

Articles

Synthesis of Ni-Ag Core-shell Nanoparticles by Polyol process and Microemulsion Process

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Ni-Ag core-shell nanoparticles were synthesized by polyol process and microemulsion technique successfully. In the polyol process, a chemical reduction method for preparing highly dispersed pure nickel and Ag shell formation have been reported. The approach involved the control of reaction temperature and reaction time in presence of organic solvent (ethylene glycol) as a reducing agent for Ag cation with poly(vinyl-pyrrolidone) (PVP. Mw = 40000) as a capping agent. In microemulsion method, the emulsion was prepared by water/cetyltrimethylammonium bromide (CTAB)/cyclohexane. The size of microemulsion droplet was determined by the molar ratio of water to surfactant (ω_0). The core-shell formation along with the change in structural phase and stability against oxidation at high temperature heat treatments of nanoparticles were investigated by X-ray diffraction and TEM analysis. Under optimum conditions the polyol process gives the Ni-Ag core-shell structures with 13 nm Ni core covered with 3 nm Ag shell, while the microemulsion method gives Ni core diameter of 8 nm with Ag shell of thickness 6 nm. The synthesized Ni-Ag core-shell nanoparticles were stable against oxidation up to 300 °C.

Key Words : Ni-Ag Core-shell, Nanoparticles, Polyol, Microemulsion, Size controllable nanoparticles

Introduction

With the development of nanomaterials and nanotechnology, more efforts have been directed toward large-scale synthesis of nanoparticles in recent years due to their potential applications in many areas.¹⁻⁵ In such uses, nanoparticles with different purity, size, shape and structure will greatly influence the ultimate performance of the device and accordingly, preparation of nanoparticles with desired quality and low cost by convenient method in large scale is of great importance. In recent years, new types of nanoparticles composed of a core and a shell of two different nano size materials have been reported for variety of applications.^{6,7} Because of the nano size of the layer, such material may have better or different chemical, magnetic, optical, and catalytic properties comparing to the individual pure metal. On the other hand, the replacement of an expensive reactive metal in the center of the particles by another less expensive material lead to substantial economic way. Nickel nanoparticles have wide range of applications in the field of permanent magnets, magnetic fluids, magnetic recording media, solar energy absorption, fuel cell electrodes, catalyst and *etc.*, and the synthesis of Ni nanoparticles has attracted considerable attention.^{8,9} Without proper protection, nickel nanoparticles are easily oxidized in air, so the usage of the nickel nanoparticles is limited seriously. Silver nanoparticles with the surface property also have many applications in

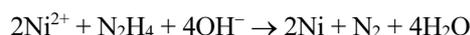
field such as: biochemical, biomedical, and *etc.* Among the various kinds of metal core-shell nanoparticles, the preparation of some metal core-shell nanoparticles such as nickel, copper and iron are relatively difficult because they are easily oxidized. Protection of Ni nanoparticles from oxidation by using Au shell layer has been reported in the literature.¹⁰ Core-shell materials may exhibit novel or multiple properties and hence have much broader applications than their single component.¹¹⁻¹⁹ In the present work we have selected Ag as a protective agent for Ni core. For common preparation of nanoparticles, chemical reduction is used frequently for its convenience and rapidity. For the preparation of uniform and size controllable nanoparticles, microemulsion method has obvious advantages.¹¹ Chen *et al.* has worked on the Ni-Ag core-shell synthesis using chemical reduction process where they employed hydrazine as a reducing agent for the synthesis of both Ni core and Ag shell.¹⁹ Here in this work, polyol process in the presence of PVP surfactant was adopted to prepare Ni-Ag core-shell. Carefully controlled preparation of silver shell on Ni nanoparticles was necessary to avoid the formation of isolated silver nanoparticles. We also prepared the Ni-Ag core-shell structure with the microemulsion technique at relatively low temperature using CTAB as new surfactant. The structure, phase, shape and stability against oxidation of the Ni-Ag core-shell particles made through each process were systematically studied and compared.

