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Synthesis of Ni Nanoparticle with Controlled Morphology via Liquid Phase Reduction Method

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ABSTRACT

This research focuses on the synthesis of nickel nanoparticles using liquid-phase reduction method, a cost-effective and scalable approach. It is discovered that the size and the morphology of the nickel nanoparticle can be control by varying the nickel ion concentration, reaction temperature as well as the pH of the solution. The results showed that the size of the nickel nanoparticles decreased with an increase of the nickel ion concentration. The results also indicate that the morphology of the nickel product strongly depend on the pH of the reaction solution. Nickel nanowires were observed at lower pH levels, while nickel nanoparticles with urchin-like particles were produced at higher pH levels. Henceforth, it will be possible to precisely change the synthesis parameters (nickel ion concentration, pH value and reaction temperature) to easily modify the morphology of the nickel nanoparticles. This research contributes valuable insights into the synthesis of well-defined nickel nanoparticles, opening avenues for their application in nanotechnology.

Keywords:
Nanostructure; nanoparticles; nickel; liquid phase reduction; control morphology

1. Introduction

Nickel nanoparticles have attracted significantly attention in recent years due to their unique optical [1,2], electronic [3,4], magnetic [5] and catalytic [6-9] properties. Precise control over the size, shape, and composition of nanoparticles is crucial for optimizing their performance in various applications. Numerous synthesis methods have been reported including chemical reduction [10-12], microwave heating [13,14], gamma irradiation-assisted [15] and solvothermal techniques [16] with an emphasis on their advantages and disadvantages. Among these methods, chemical reduction stands out as a versatile way to synthesize nickel nanoparticles [10]. This method allows for precise control over the reaction conditions, like the choice of reducing agent, temperature, stabilizing agents, nucleation agent and pH, which consequently affects the size, shape, and dispersity of the

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nanoparticles produced [10,17]. Similarly with the phase reduction method, its offer variety advantages including simplicity, cost effective and easy to scale up [18]. A number of reducing agent such as borohydride, hydrazine, ascorbic acid, and alcohol have been employed to reduce Ni2+ ions in aqueous or organic solutions. To date, various group has been working on developing a simple method, but there are still some gaps to be addresses. Therefore, the development of synthesis nickel nanoparticle with control morphology is necessary.

In this work, we synthesize nickel nano particle via liquid-phase reduction using hydrazine as the reducing agent. This study addresses the lack of consensus on optimal synthesis conditions by examining factors such as reactant concentration, pH of the solution, and reaction temperature. Thus, the project aims to control the morphology of nickel nanoparticle by varying these synthesis parameters to achieve uniform and well-defined nanoparticles, followed by analysing the microstructure and size of nickel nanoparticles using Field Emission Scanning Electron Microscopy (FESEM). Overall, this research contributes to a better understanding of nickel nanoparticle growth and properties, with potential applications in various fields.

2. Methodology

2.1 Materials

All chemicals were of analytical grade and used without further purification. Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$) was used as the nickel metal ion source and hydrazine hydrate ($N_2H_4.H_2O$) was used as the reducing agent. Sodium hydroxide (NaOH) and trisodium citrate ($Na_3C_6H_6O_7$) were used to control pH and acted as a complex agent, respectively.

2.2 Preparation and Characterization of Nickel Nanoparticle

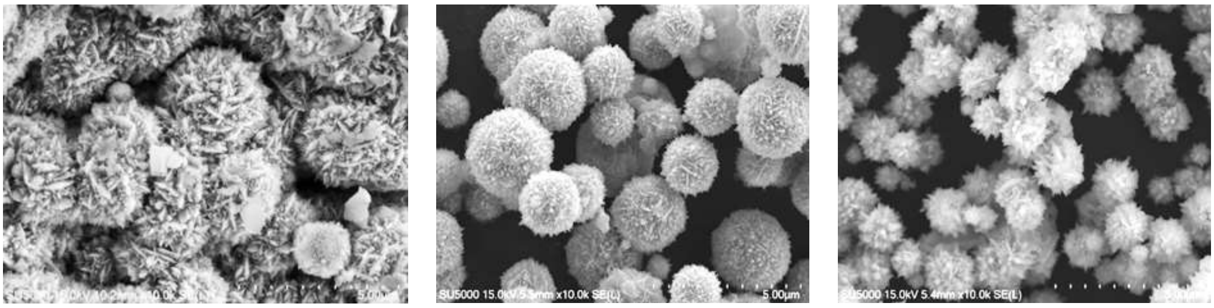
Initially, two solutions were prepared with 40 ml deionized water as the solvent. The first solution involving the dissolution of 1.0 M $NiCl_2$ in 40 ml deionized water. The second solution comprising 1.0 M N_2H_4 and 10 mM $Na_3C_6H_6O_7$ in 40 ml deionized water. The pH and reaction temperature of both solutions were adjusted to 12 and 100°C respectively. 1.0 M NaOH were added dropwise to both solutions for pH control. The metallic solution and the hydrazine solution were mixed at the predetermined temperature for about 5 hours. The reactions were agitated at a rate of 250 rpm with a magnetic stirring unit. The solutions underwent various parameter conditions, including temperature (70, 80, and 100°C), pH values (10, 11, and 12), and nickel ions concentrations (0.5, 1.0, and 5.0 M). After the reactions, a black product was formed sedimented at the bottom of a clear solution. The precipitates were then collected by centrifugation, washed several times with deionized water and ethanol to remove excess hydrazine hydrate and the solvent following with dried in an oven at 60°C for 24 hours to ensure complete removal of the moisture.

