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A Chemical Route to Large-Scale Preparation of Spherical and Monodisperse Ni Powders

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A facile chemical route to prepare a well-defined Ni powder on a mass-production scale without external heating was suggested. A highly concentrated Ni complex was formed between $NiCl_2$ and N_2H_4 solution, and subsequent addition of NaOH solution triggered serial reactions from the Ni complex decomposition via $Ni(OH)_2$ formation to the reduction of a $Ni(OH)_2$ gel into well-defined Ni spheres. The high temperature necessary for the reaction was attained not by external heating but by exothermic reactions such as complex formation and reduction. The preparation of monodisperse and spherical Ni powder was attributed to uniform distribution of the reducing agent (N_2H_4) within the $Ni(OH)_2$ gel.

I. Introduction

A MULTILAYER ceramic capacitor (MLCC) is one of the most representative passive components for highly integrated electronic and telecommunication devices.[1–4] The key concept is a large capacitance in a small volume, which is realized by the alternate stacking of $BaTiO_3$-based dielectric and Ni-based electrode layers up to several hundred layers. For the downsizing of MLCC or for achieving an ultra high capacitance, a Ni layer as well as an active layer need to be competitively being thinned down to a submicrometer scale, which requires a well-defined nanoscale Ni powder sized from 50 to 200 nm.[1,5,6]

The Ni powder for MLCC can be prepared via the vapor phase method,[7] spray pyrolysis,[8,9] and solution chemical routes such as polyol processes[10,11] and reduction in an aqueous[12–16] or non-aqueous solution.[17] Among these methods, reduction in an aqueous solution is a cost-effective and promising approach for preparing crystalline, spherical, and monodisperse Ni powders by the reduction of a complex between a Ni salt ($NiCl_2$, $NiSO_4$, $Ni(CH_3COO)_2$)[12–16] and a reducing agent (N_2H_4) in the presence of OH^- ions. This process is expected to replace the current vapor phase method. However, because a dilute solution ($[Ni^{2+}] \leq 0.1M$) is generally used, not only is large-scale production difficult but the stock solution needs to be heated up to 50°–200°C in order to induce the decomposition reaction of the Ni complex for eventual reduction into Ni.[12–16] Moreover, when the reaction volume is large, the external heating of the stock solution establishes a spatially heterogeneous temperature profile, which tends to produce polydisperse particles.

This study proposes a new wet-chemical method for preparing spherical and monodisperse Ni powder on a large scale without external heating in the following sequences: (a) the Ni complex formation between highly concentrated $NiCl_2$ ($[NiCl_2] = 1.3–1.9M$) and N_2H_4 aqueous solutions, (b) the formation of a condensed $Ni(OH)_2$ gel with a uniform N_2H_4 distribution by adding a NaOH solution, and (c) the reduction of a $Ni(OH)_2$ gel into well-defined Ni particles via a dissolution–reduction–reprecipitation process. The high temperature for the reaction was attained not by external heating but by exothermic reactions such as complex formation and reduction.

II. Experimental Procedure

$NiCl_2 \cdot 6H_2O$ (Chemical Pure, Incheon Chemical Co., Ltd., Incheon, Korea), 80% $N_2H_4 \cdot H_2O$ (Extra pure, Dae Jung Chemical & Metal Co., Ltd., Shiheung, Korea), and 50% NaOH aqueous solution (Chemical Pure, Dae Jung Chemical & Metal Co., Ltd.) were used as the source materials. During the entire reaction, the temperature of the stock solution was measured at short intervals (1 s) using a computer-interfaced thermocouple data logger (TLOG 1000, Carvolab Co., Ltd., Bucheon, Korea).

