

# On the Preparation of Nickel Nanoparticles by Chemical Reduction Method: X-ray Absorption Spectroscopy

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Nickel nanoparticles were synthesized by the chemical reduction of NiCl<sub>2</sub> with N<sub>2</sub>H<sub>4</sub> under controlled pH environment. During nucleation, polyvinyl pyrrolidone (PVP) was added as the protective agents for preventing the agglomeration of metal clusters. Color of the solution changed from green to blue during the reaction period. X-Ray Adsorption Spectroscopy (XAS), X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM) analytical methods were used to characterize the product. XAS analysis showed that the reduction reaction occurred within 5 minutes after the addition of N<sub>2</sub>H<sub>4</sub>. The length of Ni-Ni bond was 2.59 nm. The results of XRD analysis of the three cases with pH ranging from 11.0 to 13.0 suggest that the optimum pH value for the reaction appeared to be 12.0. The average particle size was 20–50 nm under this condition.

*Keywords:* chemical reduction, nanoparticle, XAS.

## 1. INTRODUCTION

Nanoparticles possess physical and chemical properties different from those of bulk materials due to their extremely small size and large specific surface area. They are expected to have many potential applications in optoelectronics, semiconductors, capacitors, catalysis, photocatalysis, environmental remediation, and so on. Nickel nanoparticles with their magnetic properties are one of the most important nanomaterials.

Many methods have been proposed to synthesize the nickel nanoparticles. Park et al [1] prepared the Ni powders directly from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution containing EDTA by chemical reduction. Massicot et al [2] used Ni(OAc)<sub>2</sub> and Al(Acac)<sub>3</sub> to get subnanometric Ni-Al clusters. Alymov and Leontieva [3] synthesized Ni and Fe powders by the hydrogen method. Monodisperse Ni nanoparticles were prepared by Hegde et al [4] by the polyol process using PVP as the protective agent. The rapid expansion of supercritical fluid solutions, coupled with chemical reduction was used by Sun et al [5] for preparing Ni, Co, and Fe nanoparticles. Li et al [6] prepared nickel ultrafine powder by chemical control reduction of NiSO<sub>4</sub> with hydrazine. Their experimental results showed that pH and temperature are the main factors to influence the reaction. Zheng et al [7] prepared PVP-protected nanoscale Ni powder in ethanol-water system. Gao et al [8] used hydrazine hydrate as reducing agent to reduce Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Wu and Chen [9] prepared Ni nanoparticles by hydrazine reduction in ethylene glycol without soluble polymer as a protective agent. Kim et al [10] discussed the effect of the kind of alcohol and volume ratio of alcohol on the reduction of nickel salt by hydrazine in aqueous solution. To enhance the reaction of chemical reduction of NiCl<sub>2</sub> in ethanol-

water solution, Kim et al [11, 12] used microwave-assisted hydrothermal method in preparing submicron nickel powders. Considering the economical aspects of the process, the chemical reduction of metal cations from the solutions of metal salt is an attractive method. Most of the previous studies concerning the preparation of nickel nanoparticles by chemical reduction were focused on the effects of nickel concentration, surfactant, solvent composition, etc. In this work, we tried to investigate the interactions between metals/metal ions during the formation of nickel nanoparticles via in-situ observation with X-Ray Absorption Spectroscopy (XAS). The final products were also characterized by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM).