The morphology of the precipitates was observed by Field Emission Scanning Electron Microscopy (FESEM). The crystalline structure of the product was investigated by X-Ray Diffraction (XRD) using Cu $K\alpha$ radiation.

3. Results

3.1 Ni Ion Concentrations Control

Figure 1 depicts the FESEM image of the product obtained from the solution at 0.5 M, 1.0 M and 5.0 M of nickel (II) after 5 hours of reaction time. It is clearly shows that the concentration nickel precursor affects the product morphology. At a concentration of 0.5 M, complex, densely aggregated sea urchin-like structures emerged, suggesting rapid, unconstrained growth with an average particle diameter of 4900 nm. This wide range in particle size indicates significant variability and suggests that lower ion concentrations may lead to less uniform particle formation due to less controlled nucleation and growth processes. When the nickel concentration was increased to 1.0 M, more distinct, variable-sized spherical particles were obtained, indicating controlled growth conditions with an average diameter of between 1628 nm. At 5.0 M nickel concentration, well-defined, sharp spiky surface with high energy were observed, indicating a well-controlled growth pattern with an average diameter of 825 nm. The study demonstrates the potential for tailored synthesis by adjusting concentration, where 5.0 M nickel concentration leads to more nucleation site and resulted a smaller particles size [19]. The crystallite size display in Table 1 is consistent with the morphology result obtained.



(a) (b) (c)

Fig. 1. A FESEM image of nickel nanoparticles synthesized at the same pH solution of 12 and reaction temperature of 80°C under different nickel ion concentrations (a) 0.5 M (b) 1.0 M (c) 5.0M

Table 1
Crystal size for different nickel ion concentration

Sample	Crystal size (nm)
A	22.423
B	12.315
C	8.6712

3.2 pH Control

Figure 2 depicts the FESEM image of nickel nanoparticles obtained from the solution at pH 8, pH 10, and pH 12. The morphology of the nickel nanoparticles was strongly dependent on the pH reactions of the solution. At a pH of 8, nickel nanowire was formed as an elongated fibrous structure with a cauliflower-like morphology. The nanowires exhibited an average diameter of 4530 nm. Upon shifting to pH 10, a mixture of nanowires and nanoparticles were obtained. The nanoparticles exhibited nearly spherical structures with a cauliflower-like morphology, suggesting a potential ripening process where smaller particles coalesce onto larger ones. The average particle diameter measured is 2520 nm. Finally, at pH 12, uniform spherical particles were obtained suggested a slowed growth stage favouring nucleation over particle enlargement with an average particle diameter of 1628 nm. This result match with the result reported by Kong *et al.,* [20] and Revathy *et al.,* [21] which emphasizing the significance of pH in shaping nickel particle morphology. Hence, this study contributes new insights to the pH-dependent synthesis of nickel nanoparticles. Table 2 presents the crystal size of the obtained nickel nanoparticle. The results indicate a decrease in size with increasing pH of the solution, which consistent with the observed morphological trends.

