



# Novel microwave assisted approach to large scale nickel nanoparticle fabrication



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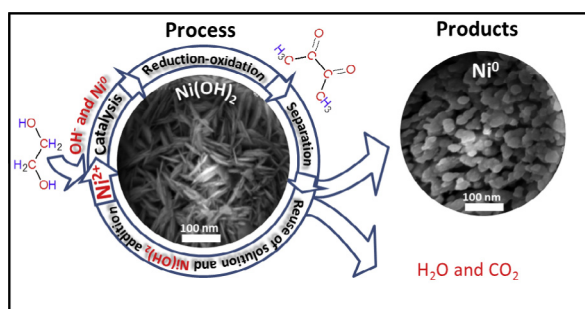
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## HIGHLIGHTS

- Nickel nanoparticles were produced by reduction of nickel hydroxide under MW-assisted heating.
- No special organic additives and pH regulators were applied.
- Auto-catalytic behavior of nickel nanoparticles was proven.
- Reduction agent (ethylene glycol) multiple usage/recyclability was demonstrated.
- Highly concentrated nickel nanoparticle suspensions were produced.

## GRAPHICAL ABSTRACT

Production of Ni<sup>0</sup> nanoparticle from Ni(OH)<sub>2</sub> and ethylene glycol under MW.



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## ABSTRACT

This work shows a novel environmentally benign microwave (MW) assisted method for the fabrication of Ni<sup>0</sup> nanoparticles. The objective was the development of a rapid and self-sustainable solvothermal method, starting from concentrated nickel hydroxide suspensions. Suspensions of nickel hydroxide (Ni(OH)<sub>2</sub>) in ethylene glycol (EG) were converted to Ni<sup>0</sup> nanoparticles at 260 °C without the need for any supplementary catalysts. The MW irradiation initiated the dissociation of nickel hydroxide to Ni<sup>2+</sup> and mobile OH<sup>-</sup> ions thus triggering the partial catalytic oxidation of EG. As a consequence, two electrons became available to reduce Ni<sup>2+</sup> to metallic Ni<sup>0</sup> nanoparticles. This process is self-sustainable as the Ni<sup>0</sup> nanoparticles then become the catalytic domains for further oxidation of EG and resulting in a faster kinetics for the complete reduction of nickel hydroxide within 60 min. Interestingly, the MW-assisted process was also effective in multiple recycling of EG, forming Ni<sup>0</sup> nanoparticles after each reduction cycle. This process dispenses the need for using a high amount of solvents as required in conventional solvothermal methods, and greatly reduces solvent waste generation. In addition, this novel process led to almost 100% conversion of highly concentrated suspensions (1.2 M Ni(OH)<sub>2</sub>) to Ni<sup>0</sup> nanoparticles, which is very attractive for a large scale production.

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## 1. Introduction

Nickel nanoparticles are versatile materials and potentially attractive for a large number of applications ranging from batteries [1], catalysis [2,3] and photocatalysis [4], to electro-oxidation [5],

magnetic devices [6], medicine [7], fuel cells [8,9], and composite materials of carbon [10] and ceramics [11]. The most common method to prepare nickel nanoparticles is based on solvothermal reduction process, a simple and facile method to control the particle size. However, the solvothermal method requires a large amount of solvents which are often wasted or require further processing for reuse. Hence, there is a need to further reduce the solvent requirement to make this method environmentally benign.

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In the solvothermal method, Ni<sup>0</sup> nanoparticles are produced in liquid media by the reduction of Ni<sup>2+</sup> ions. Ethylene glycol (EG) is a classical reducing agent which also serves as a reaction media for Ni nanoparticle formation [12–14]. Hydrazine has also been used as an efficient reducing agent instead of EG [15,16]. The use of a reducing agent requires a pH adjusting media such as NaOH, Na<sub>2</sub>CO<sub>3</sub> [16] or H<sub>2</sub>SO<sub>4</sub> [13]. However, pH adjusting media containing sodium and sulfur, both of which are undesirable in many applications. Hence, the synthesis of Ni<sup>0</sup> nanoparticles derived from Ni(OH)<sub>2</sub> without any pH additive remains an important challenge. Indeed, only the partial Ni(OH)<sub>2</sub> conversion to Ni<sup>0</sup> is generally achieved in such case [17], as the Ni<sup>2+</sup> reduction to Ni<sup>0</sup> strongly depends upon the reducing conditions.

EG based reductions by conventional heating are generally carried out at 195–198 °C. In the case of hydrazine, the reduction temperature is typically in the range 60–180 °C [15]. Microwave (MW) assisted reduction using either EG or hydrazine has been considered, though hydrazine results in a fast reaction which is difficult to control. On the other hand, EG has a high dielectric constant ( $\epsilon' = 41.0$  at 25 °C) [18] which is preferred as it favors rapid heating under MW-assisted conditions. Nevertheless, the influence of the reduction temperature is an important fundamental parameter related to Ni<sup>0</sup> particle formation, though it has yet to be reported for MW-assisted heating using EG media.

Controlling the particle size formation is another parameter of importance. There are two strategies to achieve particle size control. The first strategy is based on the addition of an easily reducible metal Pt, Pd, Au, Ag or Ni precursors or particles [13,14,19], which act as a seeding agent. The second strategy takes into consideration the steric stabilization of the early formed Ni nanoparticle in the polymeric or organic matrices such as polyvinylpyrrolidone (PVP) or n-dodecylamine [20,21], or cetyltrimethyl ammonium bromide (CTAB) [22]. The problem of the second strategy is that most of these polymers and organic additives require the supplement of other pH control ionic species (Na<sup>+</sup>, Cl<sup>-</sup>, or SO<sub>4</sub><sup>2-</sup>). Therefore, the pH controlled mixture solutions need further downstream recovery processing especially when Ni<sup>0</sup> nanoparticles are produced in a large scale. Possibly, further processing may become economically prohibitive, and the solutions can no longer be re-used or recovered and merely become waste products after the synthesis.