## 2. EXPERIMENTAL DETAILS

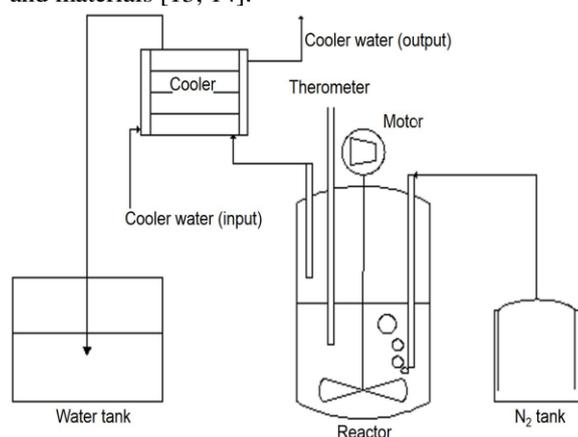
For this experimental investigation, the precursor solution was first prepared by adding appropriate NiCl<sub>2</sub> (Wako Co. Japan), di-ammonium citrate (chelating agent, Showa Co. Japan) and sodium hydroxide (Showa Co. Japan) to the reactor (Fig. 1). The pH of the solution was kept at about 12.5. Polyvinyl pyrrolidone (PVP, Showa Co. Japan) and silver nitrate (AgNO<sub>3</sub> Showa Co. Japan) were added to the precursor solution as the protecting agent and the nucleating agent to enhance the reaction rate, respectively. The solution prepared above was heated to 90 °C under a mixing rate of 250 rpm, before the reducing agent (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, Merck Germany) was added to the solution. The colors of the solution in every reaction step were observed and recorded.

A first sample was taken as soon as the reducing agent was added. Two other samples were taken at 5 and 45 minutes thereafter. All the samples were cooled, centrifuged and washed with de-ionized water and alcohol, and stocked in alcohol solution.

Analytical methods of TEM, XRD and XAS were used to characterize the properties of the samples,

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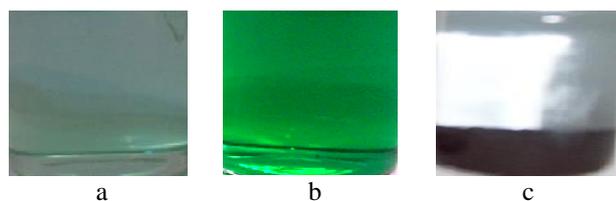
respectively, using instruments of Hitachi HF-2000, Rigaku d/max-II, and X-ray at National Synchrotron Radiation Research Center (NSRRC), Taiwan. In this study, XAS is used in analyzing the experimental results. The XAS methods used in this study were X-Ray Absorption Near Edge Structure (XANES) and Extend X-Ray Absorption Fine Structure (EXANES). XANES depicts the distribution of electrons around an atom and gives the oxidation number of the atom. EXANES is used to obtain the coordination number, bond length etc. around an atom. They are widely used in the research of catalysts and materials [13, 14].



**Fig 1.** Experimental apparatus

### 3. RESULTS AND DISCUSSION

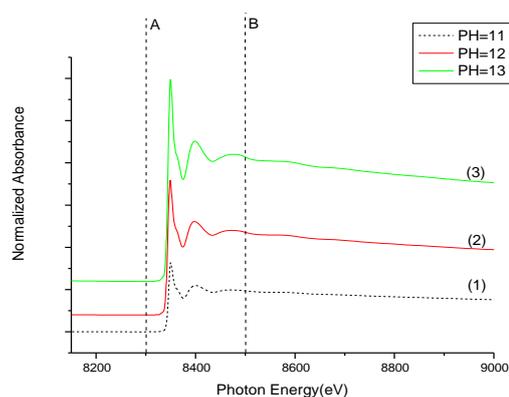
When  $\text{NiCl}_2$  was dissolved in water, green color appeared (Fig. 2 a). It is the color of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  [7]. With the addition of  $\text{NaOH}$  and di-ammonium citrate, the color turned to be dark green (Fig. 2 b). Reduction reaction occurred as soon as the addition of  $\text{N}_2\text{H}_4$  and black  $\text{Ni}$  particles precipitated (Fig. 2 c). The color of  $\text{NiCl}_2$  solution in various stages are depicted as Fig. 2.