For controlling the size of the Ni particles, three different $NiCl_2/N_2H_4/NaOH$ molar ratios, 1.35/4.5/3.6, 1/4/4, and 1/12/12, were used. The following is the procedure for preparing the $NiCl_2/N_2H_4/NaOH = 1.35/4.5/3.6$. The other reactions showed a similar behavior except for small variations in the temperature profile of the solution. First, the solutions were prepared by dissolving 321.26 g of $NiCl_2 \cdot 6H_2O$ (1.35 mol of $NiCl_2$) in 375 g of distilled water. With vigorous stirring, 282.2 g of 80% $N_2H_4 \cdot H_2O$ (4.5 mol of N_2H_4) was poured into the solution instantaneously, which resulted in a pale violet precipitate. The precipitate on the wall was washed with additional distilled water (50 g) for ~60 s. The solution temperature increased up to ~65°C by the exothermic formation of a Ni complex between $NiCl_2$ and N_2H_4. When the solution temperature became 50°C by cooling in an ambient atmosphere, 288 g of a 50 wt% NaOH solution (3.6 mol of NaOH, the temperature of NaOH solution = 20°C) was poured instantaneously into the stock solution. The solution temperature initially decreased and then increased spontaneously up to the second maximum (~54°C), after which it decreased again to room temperature. The reaction was complete 1 h after the temperature reached the second maximum (54°C). The black Ni precipitate was washed six times with distilled water and dried at room temperature for 16 h under constant ventilation. For all the experimental conditions, approximately 100% of the Ni source solution was successfully converted into Ni particles. In order to investigate the reaction intermediates, the precipitate in the solution was sampled and analyzed by X-ray diffraction (X'pert, Phillips, Eindhoven, the Netherlands). The size and morphology of Ni particles were observed by a scanning electron microscope (SEM, Model S-4300, Hitachi, Tokyo, Japan).

III. Results and Discussion

The evolution of the solution temperature, solution color, and the crystalline phase of the reaction intermediate during the re-

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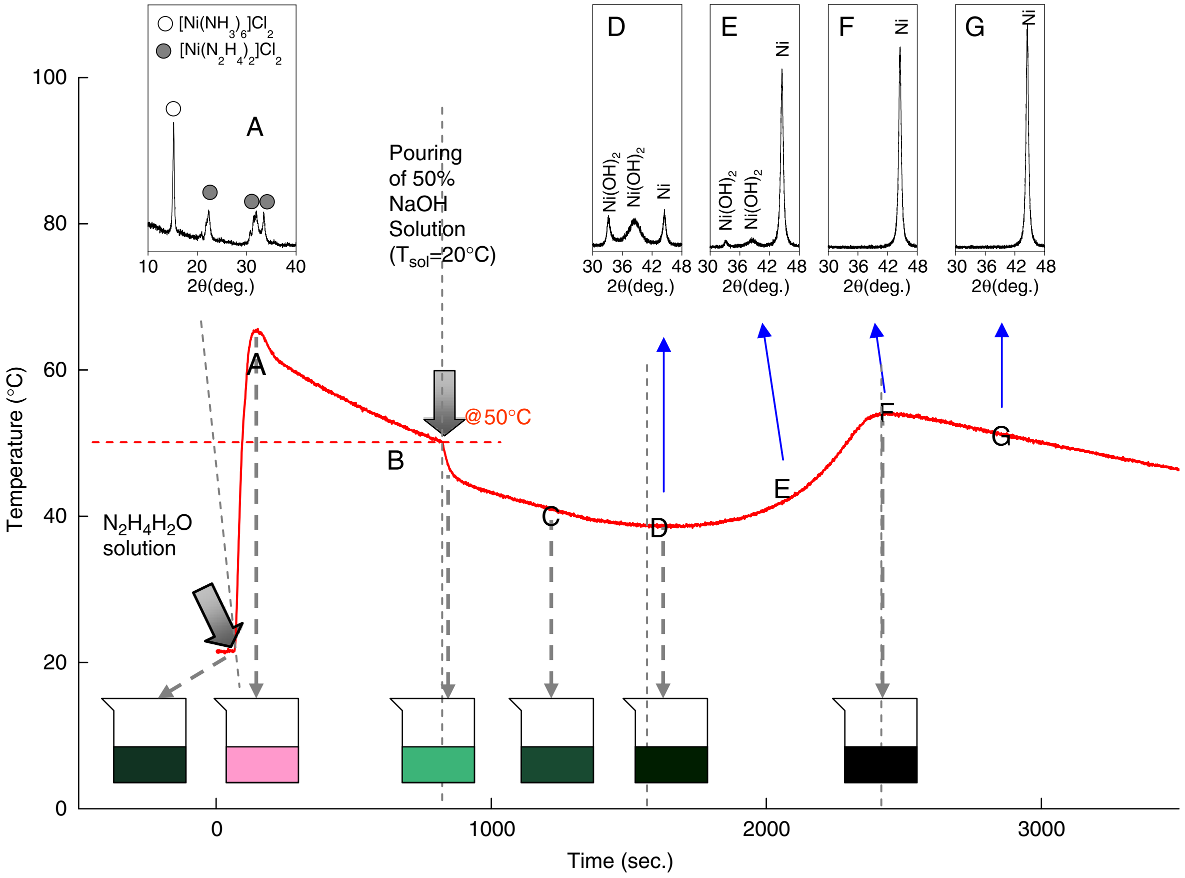

