# Synthesis of nickel nanoparticles with fcc and hcp crystal structures

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Nickel nanoparticles have been synthesized using nickel nitrate, vegetable oil and sucrose. Ethanol has been used as a solvent since the heat of reaction shows the destabilization of nickel particles if water is present in the synthesis mixture. Nickel with fcc phase is obtained by reduction with sucrose followed by stabilization using vegetable oil. Nickel or possibly nickel carbide with hcp structure is obtained by treatment with a mixture of oleylamine and methanol. The fcc and hcp crystal structures have been characterized by XRD. The calcination of nickel nanoparticles at 450 °C results in the sintering of nickel nanoparticles, thereby increasing the crystallite size. The scanning electron micrograph reveals that the particle size is in the range of 5 – 58 nm for fcc-Ni nanoparticles calcined at 450 °C for 10 min.

**Keywords:** Nanomaterials, Crystal structure, Nickel, Heat of reaction

Metallic nickel can exist in two crystalline forms with fcc[1] and hcp[2] crystal structure. Almost all common nickel powders are ferromagnetic substances with fcc crystal structure. Among the various kinds of metal nanoparticles, the preparation of some metal nanoparticles such as nickel, copper, and iron, is relatively difficult because they undergo easy oxidation. Nickel nanoparticles have attracted attention because of their applications as catalysts[3] and as magnetic materials[4]. The usual preparation methods have been carried out in organic media to avoid the formation of nickel oxide or hydroxide[5, 6]. There are reports on the preparation of Ni and Co nanoparticles; nevertheless these methods use organometallic precursors[7], reverse micelles[8] and templates[9]. Many of the applications are size dependant[10] and thus control of particle size is essential. Various physical and chemical methods, such as the pyrolysis of precursors, sputtering and milling were employed to produce nanoscale magnetic materials[11, 12]. The high surface energy of these particles makes them extremely reactive, and most nanoparticles undergo aggregation without protection or passivation of their surfaces[13-18]. Some of the commonly used methods for surface passivation include protection by thiol-functionalized organics[15], encapsulation in the water pools of reverse microemulsions[19], dispersion in polymeric matrixes[20] and passivation by ligand systems such as oleic acid, oleyl amine[21, 22] and alkylphosphine[23, 24].

In the last two decades, there has been a greater emphasis on the green chemistry and chemical processes[25-29]. These efforts aim at the elimination or minimization of generated waste and the implementation of sustainable processes. Utilization of nontoxic chemicals, environmentally benign solvents, and renewable materials are some of the key issues that merit important consideration in a green synthetic strategy. There are reports of use of $NaBH_4$ as the reducing agent and oleic acid and sodium dodecyl sulfate as the stabilizing agents. In the present study, 80 wt.% ethanol has been used as the solvent, vegetable oil as the stabilizing agent and sucrose as the reducing agent since $NaBH_4$, hydrazine, and DMF cause potential environmental and biological risks. This work provides a simple and safe process for producing nickel with fcc and hcp structures, which is nanophase and useful for magnetic recording and other applications where agglomerated particles have reduced value.

## Experimental

Nickel nitrate hexahydrate (Merck), ethanol (Hong Yang Chemical Corporation), vegetable oil (Commercial), and sucrose (SD Fine Chem Ltd) were used without further purification. Distilled water was used as a solvent.

