

Synthesis of Nickel Nanoparticles Via Non-Aqueous Polyol Method: Effect of Reaction Time

(Sintesis Mudah dan Pantas Nikel Nanozarah melalui Kaedah Tanpa-Akueus Poliol)

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ABSTRACT

This paper presents facile and rapid synthesis route of Ni nanoparticles at approximately 180°C in the mixture composed of ethylene glycol (EG) with hydrazine (N_2H_4) as a reducing agent. X-ray diffraction (XRD) analysis revealed that Ni^{2+} can be reduced completely to Ni metal in 15 min. XRD analysis also indicated that the as-synthesized nanoparticles were pure Ni with face-centered cubic (fcc) crystal structure. Transmission electron microscopy (TEM) results showed that the sample with heating duration of 15 min has the most narrow size distribution and the size increased as the reaction time increased.

Keywords: Nanoparticles; nickel; polyol

ABSTRAK

Kertas ini melaporkan cara mudah dan pantas bagi menyediakan nanozarah Ni pada suhu lebih kurang 180°C dalam campuran yang terdiri daripada etilena glikol (EG) dan hidrazina sebagai agen penurunan. Analisis XRD menunjukkan Ni^{2+} boleh diturunkan kepada logam Ni sepenuhnya dalam masa 15 minit. Ia juga menunjukkan yang terhasil adalah Ni berstruktur kubik bermuka pusat (kfm). Keputusan TEM menunjukkan bahawa sampel yang dipanaskan dengan jangka masa 15 minit menghasilkan partikel dengan taburan saiz paling kecil dan saiz bertambah dengan penambahan masa tindak balas.

Kata kunci: Nanozarah; nikel; poliol

INTRODUCTION

In recent years, Ni nanosized material has become one of the interesting materials in research communities due to the diverse promising applications in the field of catalysis (Saxena et al. 2007; Syukri et al. 2003 & Xu et al. 2007) and magnetism (Chang & Su 2008). Recently, reports on potential applications of Ni nanosized material are high-density magnetic recording media (Wang et al. 2008) and base-metal-electrode multilayer ceramic capacitor (BME-MLCC) (Hu & Sugawara 2009) due to the good properties in electrical conductivity, high melting point and inexpensive (Bai et al. 2008). Chemical and physical properties of nanoscale materials is well-known to differ from those of the bulk counterparts, Ni nanoscale material is also among one of the magnetic materials that has been reported to exhibit several interesting and unique properties in nanometer size regime that is different distinctively with their bulk counterparts (Chang & Su 2008).

Several studies on synthesis of nanoscale materials have suggested that the best method in synthesizing and tailoring nanoscale particles with desired properties may become possible and easy by manipulating reaction parameters including temperature, time, concentration, pH and capping agents which in turn, can produce Ni nanoparticles in a broad range of size and shape.

Polyol method is among the ideal methods in the past two decades by using poly-alcohol as both solvent and reducing agent (Coute et al. 2007). The poly-alcohol can be either EG, diethylene glycol or 1, 2-propanediol. Colloidal chemistry method is also another “bottom-up” approach that is cost-effective and suitable for scaling up the yields if compared with other techniques. It is also suggested that EG may be adsorbed to the surface of particles to prevent undesired surface oxidation (Hedge et al. 1997). The use of non-aqueous medium in this work is also expected to minimize the tendency of surface oxidation of Ni nanoparticles (Park et al. 2007). Another crucial part in the synthesis of Ni nanoparticles is their tendency to aggregate with each other because of their magnetic behaviour. Thus, this study was carried out for a better control and understanding of the synthesis of nickel colloidal nanoparticles.