Experimental

Materials. The chemical, nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), poly(vinyl-pyrrolidone) (PVP, $M_w = 40,000$), ethylene glycol, silver nitrate (AgNO_3), cetyltrimethylammonium bromide (CTAB), hydrazine 80% ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), butanol ($\text{C}_4\text{H}_9\text{OH}$), cyclo hexane (C_6H_{12}), sodium borohydride (NaBH_4) and sodium hydroxide (NaOH) purchased from Sigma-Aldrich. All the chemicals were analytical grade and used in the present work without any further purification.

Synthesis of Ni-Ag Core-shell Nanoparticles.

Polyol Method: Mono-dispersed Ni nanoparticles were synthesized by reduction of nickel chloride in ethylene glycol using hydrazine as reducing agent. Nickel chloride (2.5 mmol), PVP (0.1 gram) was dissolved in 50 mL ethylene glycol under mechanical stirring; the resulting solution mixture was green in color. Then, 3 mL hydrazine and 4 mL NaOH (0.5 M) were added to the solution under continuous stirring. The solution became violet after the addition. Further, the reaction mixture was heated at 60 °C until it became black indicating the formation of Ni nanoparticles. The synthesis reaction can be represented by the following equation:



For further preparation and characterization the colloid was diluted by ethanol and centrifuged at 5000 rpm for 10 minutes to separate the particles from suspension. The separated particles were re-suspended in ethanol and the centrifugation was repeated for 5 times. The resulting Ni nanoparticles were then dispersed in 50 mL fresh ethylene glycol. For comparison, the Ni nanoparticles without PVP were also synthesized. Then, 0.25 mmol silver nitrate also was separately dissolved in 50 mL ethylene glycol. Silver nitrate solution was then slowly added into the well dispersed Ni in ethylene glycol; here ethylene glycol acts itself as a reducing agent. The solution mixture was heated at different temperatures (60 °C, 80 °C and 120 °C) for various reaction times. The resulting nanopowder was collected as mentioned above for Ni nanoparticles from the suspension after centrifugation and multiple washing with ethanol.

Microemulsion Method: Water in oil (w/o) microemulsion was prepared by 1.5 g CTAB, 4 mL butanol, and 25 mL cyclohexane. The aqueous solution of nickel chloride was prepared by 1 mL H_2O with 5 mmol nickel chloride hexahydrates ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$). This aqueous solution was added into microemulsion and stirred until the emulsion became homogeneous. Two micelle solutions with same volume were prepared separately with the same procedure. The aqueous solution of silver nitrate was prepared by 1 mL H_2O with 0.5 mmol silver nitrate and the micelle solution of hydrazine was prepared by water in oil (w/o) microemulsion with 3 mL hydrazine. For preparation of the core-shell nanoparticles a two step procedure was applied. In order to have micelles with the same size the molar ratio of water to surfactant was maintained constant ($w_o = 14$). The first step in which nickel core formation was carried out. 3 mL hydrazine was added

into the microemulsion which contained $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ under vigorous stirring at 50 °C and pink nickel-hydrazine complexes were formed in the microemulsion mixture. After few minutes, the solution became black indicating the formation of Ni nanoparticles. The reaction was maintained for 1 hour, subsequently reached complete reduction, and then the solution was allowed to cool to room temperature naturally. In the second step, identical volumes of two micelle solutions containing AgNO_3 and hydrazine, respectively, were poured over the microemulsion. The micelle solution of AgNO_3 was added first followed by micelle solution of hydrazine drop by drop. After 30 minutes acetone was added to the solution to induce phase separation. The synthesized metallic nanoparticles were washed with acetone and ethanol many times in order to remove the surfactant. For comparison, small amount of the Ni nanoparticles obtained after first step was washed, collected and characterized.