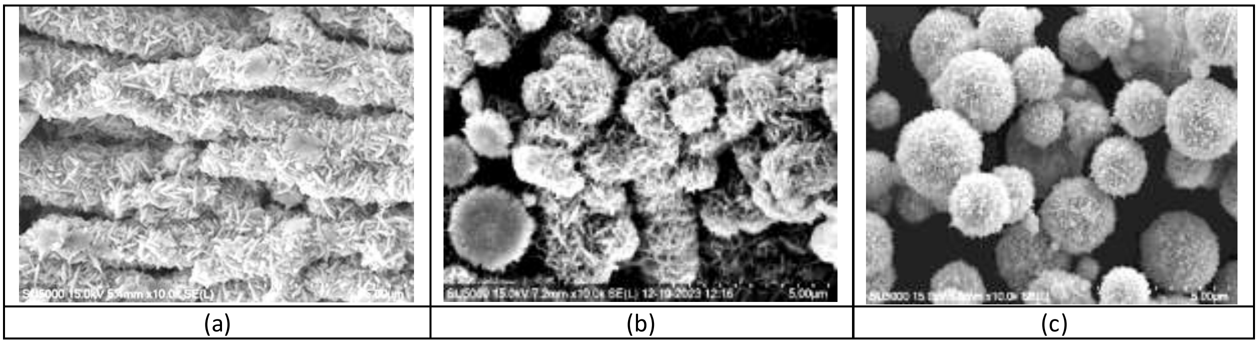

(a) (b) (c)

Fig. 2. A FESEM image of nickel nanostructures synthesized at the same nickel ion concentration of 1 M and reaction temperature of 80°C under different pH (a) 8 (b) 10 (c) 12

Table 2
Crystal size for different pH solution

Sample	Crystal size (nm)
A	18.777
B	14.776
C	12.315

3.3 Temperature Control

Figure 3 depicts the FESEM image of nickel nanoparticles obtained at varying reaction temperatures; 70°C, 80°C, and 100°C. At 70°C, the particles exhibit initial growth with a rough texture, indicative of nucleation. The average diameter is 941 nm. Moving to 80°C, an intermediate growth stage revealed larger, cauliflower-like particles as separate entities, and an average diameter of 1628 nm. At 100°C, the advanced stage shows complex, branched structures with intricate aggregates and an average diameter of 4863 nm. The growth pattern suggests progression from nucleation to coalescence, forming complex structures. During the reaction, the Ostwald ripening may occur rapidly where smaller particles dissolve preferentially and redeposit onto large particle, contributing to an increase average of the particle size [22]. The optimal temperature range for synthesizing nickel nanoparticles is identified as 80°C. The crystal diameter of the nickel nanoparticle synthesised at various reaction temperatures are shown in Table 3 which corresponds with trends shown in the FESEM image.

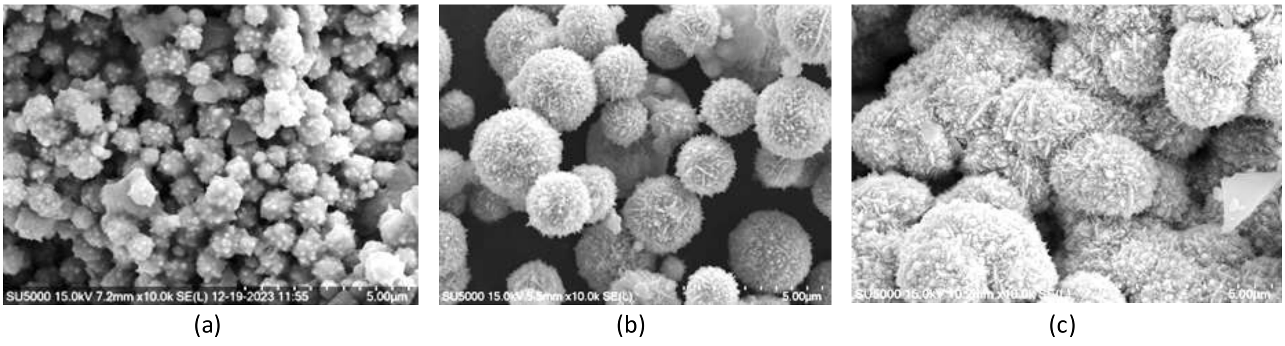

(a) (b) (c)

Fig. 3. A FESEM image of nickel nanostructure synthesized at the same nickel ion concentration of 1 M and reaction temperature of 80°C under different reaction temperature (a) 70°C (b) 80°C (c) 100°C

Table 3
Crystal size for different reaction temperature

Sample	Crystal size (nm
A	6.2554
B	12.315
C	18.889

4. Conclusions

This research aims to control the size and morphology of the nickel nanoparticle by varying the nickel concentration, pH solution and the reaction temperature. The findings revealed the optimal synthesis conditions for well-defined and controlled nickel nanoparticles: 1 M of nickel ion concentration, pH solution of 12, and 80°C of reaction temperature. FESEM results indicate that these conditions promote uniform spherical shapes, controlled growth, and a balanced morphology. It also revealed that higher nickel concentration led to a smaller size of nickel nanoparticle. The study not only enhances understanding of nickel nanoparticle growth patterns but also offers practical insights for diverse applications in catalysis, electronics, and materials science.

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