Synthesis of nanoscale materials is one of the most important prerequisite in the building blocks towards fabrication of functional-devices in nanotechnology. Although many efforts have been carried out for the past decades, studies on the size-control synthesis is rather poor. The aim of this work was to study the effect of reaction time on the Ni nanoparticles that was produced with advantages of facile and rapid synthesis without using any other protective agent such as polyvinylpyrrolidone (PVP),

polyvinyl alcohol (PVA), oleic acid and cetyltrimethyl ammonium bromide (CTAB) that may chemically interact with the surface of nanoparticles thus modify the electronic and magnetic properties of the particles (Osuna et al. 1996). These protective agents were also reported to change the shapes and morphologies of as-synthesized products (Liu et al. 2008; Wang et al. 2008; Zhang et al. 2005).

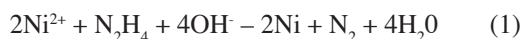
This paper describes a facile and rapid synthesis of Ni colloidal nanoparticles by utilizing polyol method with N_2H_4 acted as a reducing agent and NaOH as the catalyst. It is actually a modification of the conventional method of polyol in poly-alcohol that need long hours to complete reduction (Grisaru et al. 2003), and the synthesis of Ni nanoparticles at 60°C as reported by Chen and Wu (2003). To the best of our knowledge, there are still no reports on the synthesis of Ni nanoparticles in as fast as 15 min. It can be considered to be a very short reaction time if compared with early works (Abdel-Aal et al. 2007; Bai et al. 2008; Sidhaye et al. 2009; Wang et al. 2008). This work also may contribute to further understanding and optimization of synthesis technique, which will act as a novel route in developing Ni nanoscale materials as an advanced material via polyol method.

MATERIALS AND METHODS

All chemicals used in this experiment were analytical grade and used as received without further purifying. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), 80 wt% hydrazine hydrate ($N_2H_4 \cdot H_2O$) and sodium hydroxide (NaOH) was obtained from Merck. Ethylene glycol (EG) that was employed as a surfactant was purchased from System.

All the reactants were diluted and dissolved in EG to form desired concentration. In a typical experiment, 60 mL of 15 mM $NiCl_2 \cdot 6H_2O$, 30 mL of 0.15M N_2H_4 and appropriate amount of 1 M NaOH were mixed in a three-neck flask equipped with stirring bar, a thermometer, a dropping funnel and a condenser. Hydrazine was first heated to boiling point of the mixture, which was about 184°C. A mixture of Ni^{2+} and appropriate amount of NaOH was added quickly into the heated hydrazine as it reached the boiling point. The temperature was maintained at a constant value at the boiling temperature of mixture that was control using oil-bath. The temperature was monitored using a thermometer. Initially the green solution turned into black, indicating the formation of Ni metal. The mixture was heated for 5 min to 2 h under vigorous stirring. After the reaction was completed the colloidal was cooled to room temperature and the particles were precipitated from the solution by adding ethanol. An aliquot of the colloidal was taken for Transmission Electron Microscopy (TEM) characterization. The rest of the particles were recovered by centrifugation, thoroughly washed a few times with ethanol and acetone until colourless supernatant was obtained. In order to facilitate the x-ray diffraction analysis, the particles were then dried in vacuum for several hours under ambient

condition. The stoichiometry equation can be expressed as:



The particles size and morphologies were examined using the CM 12 Philips Transmission Electron Microscopy (TEM) operating at 120 kV. Samples were prepared by dropping a drop of colloidal sample on a carbon-coated copper grid and let dry for several minutes in air at room temperature.

The crystallographic structure and crystallite size of precipitated Ni nanoparticles were identified using Bruker X-ray powder diffraction (XRD) D8 Advanced with CuK_{α} ($\lambda = 0.154021$ nm) radiation source in the angle range of $2\theta = 20^\circ - 80^\circ$. Samples for XRD analyses were obtained by recovering the as-synthesized products from the solutions using centrifugation, followed with washing the precipitates using ethanol and acetone for a few times and were dried in a desiccator at room temperature over a few minutes.