Fig. 1. Evolution of the solution temperature, solution color, and the crystalline phase of the reaction intermediate during the reaction for the solution with the molar ratio of $NiCl_2/N_2H_4/NaOH = 1.35/4.5/3.6$.

action was investigated when a source solution with a molar ratio of $NiCl_2/N_2H_4/NaOH = 1.35/4.5/3.6$ was used (Fig. 1). By pouring 80% $N_2H_4 \cdot H_2O$ solution into a 1.9*M* $NiCl_2$ aqueous solution, a Ni complex between $NiCl_2$ and N_2H_4 (pale violet precipitate) was formed actively and the solution temperature increased because of an exothermic reaction. After ~2 min the pouring of $N_2H_4 \cdot H_2O$, the temperature reached a maximum (~65°C) (point A), and then decreased gradually as a result of the dissipation of the heat generated to the ambient. The complex phase was identified as a mixture of $[Ni(NH_3)_6]Cl_2$[‡] and $[Ni(N_2H_4)_2]Cl_2$.[§] (inset A in Fig. 1) Considering the molar ratio ($[N_2H_4]/[Ni^{2+}] = 4.5/1.35 = 3.33$) used, $Ni[(N_2H_4)_3]Cl_2$ is a probable complex species.[18]

$$NiCl_2 + 3N_2H_4 \rightarrow [Ni(N_2H_4)_3]Cl_2 \qquad (1)$$

However, it is known to be less stable than $Ni[(N_2H_4)_2]Cl_2$.[19] Therefore, it can decompose into $Ni[(N_2H_4)_2]Cl_2$ with the release of N_2H_4.

$$[Ni(N_2H_4)_3]Cl_2 \rightarrow [Ni(N_2H_4)_2]Cl_2 + N_2H_4 \qquad (2)$$

The $[Ni(NH_3)_6]Cl_2$ was reported to appear when $[Ni(N_2H_4)_2]Cl_2$ is heated to a high temperature.[20] Accordingly, $Ni[(N_2H_4)_2]Cl_2$ is believed to be transformed partly into $[Ni(NH_3)_6]Cl_2$ at high-temperature conditions (~65°C) according to the following reaction[20]:

$$\begin{aligned}&[Ni(N_2H_4)_2]Cl_2 + 5/2N_2H_4\\ &\quad\rightarrow [Ni(NH_3)_6]Cl_2 + 3/2N_2(g)\uparrow\end{aligned} \qquad (3)$$

During the initial 1.5 min after a 50% NaOH solution ($T = 20°C$) was poured into the stock solution ($T = 50°C$) (point B), the color of the solution changed rapidly from violet via blue to green. Note that the rather abrupt temperature decrease just after B is because of the introduction of the cold NaOH solution. ($T = 20°C$) Subsequently, until point D, the solution temperature decreased gradually to ~40°C for 10.5 min, and the color of the solution increasingly darkened to black. From point D, the solution temperature increased again spontaneously until the second maximum (point F, ~54°C) for 14.5 min, after which it decreased as a result of heat dissipation.