Characterization. The characterization of the as-prepared Ni and Ni-Ag core-shell nanoparticles were studied using X-ray diffractometer (XRD) (Rigaku D/max III with $\text{Cu-K}\alpha$ radiation ($\lambda \sim 0.1542$ nm)). XRD patterns were recorded in the 2θ ranging from 20° to 100° with a scanning step of 0.01°. The size and morphology of the nanoparticles were studied using transmission electron microscopy (TEM, JEOL Model JEM-1200EX). For TEM analysis, samples were prepared by dispersing the nanopowder in ethanol by using ultrasonic agitator, then placing a drop of the dilute solution (0.5% wt) onto a copper grid and then evaporating the ethanol in air at room temperature.

Results and Discussion

In polyol process the most common PVP was used as the dispersant for preparation of metal nanoparticles. The XRD pattern of the as-synthesized Ni nanoparticles with and without PVP capping agent is shown in Figure 1. The sample prepared without PVP shows peaks corresponding to the nickel oxide phase (Fig. 1(a)), which is attributed to the oxidation of Ni nanoparticles, whereas the XRD pattern of the sample prepared with PVP as capping agent shows peak with (100), (200) and (220) orientations corresponding to phase-pure Ni (Fig. 1(b)). This confirms that the protection of Ni nanoparticles against oxidation is achieved with PVP. Using the Scherer's equation particles size was calculated from the XRD pattern and the average particles size of Ni nanoparticles was about 13 nm. The particles size was further verified using TEM. Figure 2 shows the TEM image of the Ni nanoparticles, which shows the nearly uniform size and shape of the nanoparticles prepared. To further protect the Ni nanoparticles Ag shell was deposited onto it by successive polyol process by reduction of AgNO_3 . The optimum core-shell formation condition using polyol process was obtained by controlling the reaction time at difference reaction temperature. The reaction temperature was studied in the range from 60 °C to 120 °C with the reaction time varying from 1 hour to 7 days. TEM image of the sample prepared at 120 °C/1 hour (Fig. 3(a)), did not show any core-shell formation

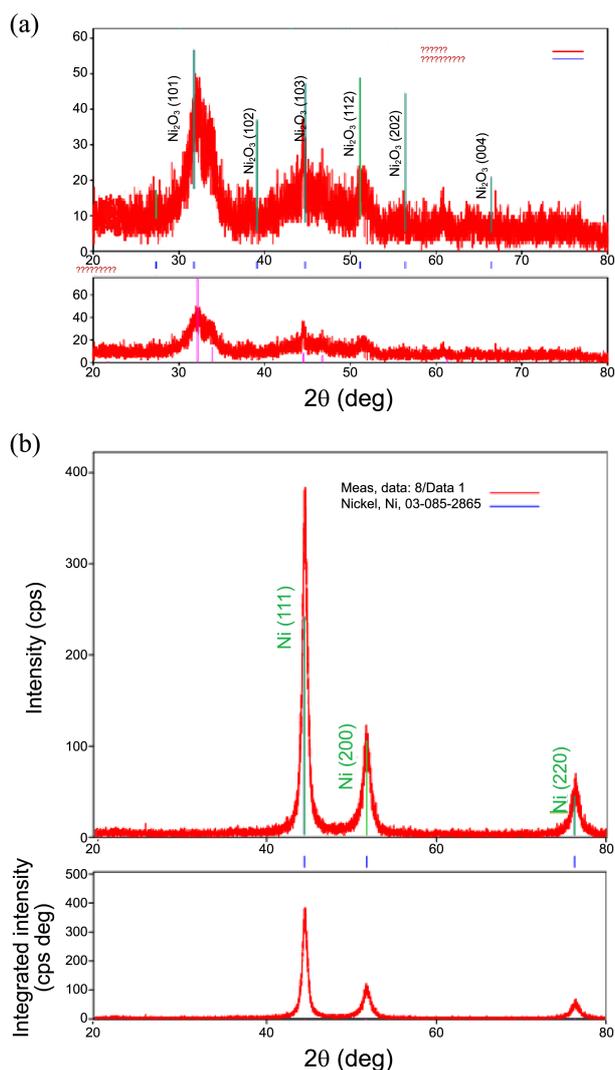


Figure 1. XRD patterns of (a) Nickel nanoparticles without capping agent and (b) Nickel nanoparticles with capping agent.