Synthesis of fcc-Ni nanoparticles was carried out as follows: Nickel nitrate hexahydrate (1.2 g) was taken in a 100 ml RB flask and dissolved in 30 g of 80 wt.% of ethanol. The flask was continuously purged with $N_2$. To this mixture, 0.3 g of vegetable oil was added and thoroughly mixed using a magnetic stirrer at room temperature. Then, 0.3 g of sucrose was added to the flask while increasing the temperature. The heating was continued until a black gel was formed. The obtained black gel was filtered and washed with water to remove any sucrose or ethanol present in the sample. The vegetable oil modified nickel nanoparticles were extracted from the product mixture with chloroform and thereafter
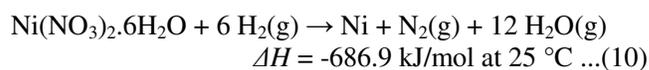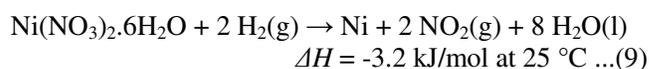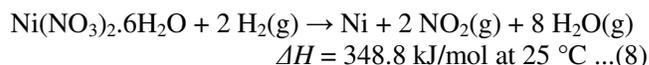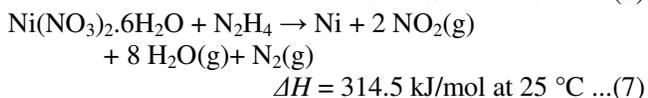
precipitated by addition of ethanol and centrifuged. The obtained nanoparticles of nickel could be re-dissolved in organic solvents, such as *n*-hexane, toluene and tetrahydrofuran.

The hcp-Ni nanoparticles were synthesized as follows: Nickel nanoparticles (0.5g) of fcc phase obtained by liquid phase reduction method using sucrose was calcined at 450 °C for 20 min. and thereafter dispersed in a mixture containing 3 ml of oleylamine and 2 ml of methanol. The contents were refluxed for 4 h and thereafter filtered and dried at vacuum.

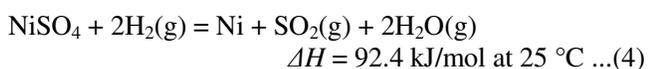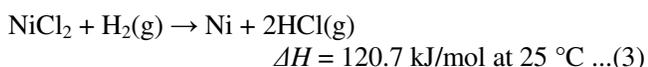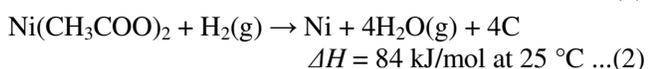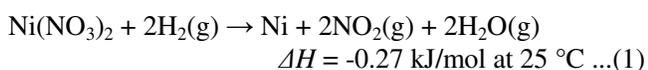The crystal structures of fcc and hcp nickel samples were analyzed on a XRD-Rigaku Miniflex II, using Cu-K$_\alpha$ irradiation. The particle size and shape were characterized using FEI Quanta FEG 200 high resolution scanning electron microscope.

## Results and discussion

The nickel nanoparticles were synthesized by the reduction of nickel nitrate hexahydrate and in the presence of vegetable oil at 170 °C. The material synthesized without vegetable oil was found to be a mixture of nickel and nickel oxides. This shows the significance of vegetable oil as stabilizing agent for nickel nanoparticles. Similar to oleic acid, the unsaturated acid present in the vegetable oil is expected to function as a capping agent and thereby prevent oxidation by air. Several precursors (nickel nitrate, nickel acetate and nickel chloride) and reducing agents (N$_2$H$_4$, NaBH$_4$ and C$_{12}$H$_{22}$O$_{11}$) were examined in order to establish a suitable precursor and reducing agent (Scheme 1).

$$Ni(NO_3)_2 + 2H_2(g) \rightarrow Ni + 2NO_2(g) + 2H_2O(g)$$
$$\Delta H = -0.27 \text{ kJ/mol at } 25 \text{ °C ...(1)}$$

$$Ni(CH_3COO)_2 + H_2(g) \rightarrow Ni + 4H_2O(g) + 4C$$
$$\Delta H = 84 \text{ kJ/mol at } 25 \text{ °C ...(2)}$$

$$NiCl_2 + H_2(g) \rightarrow Ni + 2HCl(g)$$
$$\Delta H = 120.7 \text{ kJ/mol at } 25 \text{ °C ...(3)}$$