The detailed reaction mechanism from B to F is currently under investigation. However, the decrease in NH_3 or N_2H_4 radicals in the Ni complex can be deduced from the change in the color of the solution from a short to long wavelength (from pale violet via blue to green).[8] This suggests that the supply of OH^- promotes the decomposition of the Ni complex. Another factor that needs to be considered is the temperature of the stock solution at the point of NaOH addition. The reaction took ~24 h to complete when a 50% NaOH solution ($T = 20°C$) was poured into the low-temperature stock solution ($T < 30°C$). At a higher temperature the stock solution resulted in a shorter reaction time. For the reaction to be complete within 6 h, the temperature of stock solution at the point of NaOH addition needs to be >40°C. The high solution temperature (60°–70°C) can be attained without external heating only when the Ni complex between the highly concentrated $NiCl_2$ and N_2H_4 is actively formed in a short time. Therefore, high concentrations of the source materials are an important driving force for auto-thermal reactions.

The decomposition of a Ni complex in a highly alkalic environment (pH = ~13) will result in the formation of $Ni(OH)_2$[13,15] and it can be reduced by N_2H_4 from the following reaction[12,21]:

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + N_2 + 4H_2O \qquad (4)$$

[‡] Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA (now International Centre for Diffraction Data (ICDD), Newtown Square, PA) (Card No. 76-1842).

[§] Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA (now International Centre for Diffraction Data (ICDD), Newtown Square, PA) (Card No. 28-0695).

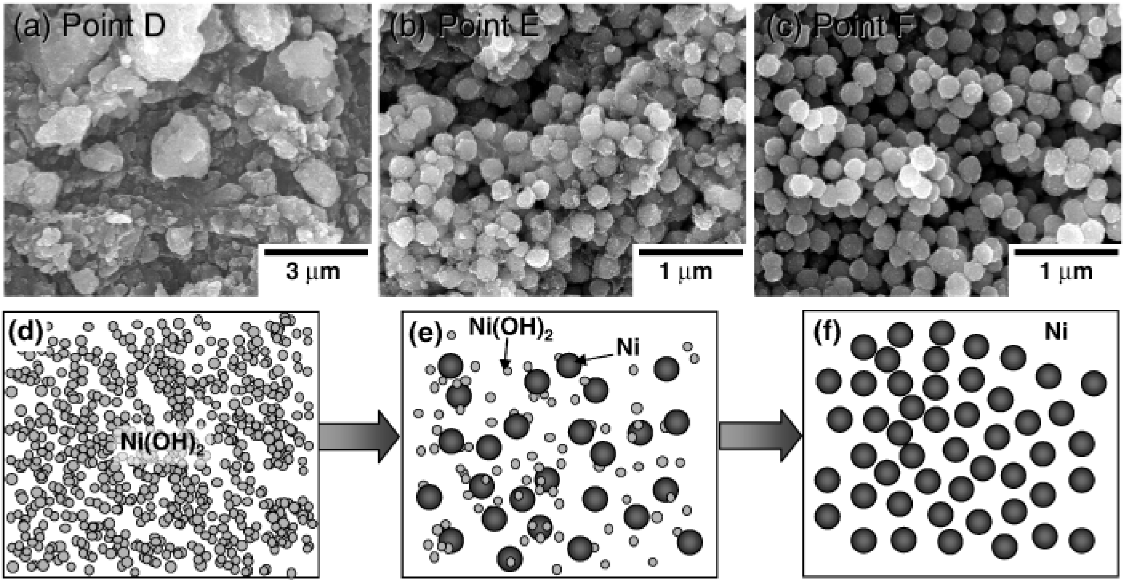

Fig. 2. Scanning electron micrographs of the reaction intermediates (a) at point D in Fig. 1, (b) at point E in Fig. 1, and (c) at point F in Fig. 1, and (d), (e), and (f) their schematic diagrams illustrating the formation of spherical Ni particles from uniform nano-scale $Ni(OH)_2$ precipitates.