RESULTS AND DISCUSSION

In the study on the effect of reaction time on the growth of Ni nanoparticles, all conditions were kept constant except for the reaction time. It should be pointed out that, reaction time in this investigation is the heating time, starting from the moment mixture of $NiCl_2 \cdot 6H_2O$ and NaOH being introduced to the preheated N_2H_4 of until the end of the synthesis. Figure 1 shows the colour changes on the solution that was taken throughout the reaction immediately after introduction of $NiCl_2 + NaOH$ mixture. It is reasonable to suggest that the colour changed from pale green gradually to black (Figure 1(a) – (e)) due to the depletion of Ni^{2+} concentration, while at the same time increase of Ni nuclei was formed with the reaction time of 2 h. Figure 1(f) is the colour of solution at 5 min reaction, where at this stage the solution turns to black completely. Increase in the reaction time further promote the precipitation of Ni particles (Figure 1(g)). Ni particles were precipitated from solution and cause the colour changes from black to grey. Colourless solution also suggests that at this stage all of the Ni^{2+} have been reduced to Ni. Prolonged reaction time gradually change the colour of solution to dark brown (Figure 1(h)).

The morphology of as-synthesized products (Figure 2), revealed that all products consisted of spherical particles with diameter of 1-200 nm. The size distribution and its normal graph for each sample are shown on the right side of corresponding micrographs in Figure 2(a – d) except for sample D5 (reaction time of 5 min) that cannot be measured due to the low yield of the particles observed in the micrograph. Increasing of the reaction time promoted abundance of particles. The size distribution produced at 15 min (Figure 2(a)) was discrete without any agglomeration and ranged from 1.2 to 2.5 nm with a mean

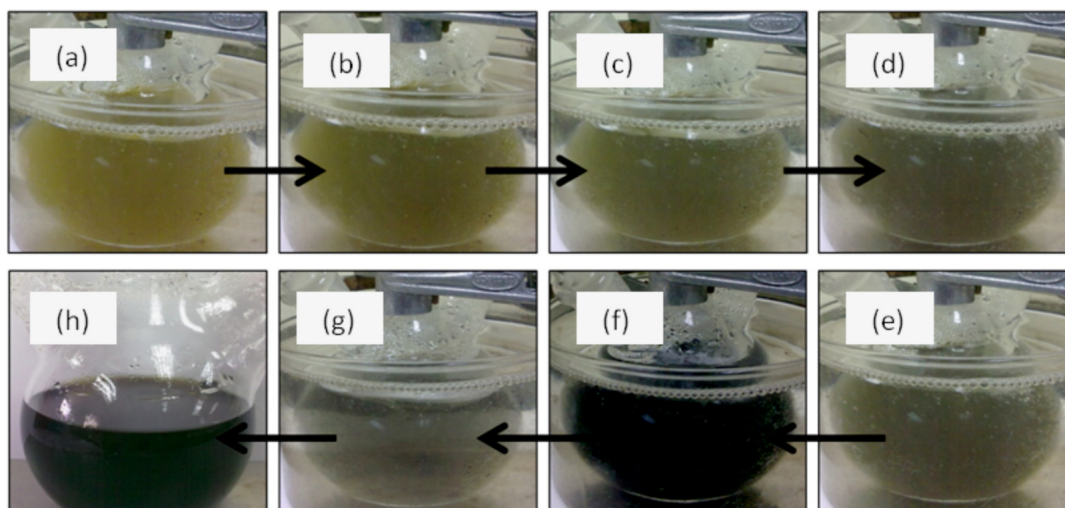


FIGURE 1. Colour changes of solution start taken (a) upon injection of NiCl_2 and NaOH mixture, and at reaction time of (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, (f) 5 min, (g) 1 h and (h) 2 h

diameter of 1.8 nm and standard deviation of 0.3. Figure 2(b) shows the micrograph of particles at 1 h reaction time, which exhibited mean particles size of 6.5 nm with the sizes ranging from 4.5 to 9.0 nm and standard deviation of 1.0. The size continues to increase at reaction time of 2 h with a mean diameter of 175.4 nm. The size varies between 93.3 and 239.8 nm with standard deviation of 36.4. Accordingly, it can be concluded that the particles size showed a significant increase in size along with the prolong of the reaction time. Although EG should have inhibited particles aggregation by physical interaction with the surface of as-synthesis nanoparticles, further heating may become the driven forces for promoting growth and agglomeration. Standard deviation also increased as reaction time increased from 0.26 to 36.4 as the function of reaction time.