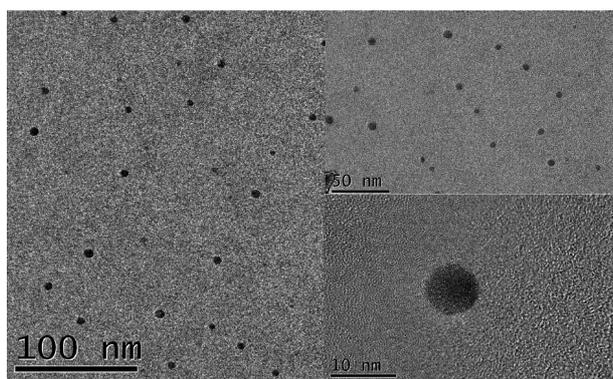


Figure 2. TEM image of Nickel nanoparticles.

and it contains only Ni nanoparticles; the EDS result also supported the presence of only Ni.

The short reaction time may not be enough for the Ag shell formation on Ni core. Figure 3(b) shows the TEM image of Ni/Ag nanoparticles synthesized at 120 °C/5 hours. EDS result confirms the Ag coating on the Ni nanoparticles,

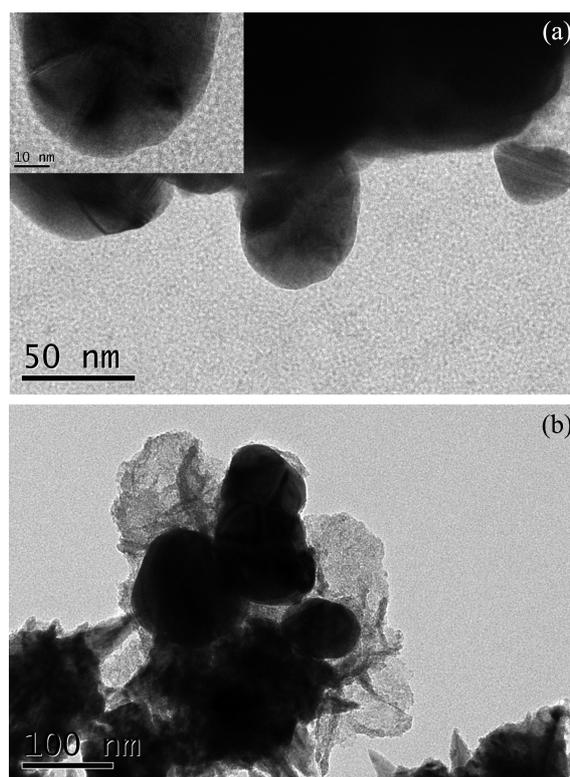


Figure 3. TEM image and EDS of (a) Ni-Ag at 120 °C/1 hour (b) TEM image of Ni-Ag at 120 °C/5 hours.

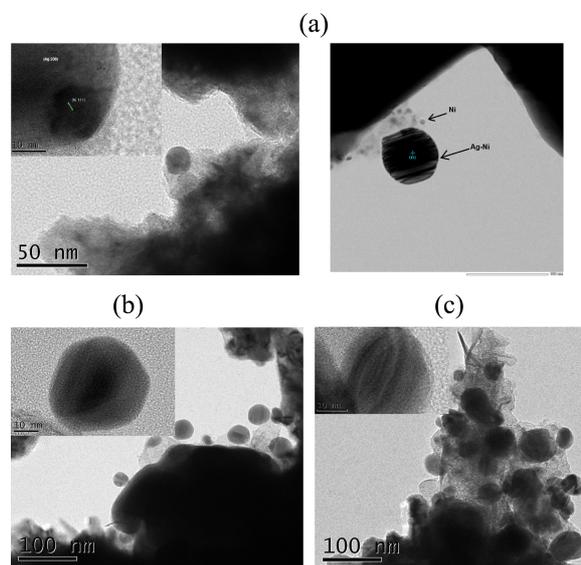


Figure 4. TEM image and EDS of (a) Ni-Ag at 80 °C/1 hour and TEM image of (b) Ni-Ag at 120 °C/5 hours and (c) Ni-Ag at 120 °C/10 hours.