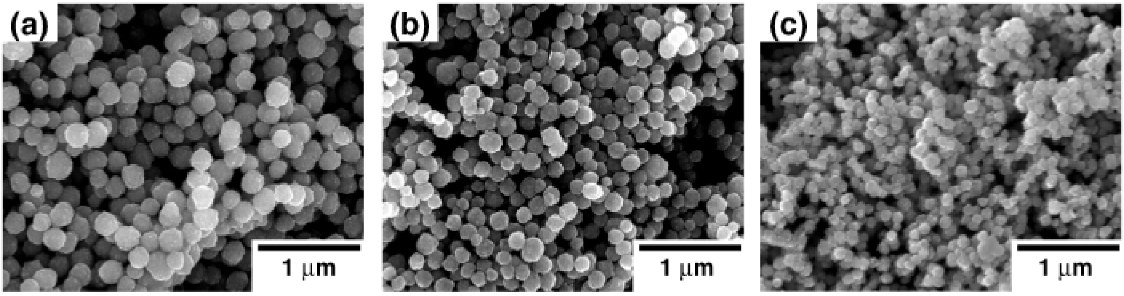

Fig. 3. Scanning electron micrographs of the spherical Ni particles prepared at (a) $NiCl_2/N_2H_4/NaOH = 1.35/4.5/3.6$ (average diameter = 203 nm), (b) $NiCl_2/N_2H_4/NaOH = 1/4/4$ (average diameter = 150 nm), and (c) $NiCl_2/N_2H_4/NaOH = 1/12/12$ (average diameter = 87 nm).

The evolution of the phase and morphology was verified by sampling the precipitate during the reaction (insets D, E, F, and G in Fig. 1, and SEM photos in Fig. 2). At point D, the Ni complex was completely transformed into a condensed $Ni(OH)_2$ gel composed of uniform nanoscale precipitates (inset D in Fig. 1, and Fig. 2(d)), which was confirmed by TEM. The irregular morphology of the $Ni(OH)_2$ shown in the SEM photo (Fig. 2(a)) was caused by agglomeration during the drying process. When Ni becomes predominant over $Ni(OH)_2$ (inset E in Fig. 1), spherical particles with a uniform size ($\sim$200 nm) and a number of nanoscale $Ni(OH)_2$ precipitates (Fig. 2(e)) appear, which could be observed as the small non-spherical particles after the drying process (Fig. 2(b)) decreased significantly. This suggests that the spherical Ni particles form at the cost of a uniform $Ni(OH)_2$ matrix. Finally, the remaining $Ni(OH)_2$ precipitates had completely disappeared as a result of further reduction into Ni (insets F and G in Fig. 1 and Figs. 2(c) and (f)), which resulted in spherical and monodisperse Ni particles. X-ray photoelectron spectroscopy (XPS) analysis on sputtering of the surface of Ni particles confirmed that the small amount of $(OH)^-$ ion presents only at the surface. The key reasons why the $Ni(OH)_2$ phase was prepared not by simple precipitation but by the decomposition of a Ni complex could be the uniform distribution of the reducing agent (N_2H_4) throughout the $Ni(OH)_2$ matrix as a result of complex decomposition and the molecular-scale uniformity of the reaction temperature as a result of the chemical reaction-induced self-heating. This will lead to uniform and homogenous nucleation of spherical Ni particles.

As stated above, the monodisperse, spherical, and non-agglomerated Ni particles were prepared from a homogenous matrix of $Ni(OH)_2$ precipitates. This is analogous to the process known as the "gel–sol" method to prepare monodisperse oxide powders from a condensed metal hydroxide gel, which was suggested by Sugimoto *et al.*[22] and Muramatsu and Sugimoto[23] The core concept is that the solutes in a condensed metal hydroxide gel are dissolved and subsequently recrystallize as a monodisperse metal or metal oxide sol. Agglomeration can be avoided effectively because the precursory solid network plays the role of a protective matrix against the coagulation of subsequently formed particles. In this study, the Ni^{2+} ions, which were dissolved from a condensed $Ni(OH)_2$ gel, are thought to recrystallize into spherical and non-agglomerated Ni particles via the reduction reaction (4). This gel–sol conversion mechanism in this study strongly suggests that a well-defined and non-agglomerated Ni powder can be prepared on a mass-production scale. Indeed, this idea was confirmed by the preparation of $\sim$700 g of monodisperse Ni powders using a 20 L reactor via a one-pot reaction.