$$NiSO_4 + 2H_2(g) = Ni + SO_2(g) + 2H_2O(g)$$
$$\Delta H = 92.4 \text{ kJ/mol at } 25 \text{ °C ...(4)}$$

$$Ni(NO_3)_2.6H_2O + NaBH_4 \rightarrow$$
$$Ni + 2 NO_2(g) + 6 H_2O(g) + NaBO_2 + 2 H_2(g)$$
$$\Delta H = 48.6 \text{ kJ/mol at } 25 \text{ °C ...(5)}$$

$$Ni(NO_3)_2.6H_2O + C_{12}H_{22}O_{11} \rightarrow Ni + 2 NO_2(g) + 1.5 CO_2(g)$$
$$+ 10.5 C + 16H_2O(g) + H_2(g)$$
$$\Delta H = 45.1 \text{ kJ/mol at } 25 \text{ °C ...(6)}$$

$$Ni(NO_3)_2.6H_2O + N_2H_4 \rightarrow Ni + 2 NO_2(g)$$
$$+ 8 H_2O(g) + N_2(g)$$
$$\Delta H = 314.5 \text{ kJ/mol at } 25 \text{ °C ...(7)}$$

$$Ni(NO_3)_2.6H_2O + 2 H_2(g) \rightarrow Ni + 2 NO_2(g) + 8 H_2O(g)$$
$$\Delta H = 348.8 \text{ kJ/mol at } 25 \text{ °C ...(8)}$$

$$Ni(NO_3)_2.6H_2O + 2 H_2(g) \rightarrow Ni + 2 NO_2(g) + 8 H_2O(l)$$
$$\Delta H = -3.2 \text{ kJ/mol at } 25 \text{ °C ...(9)}$$

$$Ni(NO_3)_2.6H_2O + 6 H_2(g) \rightarrow Ni + N_2(g) + 12 H_2O(g)$$
$$\Delta H = -686.9 \text{ kJ/mol at } 25 \text{ °C ...(10)}$$

**Scheme 1**

Eqs (1) – (4) suggest that reduction of nickel nitrate to nickel requires lower energy than that required by the other precursors such as Ni(OOCCH$_3$)$_2$, NiCl$_2$ and NiSO$_4$. This shows that pure nickel nanoparticles can be synthesized from Ni(NO$_3$)$_2$ as the removal of nitrates and water requires lower energy than the removal of water, HCl, SO$_2$ and carbon from other precursors. In addition, nickel acetate leaves carbon with the nickel nanoparticles. NiCl$_2$ can produce pure nickel nanoparticles, nevertheless as shown in Eq. (3) it requires about 120 times higher energy than Ni(NO$_3$)$_2$. In addition to higher energy (92.4 kJ/mol), NiSO$_4$ requires 2 moles of hydrogen for its reduction to Ni. Notwithstanding the fact of two moles of hydrogen consumption by Ni(NO$_3$)$_2$ for its reduction to nickel, the calculated heat of reaction for various precursors shows the preference of Ni(NO$_3$)$_2$ over the other precursors for the synthesis of nickel nanoparticles.

Among the various reducing agents studied, Eqs (5) – (8) suggest that sucrose is a better reducing agent than sodium borohydride, hydrazine and molecular hydrogen. Although NaBH$_4$ shows nearly same energy for the reduction, considering the difficulties of removing sodium and boron, sucrose was preferred over sodium borohydride. The two other reducing agents (N$_2$H$_4$ and H$_2$) as shown in Eqs (7) and (8) require about 7 - 8 times higher energy for the reduction of nickel nitrate than sucrose and NaBH$_4$. The use of sucrose as reducing agent leaves considerable amount of carbon with the nickel particles which compels the extraction of nickel nanoparticles with polar solvents.