but still the core/shell structure is not observed. In order to prepare the aggregation free core/shell structure, the preparation was carried out at the reaction temperature of 80 °C. The sample prepared at 1 hour reaction time showed the presence of Ni and also Ni/Ag core/shell structure (Fig. 4(a)), but the Ag shell layer thickness was non-uniform. The average size of the core Ni nanoparticles was about 13 nm

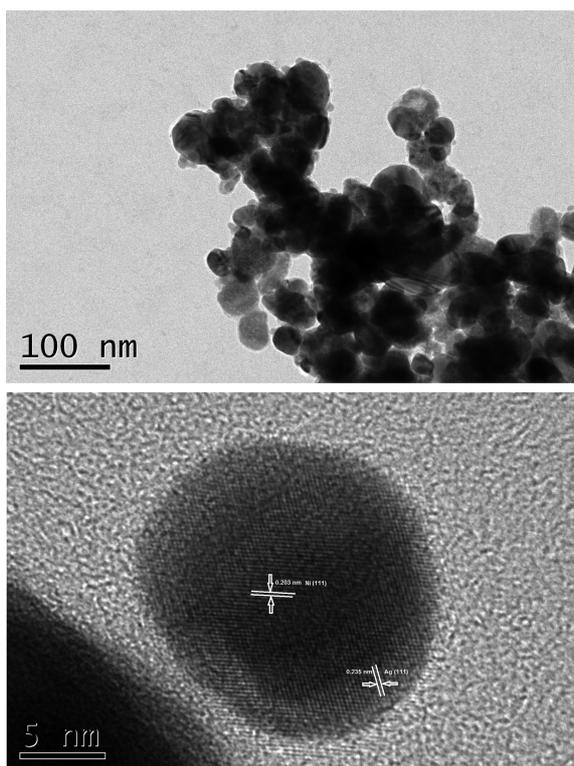


Figure 5. TEM image of Ni-Ag at 60 °C/7 days.

which is similar to the particles size estimated from the XRD. With the samples prepared after 5 hours of reaction time, particles were chosen randomly and studied by EDS (Fig. 4(b)). All the particles showed the presence of both Ag and Ni, difference in composition from particles to particles was high due to the non-uniformity of the Ag shell on Ni core and possibly due to presence of some unprotected Ni nanoparticles. To realize more uniform shell growth, the reaction time was increased to 10 hours, the TEM image (Fig. 4(c)) and EDS result of the samples show the formation of core-shell nanoparticles with nearly uniform size and composition. Further, we decreased the reaction temperature to 60 °C with increase in reaction time to 7 days.

With this optimum condition, the formation of core-shell structure is observed clearly and the TEM image of the sample is shown in Figure 5. The resulting core/shell nanoparticles were of the size of ~13 nm diameter Ni core with a thin Ag shell of thickness about ~3 nm. This polyol method is cheap and good for bulk synthesis of Ni-Ag core-shell. At controlled reaction conditions under extended reaction time and reduced reaction temperature, particle aggregation could be avoided, uniform Ni-Ag core-shell particles could be obtained with an yield of 80%. However, small amount of uniform nanoparticles was obtained through micelle solutions in microemulsion technique. The XRD pattern of the Ni nanoparticles synthesized using the microemulsion technique is shown in Figure 6(a), which shows peaks at 2θ values 44.45, 51.95, 76.18 and 92.87 corresponding to the orientations (111), (200), (220), (311) of phase on pure FCC Ni, no oxides or hydroxide such as NiO, Ni₂O₃, Ni(OH)₂ were