The manipulation of the Ni particle size is another important concern in the fabrication of a highly integrated MLCC. Therefore, the Ni powders were prepared from various $NiCl_2/N_2H_4/NaOH$ ratios. Figure 3 shows the Ni powders prepared at $NiCl_2/N_2H_4/NaOH = 1.35/4.5/3.6$, 1/4/4, and 1/12/12. The average particle sizes were 203, 150, and 87 nm, respectively. The particle sizes tended to decrease with increasing $N_2H_4/NiCl_2$ (3.3, 4, 12 in molar ratio), which can be explained by the promotion of Ni nucleation as a result of the enhanced reduction rate.[9] This shows that the particle size can be controlled easily by changing the reaction conditions.

The serial reactions from Ni-complex decomposition via $Ni(OH)_2$ formation to the reduction of $Ni(OH)_2$ into spherical

Ni particles were triggered by the addition of 50% NaOH ($T = 20°C$) to the stock solution ($T = 50°C$). In order to determine the reason for the monodispersity, the 50% NaOH solution at $T = 50°C$ was poured instantaneously but there was no significant change in the size and morphology. This means that the temperature of the NaOH solution is not a key parameter. However, the Ni powder showed a polydisperse size distribution when the 50% NaOH solution ($T = 20°C$) was not poured within a few seconds was dripped for ~60 min. This could be attributed to the overlapping of three sequential reactions by the gradual addition of the NaOH addition. Therefore, the abrupt addition of the NaOH solution is effective in separating the nucleation and growth process, which is a prerequisite for preparing monodisperse Ni particles.

IV. Conclusion

A new and simple chemical route for preparing a well-defined Ni powder on a mass-production scale without external heating was suggested. The active formation of the Ni complex between highly concentrated $NiCl_2$ and N_2H_4 solutions not only provided sufficient thermal energy for a spontaneous reaction but also enabled a large-scale synthesis. Moreover, the instantaneous addition of the NaOH solution was effective in separating three sequential reactions from the Ni-complex decomposition via $Ni(OH)_2$ formation to reduction into Ni. The formation of a concentrated Ni complex and a uniform distribution of a reducing agent (N_2H_4) within a $Ni(OH)_2$ matrix gel were suggested as the main reasons for the preparation of monodisperse and spherical Ni powder. The size of the Ni particle could be controlled by changing $[N_2H_4]/[Ni^{2+}]$ in the solution, which was attributed to the promotion of Ni nucleation by the enhanced reduction reaction.

References

[1] H. Kishi, Y. Mizuno, and H. Chaozono, "Base-Metal Electrode-Multilayer Ceramic Capacitors: Past, Present, and Future Perspectives," *Jpn. J. Appl. Phys.*, **42**, 1–15 (2003).

[2] Y. Sakabe and T. Reynolds, "Base-Metal Electrode Capacitors," *Am. Ceram. Soc. Bull.*, **81** [10] 24–6 (2001).

[3] S. Sato, Y. Nakano, A. Sato, and T. Nomura, "Mechanism of Improvement of Resistance Degradation in Y-Doped $BaTiO_3$ Based MLCCs with Ni Electrodes Under Highly Accelerated Life Testing," *J. Eur. Ceram. Soc.*, **19**, 1061–5 (1999).

[4] J. G. Pepin, W. Borland, P. O'Callaghan, and R. J. S. Young, "Electrode-Based Causes of Delaminations in Multilayer Ceramic Capacitors," *J. Am. Ceram. Soc.*, **72** [12] 2287–91 (1989).

[5] J.-Y. Lee, J.-H. Lee, S.-H. Hong, Y. K. Lee, and J.-Y. Choi, "Coating $BaTiO_3$ Nanolayers on Spherical Ni Powders for Multilayer Ceramic Capacitor," *Adv. Mater.*, **15**, 1655–7 (2003).

[6] J.-Y. Lee, S.-H. Hong, J.-H. Lee, Y. K. Lee, and J.-Y. Choi, "Uniform Coating of Nanometer-Scale $BaTiO_3$ Layer on Spherical Ni Particles Via Hydrothermal Conversion of Ti-Hydroxide," *J. Am. Ceram. Soc.*, **88** [2] 303–7 (2005).

[7] J.-H. Hwang, V. P. Dravid, M. H. Teng, J. J. Host, B. R. Elliott, D. L. Johnson, and T. O. Mason, "Magnetic Properties of Graphically Encapsulated Nickel Nano Crystals," *J. Mater. Res.*, **12** [4] 1076 (1997).