**Fig. 2.** Color of  $\text{NiCl}_2$  solution in various stages (in colour on-line)

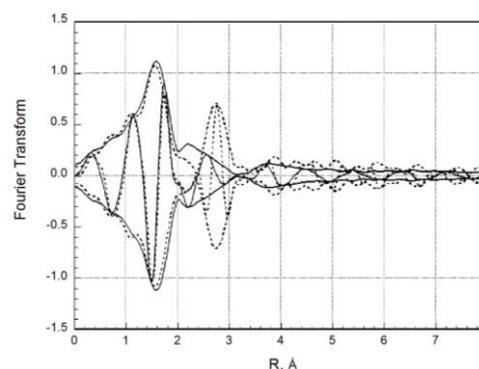
Three samples taken immediately, 5 and 45 minutes after the addition of the reducing agent were analyzed with the XAS, TEM and XRD methods. Fig. 3 is an XANES spectrum. It shows that the photo energies are 8346.59 eV, 8343.8 eV and 8346.99 eV at pH = 11, 12, and 13, individually. At pH = 12, the system has the lowest photo energy. It means that at pH = 12, nickel has lower oxidation number than that of the other two conditions and there are less  $\text{Ni}(\text{OH})_2$ . Less  $\text{Ni}(\text{OH})_2$  is helpful for reducing nickel ions to nickel nanoparticles.

Fig. 4 shows the magnitude and imaginary of EXAFS functions. To obtain this result, a program for data analysis and Fourier Transform is used, and  $k$  is the structure parameter used in this program.



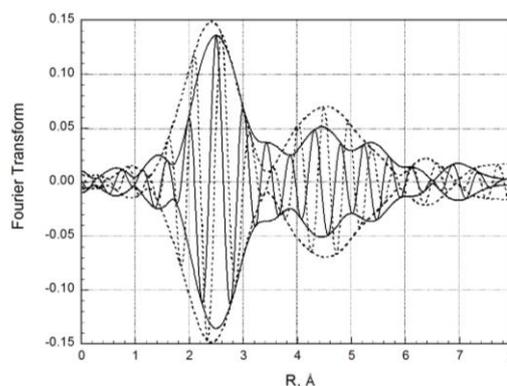
**Fig. 3.** The XANES spectrum. photon energy at various pH conditions: 1–pH = 11 photon energy = 8346.59 eV; 2–pH = 12 photon energy = 8343.8 eV; 3–pH = 13 photon energy = 8346.99 eV

As demonstrated in Fig. 4, as soon as the addition of  $\text{N}_2\text{H}_4$  to the pH controlled aqueous solution containing di-ammonium citrate,  $\text{NiCl}_2$  and PVP, the appearance of  $\text{NiCl}_2$  aggregates was considered as the evidence of formation of Ni-Ni bond at about 3.0 Å as discussed by Gaidelene et al. [13, 14].

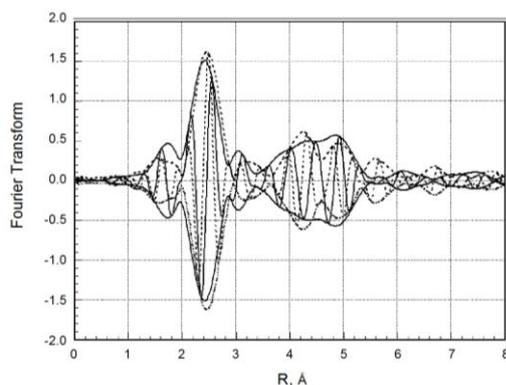


**Fig. 4.** Magnitude and imaginary ( $3.5 < k^2 < 12 \text{Å}^{-1}$ ) of EXAFS functions characterizing structure of  $\text{NiCl}_2$  before (solid line) and after (dashed line) the addition of  $\text{N}_2\text{H}_4$

Fig. 5 and Fig. 6 show that after 5 minutes into the reaction,  $\text{NiCl}_2$  was reduced to Ni cluster with the Ni-Ni bond distance of about 2.50 Å.

