Journal of Alloys and Compounds 635 (2015) 118–123

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Effect of experimental factors on magnetic properties of nickel nanoparticles produced by chemical reduction method using a statistical design

M.R. Vaezi [a], M. Barzgar Vishlaghi [b,*], M. Farzalipour Tabriz [b], O. Mohammad Moradi [c]

[a] Division of Nanotechnology and Advanced Materials, Materials and Energy Research Center, Karaj, Iran
[b] Graduate School of Science and Engineering, Koç University, Rumeli Feneri Yolu, Sarıyer, Istanbul 34450, Turkey
[c] Faculty of Engineering and Natural Sciences, Sabancı University, Tuzla/Orhanli, Istanbul 34956, Turkey

ARTICLE INFO

Article history:
Received 14 January 2015
Accepted 14 February 2015
Available online 21 February 2015

Keywords:
Nanostructured materials
Chemical synthesis
Magnetization
Magnetic measurements
Transmission Electron Microscopy

ABSTRACT

Nickel nanoparticles were synthesized by chemical reduction method in the absence of any surface capping agent. The effect of reactants mixing rate and the volume ratio of methanol/ethanol as solvent on the morphology and magnetic properties of nickel nanoparticles were studied by design of experiment using central composite design. X-ray diffraction (XRD) technique and Transmission Electron Microscopy (TEM) were utilized to characterize the synthesized nanoparticles. Size distribution of particles was studied by Dynamic Light Scattering (DLS) technique and magnetic properties of produced nanoparticles were investigated by Vibrating Sample Magnetometer (VSM) apparatus. The results showed that the magnetic properties of nickel nanoparticles were more influenced by volume ratio of methanol/ethanol than the reactants mixing rate. Super-paramagnetic nickel nanoparticles with size range between 20 and 50 nm were achieved when solvent was pure methanol and the reactants mixing rate was kept at 70 ml/h. But addition of more ethanol to precursor solvent leads to the formation of larger particles with broader size distribution and weak ferromagnetic or super-paramagnetic behavior.

1. Introduction

Transition metal nanoparticles have attracted a lot of interest in recent years since they have intriguing physical and chemical properties which makes them a promising candidate in various applications [1]. Among transition metal nanoparticles, nickel nanoparticles have attracted considerable attention which is mostly due to their magnetic and catalytic properties [2–5]. Nickel nanoparticles have a wide range of applications in rechargeable batteries [6], chemical catalysts [7], supercapacitors [8], etc. Various chemical methods have been developed for preparation of Ni nanoparticles such as chemical vapor deposition [9], electroless plating [10], polyol process [11], hydrothermal method [12], wet chemical reduction [8] and microemulsion method [13]. Chemical reduction method has many advantages over other synthesis methods. It is a simple, inexpensive and very versatile method for preparing the metallic nanoparticles. In the chemical reduction method, metal ions in metal salt solution are reduced to metal particles by reducing agent. Due to easily oxidizing nature of transition metal nanoparticles and their high tendency to agglomeration, it is inevitable to use the suitable surfactants or capping agents [16,17]. However, presence of the surfactants can change the physical properties of produced nanoparticles [14,15] and leads to the formation of stable solutions which makes the precipitation and separation of nanoparticles more difficult [16]. In magnetic nanoparticles, as the size of particles is reduced to a critical amount, they become single magnetic domain. In this case, the thermal energy overcomes the magnetic anisotropy energy barriers of single domain particles and results in super-paramagnetic behavior [17]. Super-paramagnetic nanoparticles have proven to be ideal for many biomedical applications such as magnetic resonance imaging, cancer treatments, biological and chemical sensing and targeted drug delivery [18–21]. Due to the strong dependence of physical and particularly magnetic properties of metal nanoparticles on their shape and size [22,23], it is important to control synthesis parameters to achieve desirable morphology and size distribution. It has been shown that the parameters such as solvent composition, reactants concentration, reaction temperature and surfactant concentration can be easily adjusted in the chemical reduction method [24–27]. The conventional approaches for optimization of process variables require large number of experiments

* Corresponding author. Tel.: +98 9144453947.
E-mail address: mahsabarzgar@gmail.com (M. Barzgar Vishlaghi).

http://dx.doi.org/10.1016/j.jallcom.2015.02.112
0925-8388/

which would be very expensive and time consuming. However, a statistical experimental design can provide an appropriate model for optimizing the process which decrease the number of examinations and evaluate the influence of variables interactions on the process outcome [12,28]. Some researchers investigated the relationship between process variables and the yield of nickel nanoparticles [29] or their size [12] by design of experiment. However, no systematic study has been done yet for investigating the effect of variables such as the solvents ratio or the rate of adding the precursor solutions to each other, on the magnetic properties of nickel nanoparticles. In previous study [30], we synthesized the metallic nickel nanoparticles using electrohydrodynamic atomization (EHDA) assisted chemical reduction method, which is a useful method for producing fine nanoparticles [31]. It has been shown that the atomization of nickel precursor into the reductive bath was very efficient for decreasing the size of nickel nanoparticles. It was also found out that separation of fine nanoparticles from the precursor solution is difficult due to their high stability in presence of the surfactant [30]. Thus, in present study, we synthesized nickel nanoparticles by reduction of nickel acetate precursor with sodium borohydride without using any surface capping agent.