XRD analyses (Figure 3(a)) revealed that sample D5 existed in the amorphous structure with main reflection peak at crystal-plane of [111] present. The crystallinity of the sample D5 was very low as the intensity of peaks are very low as compared with sample D15, D60 and D120. Further increasing of the reaction time improved the crystallinity and Ni(OH)_2 peak absent in the diffractions patterns. Three characteristic peaks at $2\theta = 44.5^\circ$, 51.8° and 76.4° in all samples can be indexed (JCPDS 01-1260) to the standard pattern of Ni with face centered cubic (fcc) phase, which were in the good agreement with JCPDS card of Ni (Tian et al. 2008). After the reaction time of 15 min, all samples can be indexed to standard Ni and Ni nanoparticles with high yield can only be obtained with reaction time longer than or at 15 min. The particles size at 15 min with the diameter of 1.8 nm can be regarded as primary particles as it is the smallest particles size and only contain pure Ni sample without any amorphous structure.

The findings of this study inferred that the 2 h reaction might proceed through three steps process. Figure 4 shows the proposed growth mechanism of Ni nanoparticles

as reaction time increase. It is postulated that the first step involved reduction followed by nucleation, where formation of Ni^{2+} to Ni(OH)_2 followed by Ni metal took place. Ni(OH)_2 can be regarded as intermediate phase before it was fully reduced by N_2H_4 into Ni nanoparticles. The first 5 min reaction time did not fully convert all of Ni(OH)_2 into Ni metal but the nucleation continue and completed at 15 min and this process consumed high amount of Ni^{2+} . The next 15 min reaction can be thought as the second step where particle size increased through agglomeration, while the third step was the further increased of particles size that may involved Ostwald ripening in which smaller particles dissolved in favour of the growth of larger particles (Ahrenstorf et al. 2008). The size of particles also become inhomogeneous and this has caused the increase of the size distribution of particles size with the prolong reaction times (Wang et al. 2008).

Since all conditions were kept constant in the whole experiments except for the reaction time, reaction rate were assumed to be the same in the whole process. Another set of test was carried out where all the samples were synthesis separately according to their reaction time. It was found that colour eventually changes from pale green to black, indicating Ni nucleation was almost the same for all the samples D5 to D120, in which further confirmed that 5 min was the stage of nucleation. These results showed that by using the identical synthesis condition (concentration of reactants, temperature, pH and method) with variation of reaction time was feasible to produce colloidal Ni nanoparticles.

CONCLUSION

In conclusion, a facile and rapid synthesis of Ni nanoparticles by non-aqueous polyol method was investigated. Reaction time has been found to play a crucial role in tuning the size of the particles. The mean particles size of the as-