This work focuses on the development of an environmentally benign method adapted to large scale production of Ni<sup>0</sup> nanoparticles preferably in concentrated suspensions, thus preventing large generation of solvent wastes. Therefore, we have developed a novel method based on a key strategy which (i) encompasses an initial synthesis process from concentrated suspensions of commercial Ni hydroxide (Ni(OH)<sub>2</sub>) in EG and (ii) carries out the nickel reduction rapidly by coupling metal basic catalysis and MW heating, without any further additives or pH adjusting media. To further understand the outcomes of the proposed novel method for large scale production, this work studies the effect of temperature by MW assisted reduction in the formation of Ni<sup>0</sup> nanoparticles. The solutions and resultant Ni<sup>0</sup> nanoparticles are analyzed by microscopy and spectroscopy techniques involving XRD, SEM, TEM, FT-IR to elucidate the important parameters leading to particle size and reaction completion.

## 2. Experimental

### 2.1. Nanoparticle synthesis

Nickel hydroxide (Ni(OH)<sub>2</sub>, 99% – AlfaAesar), and ethylene glycol (C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, 98% – Sigma), were used for the synthesis of metallic nickel nanoparticles.

Homogeneous suspensions of Ni(OH)<sub>2</sub> (0.3, 1.2, 2.4, 3.6 and 4.8 M) in ethylene glycol (EG) were prepared by mixing 20 g of EG with the corresponding amount of Ni(OH)<sub>2</sub>. In order to investigate the catalytic effect of the seeds on the formation of Ni<sup>0</sup> nanoparticles, the suspension was seeded with either (i) Ni<sup>0</sup> nanoparticles, using a molar ratio [Ni<sup>0</sup>]/[Ni(OH)<sub>2</sub>] = 10<sup>-2</sup> or (ii) hexachloroplatinic acid (IV) hexahydrate Premion<sup>®</sup> (H<sub>2</sub>PtCl<sub>6</sub>\*6H<sub>2</sub>O, 99.9% metal basis – AlfaAesar) using a molar ratio [H<sub>2</sub>PtCl<sub>6</sub>\*6H<sub>2</sub>O]/[Ni(OH)<sub>2</sub>] = 10<sup>-3</sup>.

The suspensions were poured into high pressure Teflon<sup>®</sup> autoclaves fitting the MW reactor. A scientific MW oven (Milestone Ethos 1600) was used for the synthesis of Ni<sup>0</sup> nanoparticles. Sols were irradiated for specific times (10–120 min) at temperatures in the range 160–260 °C, with a maximum MW power fixed at 300 W only in order to better control the temperature regulation at the set-point.

All experiments have been made with 20 g of EG in closed pressure vessels under autogenic vapor pressure of the reaction mixture. Although the pressure has not been measured in the reactors, it increased with the synthesis temperature but never exceeded 25 bar (security limit).

After the desired reaction time, the reaction mixture was cooled down to 60 °C prior to opening the autoclaves. The solid product was separated from the suspension by magnetic field and the liquid phase was recovered. The recovered solid was dispersed in water and placed into an ultrasonic bath to remove any remaining EG. The washed solid was dried in air at 80 °C for 2 h.

### 2.2. Characterization

The recovered liquids were used for ATR-FTIR analysis (Nicolet NEXUS). The resulting particles were analyzed by FESEM (Hitachi 4800) operated at 5 kV and an X-ray analysis was performed using Panalytical X'Pert Pro diffractometer using Cu-K $\alpha$  radiation (wavelength of 1.5418 nm) with 40 mA current and 40 kV voltage. Recorded XRD patterns were compared to the references in an ICDD X-ray diffraction database PDF2. To further support XRD studies, FT-IR spectroscopy (Nicolet NEXUS) was also used. The TEM studies were made on a JEOL JEM-2100F transmission electron microscope equipped with a slow-scan CCD camera and an accelerating voltage of the electron beam 200 kV. The preparation of samples for these analysis involved sonication in ethanol for 5 min and deposition on a copper grid.

## 3. Results

### 3.1. Effect of temperature

XRD patterns of the derived powders using MW assisted heating in the temperature range 160–260 °C during one hour in presence of H<sub>6</sub>PtCl<sub>6</sub>\*6H<sub>2</sub>O are shown in Fig. 1. Traces of the Ni(OH)<sub>2</sub> precursor were detected in the temperature range 200 °C–220 °C as displayed by the X-ray diffraction lines at 2 19.01°, 32.96°, 38.47°, 51.74°, 58.81° and 62.68° (ICDD Ref. 01-1047).

On the other hand, the peaks assigned to Ni<sup>0</sup> are hardly detected below 200 °C (Fig. 1a–b), thus indicating that the reduction process leading to the formation of Ni<sup>0</sup> requires temperatures higher than 200 °C. Pure Ni<sup>0</sup> was the only product observed for the sample heated above 220 °C (i.e. at 260 °C) corresponding to the metallic nickel with the main diffraction lines at 2 44.42°, 54.85° and 76.27° (ICDD Ref. 04-0850).

FT-IR analysis (results not shown) was also used to check the complete conversion of the hydroxide precursor. The IR absorption band at about 650 cm<sup>-1</sup>, attributed to the  $\delta$ Ni–O–H vibration, was used as a fingerprint for detecting the presence of unconverted

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