Equations (1) and (8) suggest that anhydrous precursor requires lower energy than the hydrated precursor. If the precursor does not contain water of hydration or the water of hydration is lower, then the heat of reaction is also lower. This suggests that the presence of water in the synthesis mixture may destabilize the formation of metallic nanoparticles. This also shows that the synthesis of nickel nanoparticles using water as the solvent can be

detrimental since it will lead to the formation of the respective oxides. In the present study, 80 wt.% ethanol was used as a solvent for the synthesis of nickel nanoparticles in order to ensure the synthesis of metallic nickel. The experiments performed with isopropanol and *n*-butanol show rapid settling of the particles. Equations (8) and (9) show that the synthesis of nickel without eliminating moisture from the sample is energetically more favored than that by removing moisture from the sample. However, the metallic nanoparticles containing moisture is more vulnerable as it will react with the moisture present in the sample and consequently the metallic nickel will be converted to NiO or Ni(OH)$_2$. Although removal of water from the sample requires higher energy, the removal of water was found to enhance the stability of the material.

Equations (8) and (10) show that the increase in concentration of reducing agents can control the emission of NO$_2$ as this can react with excess hydrogen in the reaction mixture to form H$_2$O and N$_2$. Hence, increasing concentration of reducing agents will lead to a green process for producing nanoparticles from nitrate precursors. The three-fold increase of reducing agent shows the reaction occurring at a rapid rate as compared to reaction with two moles of hydrogen for a mole of nickel nitrate.

The crystal structures of the as-synthesized, calcined fcc-Ni and hcp-Ni or nickel carbide nanoparticles were determined by XRD and are shown in Fig. 1. The samples were calcined at 450 $^o$C as the maximum loss is obtained at 450 °C. The XRD

patterns obtained for the calcined samples show the presence of metallic nickel nanoparticles. The peaks observed at a 2θ° of 44.5, 51.8 and 76.4 are characteristic of fcc nickel phase[1]. The hcp nickel phase[2] is not per se obtained by the present synthesis procedure. Nevertheless, the fcc crystal structure could be converted to hcp phase by post synthesis modification (*vide infra*). The enhanced crystallinity of the calcined samples is seen from the XRD patterns presented in Fig. 1(a-c). However, the as-synthesised sample (Fig. 1a) does not show any apparent peaks characteristic of metallic Ni. XRD patterns show no peaks related to nickel oxides. The sintering of nickel nanoparticles is also demonstrated when the sample is calcined under inert and reducing atmosphere. The XRD pattern for these samples is not shown as they are similar to the pattern obtained in Fig. 1(c). The crystallite size for the calcined samples was determined by Scherrer formula. The average crystallite size obtained is 6.6 nm and 26 nm for the materials calcined at 450 °C for 10 and 20 min. respectively. The increase of crystallite size with