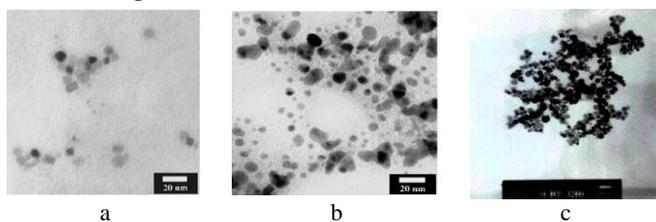


**Fig. 5.** Magnitude and imaginary ( $3.5 < k^1 < 8.0 \text{Å}^{-1}$ ) EXAFS functions characterizing structure of Ni clusters after 5 min reaction (solid line) and after 45 min reaction (dashed line)



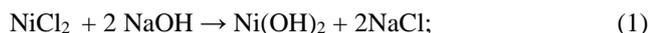
**Fig. 6.** Magnitude and imaginary ( $3.5 < k^2 < 13 \text{ \AA}^{-1}$ , Ni-Ni phase and amplitude corrected) EXAFS functions characterizing structure of Ni clusters after 5 min reaction (solid line) and after 45 min reaction (dashed line)

Fig. 7 depicts the TEM images in various stages. The number of nickel nanoparticles increases with time and their average diameters are between 10 – 20 nm. Because nickel is magnetic metal, aggregation occurred as the number of particles increased.

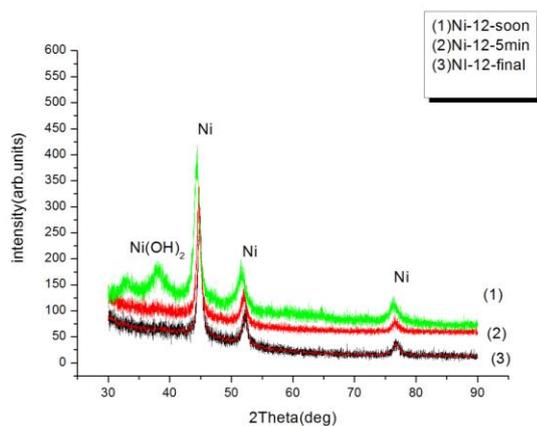


**Fig. 7.** TEM images of the synthesized nickel nanoparticles: a – soon; b – 5 min; c – 45 min

The results of XRD analysis are shown in Fig. 8. They are consistent with the experimental results conducted by Park et al [15] and Park et al [16]. XRD results showed that nickel hydroxide was formed first and then reduced to nickel metal by  $\text{N}_2\text{H}_4$ . With these experimental results, it is believed that nickel hydroxide formation and its reduction to nickel particles by  $\text{N}_2\text{H}_4$  are two competition reactions.



The strong bonding of Ni-O<sub>x</sub> in the first reaction will decrease the rate of reduction reaction. Therefore a proper chelating agent is needed in order to enhance the reaction, such as di-ammonium citrate.



**Fig. 8.** XRD patterns of the samples at the beginning (1), 5 min exposure (2), and the final product (3)

## 4. CONCLUSIONS

The information about valence and local structure of metals/metal ions was obtained at different pH values of the reaction system. As concluded below, interaction between metals/metal ions and protective polymers could be fully characterized and the role of pH in affecting the structure of Ni nano-particles was better understood:

1. The formation of NiO<sub>x</sub> not only affects the morphology of Ni cluster, but also influences the oxidation state leading to a change of the character of Ni nano-particles.
2. pH of the solution and the chelating agent are very important in the competition reactions between the reduction of NiCl<sub>2</sub> and the formation of NiO<sub>x</sub>.
3. XAS is a powerful tool to identify the interaction between the metal ion and the approaching agent. By incorporating XAS, TEM, and XRD, the relationship between the structure of Ni nano-particles and operating condition can be explored.

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