Response surface methodology (RSM) is an experimental design technique that uses mathematical and statistical techniques to analyze the influence of independent variables (inputs) on a specific dependent variable (response). RSM is an effective alternative to the factorial design. Central composite design (CCD) which is a widely used form of RSM, was used to investigate the effect of the pouring rate of metal precursor into the reductive bath and solvents ratio on the morphological and magnetic properties of nickel nanoparticles. The use of CCD allows determination of the effects of various parameters and also the interrelation between them simultaneously [32].

Table 1
Levels of variables and coded levels in CCD experiment design for two variables and three central points.

*L*2	*L*1	*X*1	*X*2	Run
−1	−1	−0.7072	−0.7072	P6
1	−1	0.7072	−0.7072	P1
−1	1	−0.7072	0.7072	P2
1	1	0.7072	0.7072	P7
0	−α	0	−1	P3
0	α	0	1	P4
−α	0	−1	0	P8
α	0	1	0	P9
0	0	0	0	P5
0	0	0	0	P11
0	0	0	0	P10

2. Experimental

Nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), sodium borohydride ($NaBH_4$), methanol and ethanol were purchased from Merck and used without further purification. Nickel nanoparticles were synthesized by reduction of Ni^{2+} cations dissolved in nickel precursor solution. Different solvents were tried as precursor/reductive solutions medium in order to achieve suitable solutions for reduction processes. Methanol and ethanol were chosen as synthesis media due to the high solubility of reactants in both solvents. No water was used in the solvent in order to avoid the formation of nickel hydroxide. Concentration of nickel salt solution was 0.42 M and its volume was 30 ml. For preparing the reductive bath, $NaBH_4$ was added to the methanol solution as a reducing agent. Due to the spontaneous reaction of $NaBH_4$ with methanol, about twice more than calculated stoichiometric amount of $NaBH_4$ was added to the bath to ensure complete reduction of precursor. The precursor solution was dripped into the reductive bath using a syringe pump with various pumping rates. The experiment setup was the same as the previous work [30], but no high voltage was applied. Volume ratio of methanol/ethanol and the rate of the mixing reactants or dripping rate were chosen as process variables.

For studying the effect of variables on the morphology and magnetic properties of nickel nanoparticles, rotatable central composite design with two variables and three central points were used. Variable levels ($-\alpha$, $+\alpha$) are chosen as (0, 100)% for methanol volume and (20, 120) ml/h for dripping rate, respectively.

The order of runs is chosen randomly to minimize the effects of systematic errors on our observations. Experiment design and experiment conditions for 11 runs are listed in Tables 1 and 2, respectively. The results were used to develop appropriate empirical equations in form of second order polynomial. The statistical calculations are done using SAS JMP 10 package.

The experiments were carried out in air and at room temperature. A strong black color was observed immediately after dripping started, which is corresponded to the reduction of nickel ions into metallic nickel. Precipitates were separated from solution by centrifugation, washed with methanol and acetone several times and dried at 70 °C. The obtained particles were characterized by X-ray diffraction using a Siemens D-5000 X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm). The particles shape and size were studied by Philips EM208S (100 kV) Transmission Electron Microscope (TEM) and size distribution was examined by Microtrac, Nanotrac Wave Dynamic Light Scattering (DLS) technique. The magnetic properties of nickel nanoparticles were investigated using 4 inch, Daghigh Meghnatis Kashan Vibrating Sample Magnetometer (VSM) apparatus under the maximum magnetic field of 8 kOe.

3. Results and discussion

There was no crystalline peak in the X-ray diffraction patterns of samples. XRD pattern of a typical sample P9 is shown in Fig. 1. This is in agreement with previous work [30] which corroborates the weakly ordered, small size and large surface areas of nanoparticles produced by reduction precipitation using $NaBH_4$ due to its fast reducing nature [28,29]. A broad diffraction peak around $2\theta = 45°$ is observable in Fig. 1 which is near the characteristic (1 1 1) peak position of metallic nickel. This indicates that the sample consists of fine metallic nickel particles.

Morphology of samples was investigated by TEM. Fig. 2 shows TEM image of sample P9 and its Selected Area Electron Diffraction (SAED) pattern. It can be seen that the sample consists of semi-spherical particles with size range between 20 and 50 nm. Agglomeration of particles was expected due to the high surface energy of fine particles and the absence of surfactant in synthesis media.

Table 2
Experiment conditions, DLS results and magnetic properties of samples.

Run	Methanol vol.%	Dripping rate (ml/h)	Minimum particle size (nm)	Maximum particle size (μm)	Median (μm)	*Hc* (Oe)	Maximum magnetization (emu/g)	M_r (emu/g) × 10^{-3}
P1	85.36	34.64	170	0.81	0.64	13.0	0.240	0.40
P2	14.64	105.36	480	5.5	5	19.5	0.011	0.04
P3	50.00	20.00	171	1.3	1.2	11.5	0.077	0.10
P4	50.00	120.00	120	1.1	1	6.0	0.061	0.05
P5	50.00	70.00	537	2.2	1.6	4.2	0.055	0.05
P6	14.64	34.64	818	3.8	3	5.0	0.052	0.04
P7	85.36	105.36	80	0.88	0.73	4.0	0.200	0.10
P8	0.00	70.00	120	1.6	1.5	7.1	0.053	0.05
P9	100.00	70.00	144	0.88	0.67	6.8	0.250	0.21
P10	50.00	70.00	578	2.3	1.7	4.2	0.053	0.03
P11	50.00	70.00	438	1.8	1.3	4.6	0.056	0.08