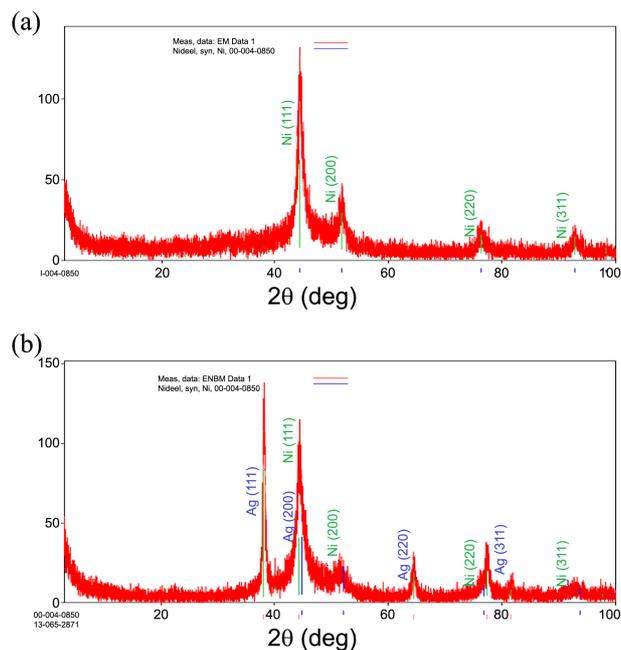


Figure 6. X-ray diffraction spectrum of (a) Ni nanoparticles (b) and Ni-Ag nanoparticles by microemulsion.

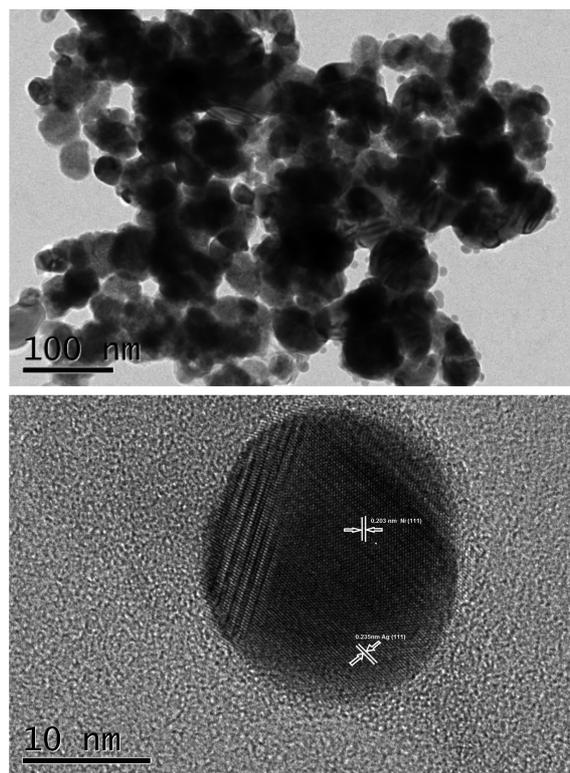


Figure 7. TEM image of Ni-Ag core-shell nanoparticles.

formed revealing the complete reduction process. Figure 6(b) shows the XRD pattern of the Ni-Ag core-shell nanoparticles. Here, in addition to the Ni peaks, the peaks of pure Ag also appeared at $2\theta = 38.12, 44.31, 64.46, 77.41,$ and 81.56 without any oxides. The TEM image in the Figure 7 shows the formation of nearly uniform core-shell nano

