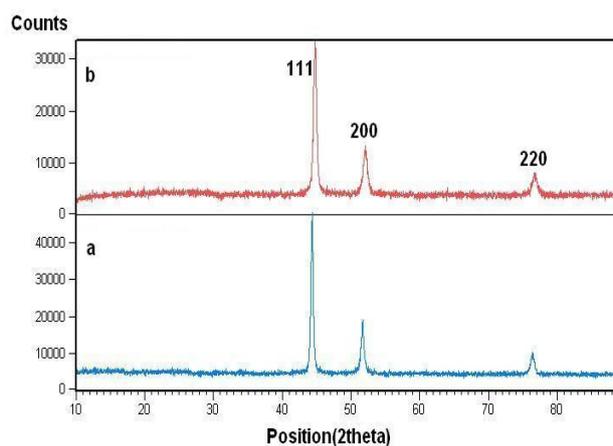


Fig.1 . The XRD Pattern of (a): S1 and (b): S4.

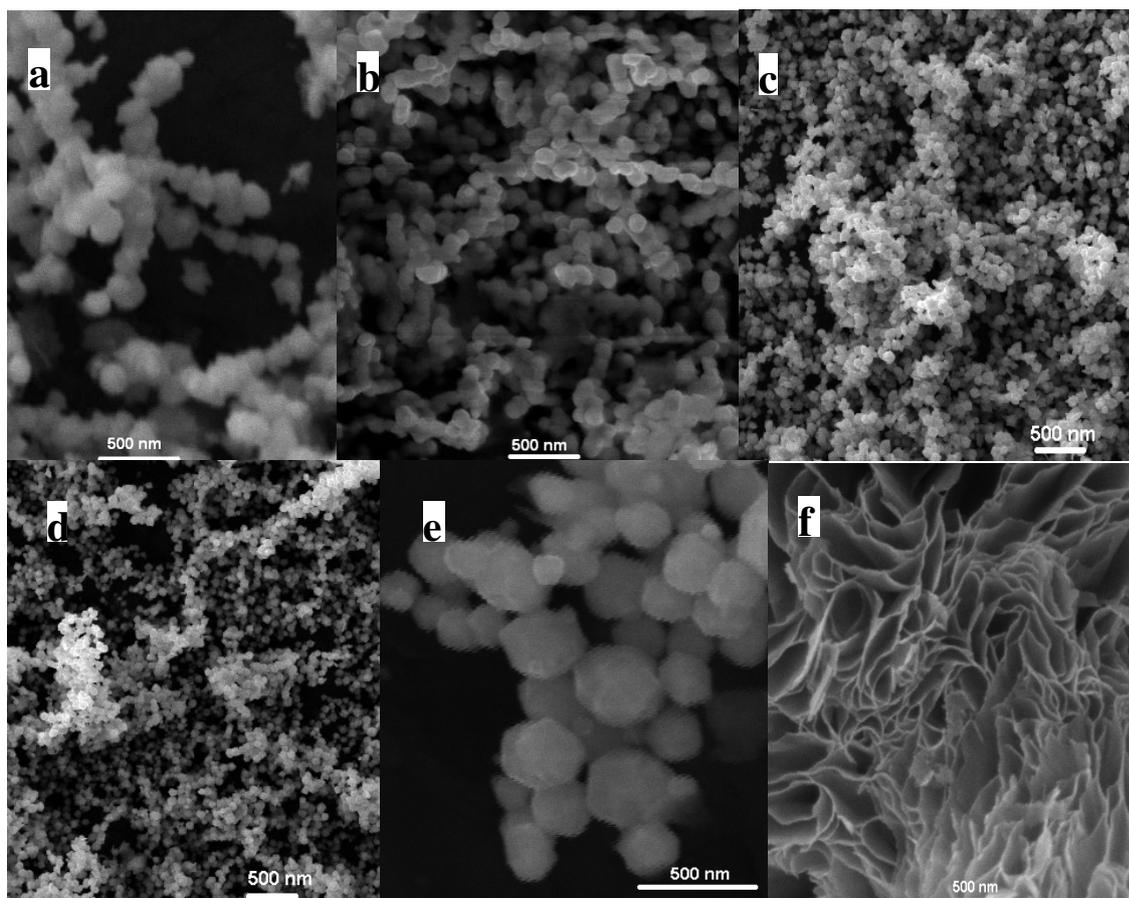


Fig. 2 (a): S1, (b): S2, (c):S3, (d) S4, (e):S5 and (f):NiO nanowall.

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