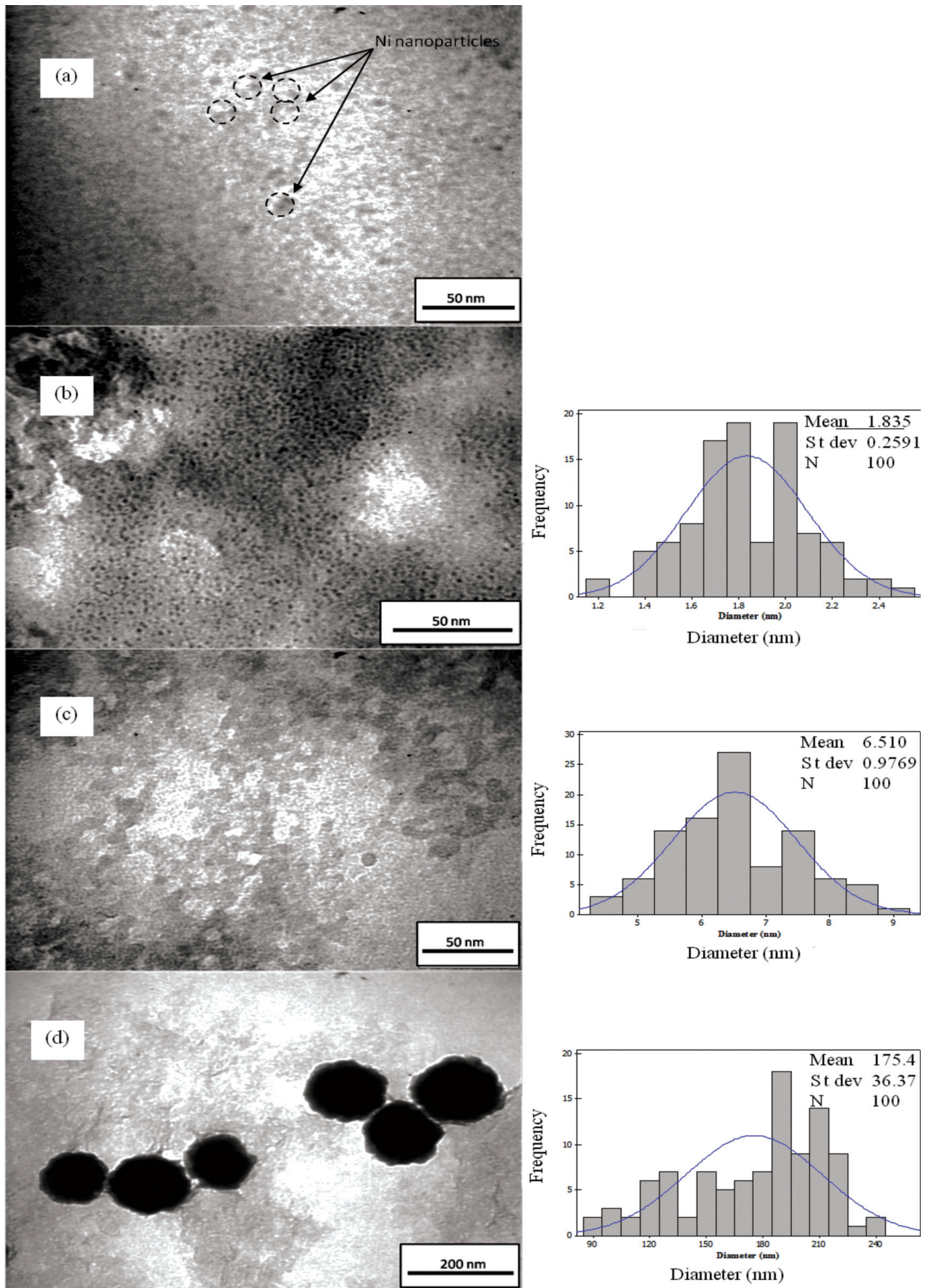


FIGURE 2. TEM micrographs and particles size distributions histogram of (a) D5 ($t = 5$ min), (b) D15 ($t = 15$ min), (c) D60 ($t = 1$ h) and (d) D120 ($t = 2$ h), respectively. Size distribution was determined by counting 100 particles using ImageJ software