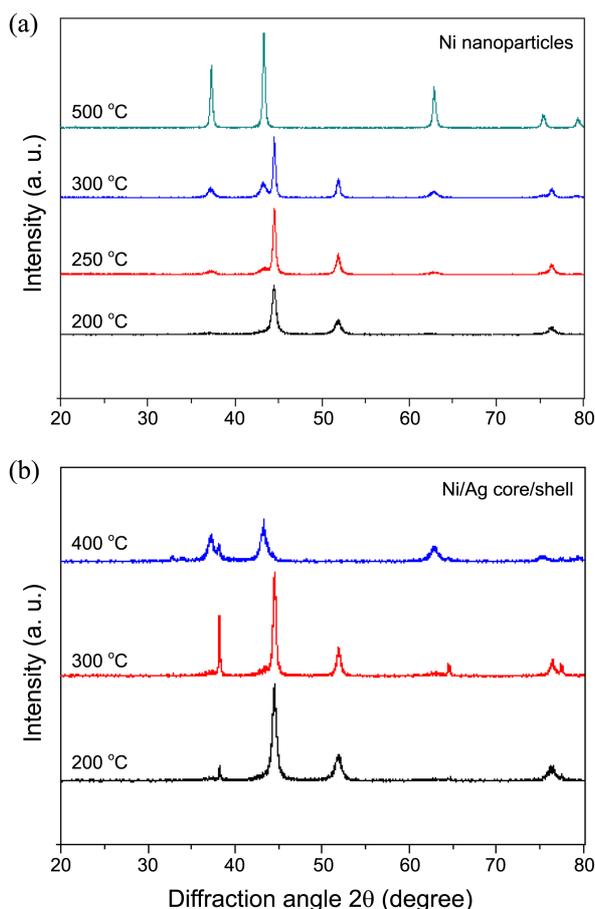


Figure 8. X-ray diffraction of (a) Nickel nanoparticles and (b) Ni-Ag nanoparticles at different temperatures.

structure; the Ni core size was about 8 nm while the Ag shell thickness was 6 nm. The particles in this case were more uniform than the particles obtained from polyol process.

To investigate the resistance against the thermal oxidation, Ni-Ag core-shell nanoparticles synthesized by polyol process and microemulsion technique were heat treated at different temperatures and the change in structure and phase was studied using XRD. The Ni nanoparticles prepared using the polyol process after washing were heated at 200 °C, 250 °C, 300 °C, 350 °C and 500 °C. The XRD pattern of the samples (Fig. 8(a)) heat treated at 200 °C shows only Ni phase, whereas the sample dried at 250 °C showed in addition to the strong Ni peak, small diffraction peaks corresponding to the nickel oxide phase, further at high drying temperature (500 °C) the nanoparticles phase completely turns into nickel oxide. To check the role of Ag shell layer on the oxidation of Ni nanoparticles the Ni-Ag core-shell nanoparticles were sintered at different temperatures and the oxidation of the samples were monitored. The XRD pattern of the Ni-Ag core-shell nanoparticles (Fig. 8(b)) the sample showed only the presence of pure Ni and Ag phase until 300 °C with no oxide peak observed. This result indicates that the Ag shell layer protect Ni core particles against oxidation until 300 °C, however, the samples showed the presence of oxide above 300 °C. Similarly, Ni and Ni-Ag

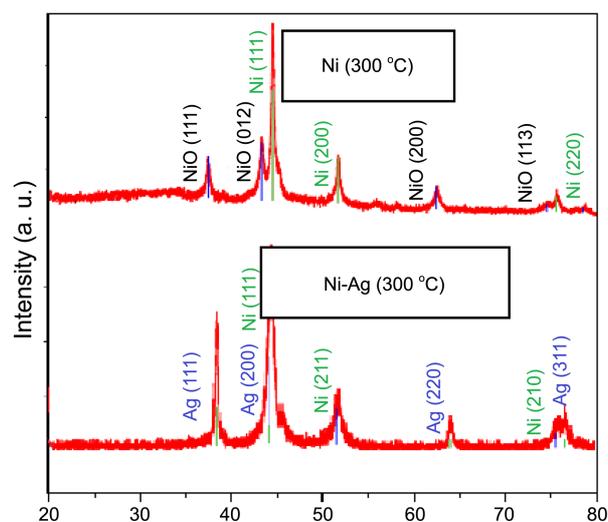


Figure 9. X-ray diffraction spectrum of Nickel and Ni-Ag nanoparticles after heating at 300 °C.

nanoparticles synthesized using the microemulsion technique was heated up to 300 °C. The XRD pattern of the Ni nanoparticles sintered at 300 °C showed a small peak corresponding to the nickel oxide, whereas the Ag coated Ni nanoparticles sintered at 300 °C does not show any oxide phase of Ni, showing the protecting ability of Ag shell against the oxidation (Figure 9). Compared to the polyol technique, the microemulsion method is more complicated. It is not good for bulk synthesis as the yield is almost half of the polyol process. But using this method uniform, monodispersed, aggregation free nanoparticles could be prepared. Because micelle covers particles and control the growth of particles. By varying the H₂O to surfactant (*w*_o) ratio size of the particles could be changed.