Fig. 2 – High-resolution SEM image of nickel nanoparticles calcined at 450 °C for 20 min. [(a) × 50000; (b) × 93000].
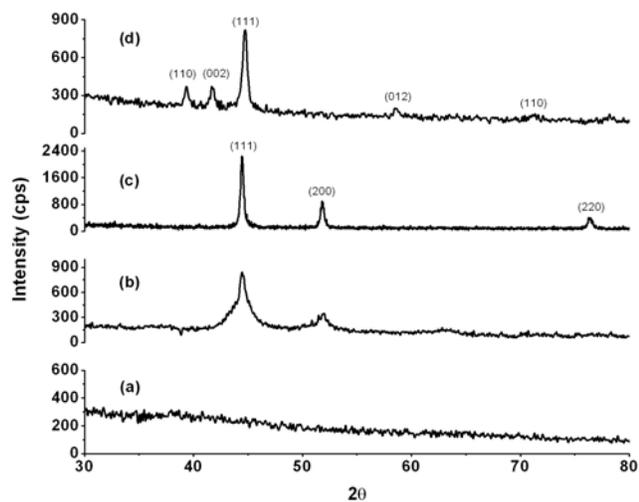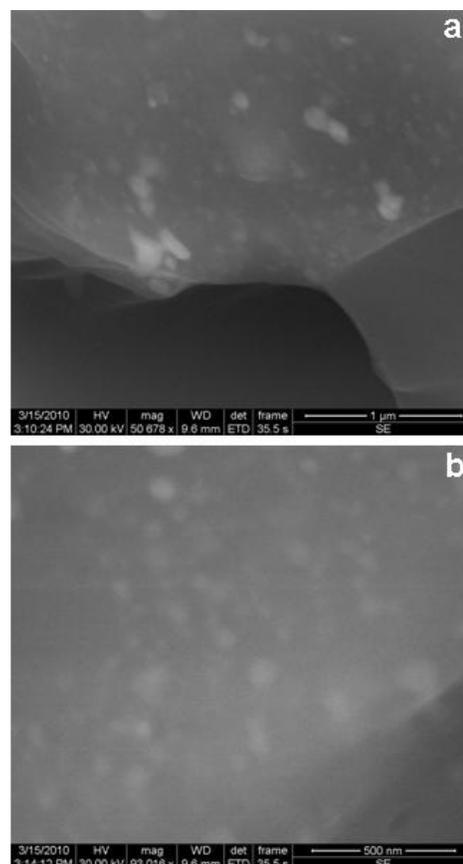


Fig. 1 – XRD patterns of nickel nanoparticles. [(a) as-synthesised; (b) calcined at 450 °C for 10 min; (c) calcined at 450 °C for 20 min; (d) oleylamine treated-(c)].

increasing time of treatment at 450 °C shows the aggregation of the nickel particles.

The XRD pattern obtained for the oleylamine treated sample showed lower crystallinity, crystallite size (19 nm) and a pure hcp phase (Fig. 1d). The peaks at 51.8 and 76.4 which are due to fcc phase (Fig. 1b and 1c) are not seen for the oleylamine treated sample (Fig. 1d). The characteristic peaks due to hcp phase are formed at $2\theta$ of 9.3°, 41.7°, 44.6°, 58.6° and 71.2°, yet again confirming the total conversion of fcc to hcp crystal structure. The XRD pattern obtained for hcp phase could also be due to the formation of nickel carbide.

Figure 2 shows the high-resolution SEM image obtained for the nickel nanoparticles calcined at 450 °C for 20 min. SEM could not be recorded for the as-synthesised sample as the material is amorphous and also the particle size is smaller than that of the heat treated sample. The different magnifications (Fig. 2a and 2b) of SEM images show virtually spherical morphology and moderately agglomerated particles with a particle size ranging from 5 – 58 nm. This shows that the crystallite size (6.6 nm) obtained from XRD is smaller than the average particle size observed from SEM analysis. The enhanced magnification shows clear images of the Ni particles (Fig. 2b). The dissimilarity in particle and crystallite size may be attributed to the limitations of determining the particle size for the samples with less than 10 nm by SEM.

In the present study, nickel nanoparticles have been prepared by an environmentally benign method using nickel nitrate, vegetable oil and sucrose. The evaluation of heat of reaction for various nickel precursors shows the advantage of nickel nitrate over the other precursors as the removal of nitrates and water requires lower energy. Ethanol is used as a solvent as the heat of reaction shows destabilization of nickel particles when water is present in the sample. The present study describes the synthesis of fcc and hcp crystal structures of Ni or nickel carbide nanoparticles. The calcination of nickel nanoparticles at 450 °C demonstrates the sintering of nickel nanoparticles and increasing of crystallite size. The XRD data reveals fcc structure for the nickel particles and a crystallite size of 6.6 nm. The scanning electron micrograph shows a particle size of 5 – 58 nm for the fcc-Ni nanoparticles calcined at 450 °C for 10 min. Vegetable oil is found to stabilize the surface of the nickel nanoparticles.

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