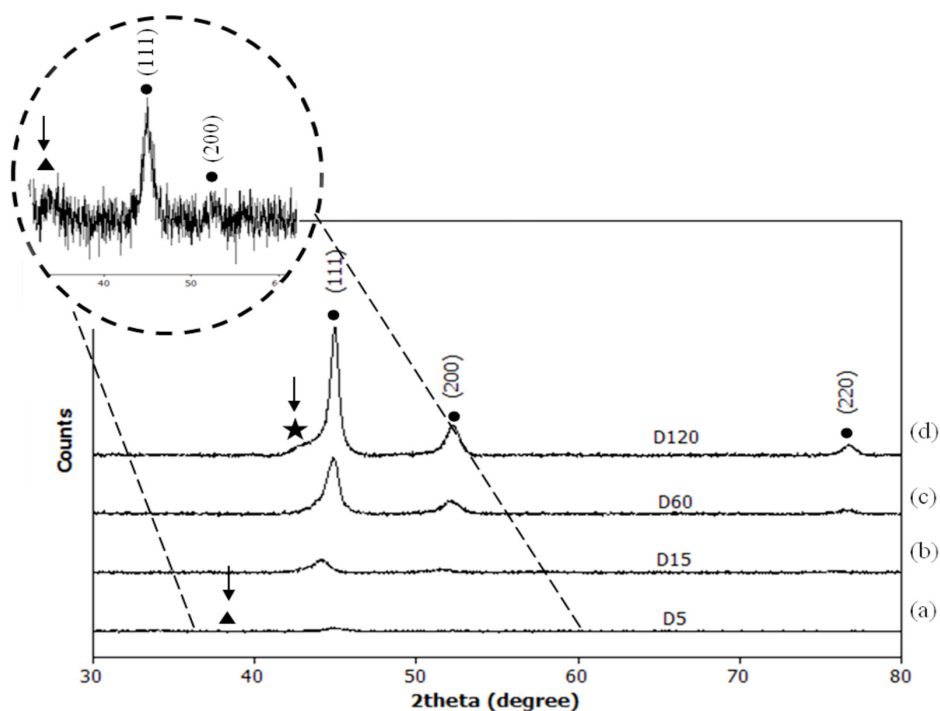


FIGURE 3. XRD patterns of (a) D5 ($t = 5$ min), (b) D15 ($t = 15$ min), (c) D60 ($t = 1$ h) and (d) D120 ($t = 2$ h). (Inset is the magnification of diffraction pattern of sample D5) ($\blacktriangle = \text{NiO}$, $\bullet = \text{Ni(OH)}_2$)

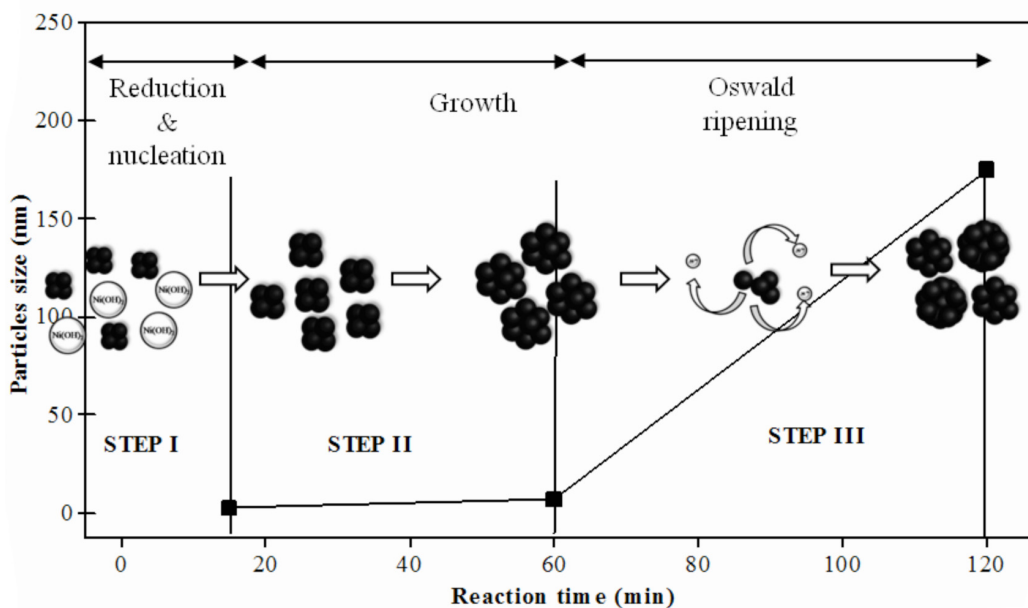


FIGURE 4. Schematic diagram of the reaction procedure at different reaction times

synthesized particles can be synthesized within the range of 1 to 175 nm by manipulating the reaction time. This facile and rapid synthesis may provide a route and understanding in the production of Ni nanoparticles as well as other nanostructures.

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