Conclusion

The Ag coated Ni nanoparticles have been synthesized successfully by polyol process and also by microemulsion technique. In polyol technique with low reaction temperature and with long reaction time high quality Ni-Ag core-shell were formed with 13 nm diameter Ni core with 3 nm thick Ag shell. The advantage of this method are: cheap and good for bulk synthesis. But the particle control is usually difficult because of the aggregation and formation of separated Ag particles. But by controlled reaction time and reaction temperature, we can obtain the core-shell particles. In the contrary with polyol technique, microemulsion technique is more expensive. It is not appropriate for large-scale manufacturing of Ni-Ag core-shell particles by emulsion technique. But by microemulsion technique, we can obtain the particles with uniform size. The core-shell nanoparticles synthesized in both methods show good resistance against the thermal oxidation up to 300 °C. The core-shell with inert silver coatings presented here will have more attractive applications. The ink preparation process of the prepared nanoparticles for inkjet printing application is

currently being investigated.

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References

1. Chen, D. H.; Wang, S. R. *Materials Chemistry and Physics* **2006**, *100*, 468.
 2. Lee, C. C.; Chen, D. H. *Applied Physics Letters* **2007**, *90*, 193102.
 3. Wang, H.; Kou, X.; Zhang, J.; Li, J. *Bull. Mater. Sci.* **2008**, *31*(1), 97.
 4. Chen, D. H.; Wu, S. H. *Chem. Mater.* **2000**, *12*, 1354.
 5. Toshima, Y.; Hayashi, T.; Yamaguchi, Y.; Shimamura, H. *U.S Patent*, 6,632,524, 2003.
 6. Chen, D.; Liu, S.; Li, J.; Zhao, N.; Shi, C.; Dua, X.; Sheng, J. *Journal of Alloys and Compounds* **2009**, *475*, 494.
 7. Bala, T.; Swami, A.; Prasad, B. L. V.; Sastry, M. *Journal of Colloid and Interface Science* **2005**, *283*, 422.
 8. Chen, D. H.; Hsieh, C. H. *J. Mater. Chem.* **2002**, *12*, 2412.
 9. Joshi, R.; Mukherjee, T. *Radiation Physics and Chemistry* **2003**, *66*, 397.
 10. Chiu, H. K.; Chiang, I. C.; Chen, D. H. *J. Nanopart. Res.* **2009**, *11*, 1137.
 11. Lopez, F.; Cinelli, G.; Ambrosone, L.; Colafemmina, G.; Ceglie, A.; Palazzo, G. *Colloids and Surface A: Physicochem. Eng. Aspects* **2004**, *237*, 49.
 12. Chen, D.; Li, J.; Shi, C.; Du, X.; Zhao, N.; Sheng, J.; Liu, S. *Chem. Mater* **2007**, *19*, 3399.
 13. Capek, I. *Advances in Colloids and Interface Science* **2004**, *110*, 49.
 14. Li, X.; He, G.; Zheng, W.; Xiao, G. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2010**, *360*, 150.
 15. Gan, L. M.; Chieng, T. H.; Chew, C. H.; Ng, S. C. *Langmuir* **1994**, *10*, 4022.
 16. Ganesh, V.; Lakshminarayanan, V. *Journal of Colloids and Interface Science* **2010**, *349*, 300.
 17. Zhang, W.; Qiao, X.; Chen, J. *Materials Science and Engineering B* **2007**, *142*, 1.
 18. Valiente, M.; Rodenas, E. *Colloid Polym. Sci.* **1993**, *271*, 494.
 19. Chen, M.; Zhou, J.; Xie, L.; Gu, G.; Wu, L. *J. Phys. Chem. C* **2007**, *111*(32), 11829.
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