[8] S. Stopić, J. Nedeljković, S. Rakočević, and D. Uskoković, "Influence of Additives on the Properties of Spherical Nickel Particles Prepared by Ultrasonic Spray Pyrolysis," *J. Mater. Res.*, **14** [7] 3059–65 (1999).

[9] B. Xia, I. W. Lenggoro, and K. Okuyama, "The Role of Ammonia and Ammonium Bicarbonate in the Preparation of Nickel Particles from Nickel Chloride," *J. Mater. Res.*, **15** [10] 2157–66 (2000).

[10] F. Fiévet, J. P. Lagier, and M. Figlarz, "Preparing Monodisperse Metal Powders in Micrometer, and Submicrometer Sizes by the Polyol Process," *MRS. Bull.*, **14**, 29–33 (1989).

[11] V. Viau, F. Fiévet-Vincent, and F. Fiévet, "Nucleation and Growth of Bimetallic CoNi and FeNi Monodisperse Particles Prepared in Polyols," *Solid State Ionics*, **84**, 259–70 (1996).

[12] D.-H. Chen and S.-H. Wu, "Synthesis of Nickel Nanoparticles in Water-in-Oil Microemulsion," *Chem. Mater.*, **12**, 1354–60 (2000).

[13] Y. D. Li, C. W. Li, H. R. Wang, L. Q. Li, and Y. T. Qian, "Preparation of Nickel Ultrafine Powder and Crystalline Film by Chemical Control Reduction," *Mater. Chem. Phys.*, **59**, 88–90 (1999).

[14] Z. Gui, R. Fan, W. Mo, X. Chen, L. Yang, and Y. Hu, "Synthesis and Characterization of Reduced Transition Metal Oxides and Nanophase Metals with Hydrazine in Aqueous Solution," *Mater. Res. Bull.*, **38**, 169–76 (2003).

[15] J. Gao, F. Guan, Y. Zhao, W. Yang, Y. Ma, X. Lu, J. Hou, and J. Kang, "Preparation of Ultrafine Nickel Powder and its Catalytic Dehydration Activity," *Mater. Sci. Commun.*, **71**, 215–9 (2001).

[16] R. S. Sapieszko and E. Matijevi, "Preparation of Well Defined Colloidal Particles by Thermal Decomposition of Metal Chelates: II. Cobalt and Nickel," *Corrosion-Nace*, **36** [10] 522–30 (1980).

[17] A. Degan and J. Maèek, "Preparation of Submicrometer Nickel Powders by the Reduction from Nonaqueous Media," *Nanostruct. Mater.*, **12**, 225–8 (1999).

[18] D. Nicholls and S. Swindells, "Hydrazine Complexes of Nickel(II) Chloride," *J. Inorg. Nucl. Chem.*, **30**, 2211–7 (1968).

[19] G. A. Konin, A. M. Bol'shakov, and L. V. Khmelevskaya, "Autocatalytic Decomposition of Nickel(II) Hydrazine Complexes in Aqueous Solutions," *Russ. J. Coord. Chem.*, **22**, 870–2 (1996).

[20] L. Guo, C. Liu, R. Wang, H. Xu, Z. Wu, and S. Yang, "Large-Scale Synthesis of Uniform Nanotubes of a Nickel Complex by a Solution Chemical Route," *J. Am. Chem. Soc.*, **126**, 4530–1 (2004).

[21] A.-G. Boudjahem, S. Monteverdi, M. Mercy, and M. M. Bettahar, "Study of Support Effects on the Reduction of Ni^{2+} Ions in Aqueous Hydrazine," *Langmuir*, **20**, 208–13 (2004).

[22] T. Sugimoto, X. Zhou, and A. Muramatsu, "Synthesis of Uniform TiO_2 Nanoparticles by Gel–Sol Method: 3. Formation Process and Size Control," *J. Colloid Interface Sci.*, **259**, 43–52 (2003).

[23] A. Muramatsu and T. Sugimoto, "Synthesis of Uniform Spherical Cu_2O Particles from Condensed CuO Suspensions," *J. Colloid Interface Sci.*, **189**, 167–73 (1997).

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