

Effect of liquid media on nanoparticles synthesized of nickel oxide by pulsed laser ablation

Suk Hyun Kang^a, Tian Yi Liu^a, Bong Geun Choi^a, Jun Han Yuh^b and Kwang Bo Shim^{a,*}

^aDivision of advanced Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea

^bGlobal Technology Center, POSCO, 892 Daechi-dong, Gangnam-gu, Seoul 135-777, Korea

Since nano science and technology has been developed at the end of the 20st century, the key technical issues is how to get a large number of high purity nano materials which were precisely controlled on the morphology, size and structure, and improve the dispersion and stability of nano materials. Among the numerous methods, laser as an advanced technology has got more and more attention. And the introduction of liquid medium makes the laser ablation process become more complex. This work presents the characteristics of nano-sized magnetic material. Focus on the application and preparation of NiO nanoparticles. By using liquid phase pulsed laser ablation method, NiO nanoparticles have been made in different liquid media. The comparison of the effect of different liquid medium on composition, size and shape, and process mechanism of the preparation by this method were discussed. In addition, because of the magnetic properties of the NiO nanoparticles obtained, it can be better applied in many fields. This unique method of liquid phase pulsed laser ablation, is expected to obtain new nano structure and material, show better physical and chemical properties of material.

Key words: Nio, Nano particles, Laser ablation.

Introduction

21st century is full of opportunities and challenges. The rapid development of information technology, biotechnology, manufacturing technology, energy sector, Energy Sector environmental science and national defense made new requirements on material science. In order to be smaller in size and heighten in properties, nanometer material became the most important role. Nanometer material is composed of nanoparticles which heighten heighten New Requirements New Requirements refer to the ultrafine particles whose particle size is ranged in diameter of 1-100 nm. When the particle size comes into nanometer scale, the particles are provided with quantum size effect, small size effect, surface effect and macroscopic quantum tunnel effect [1]. Because of these properties, nanoparticles have broad application prospects in magnetic materials, electronic material, optical material, catalyst, ceramic toughening and medicine. ceramic toughenin small size effects small size effect Nickel (II) oxide is a kind of common inorganic compounds with the chemical formula of NiO. It is green powder, the melting point is 1980 ± 20 °C and the density is 6.67 g/cm³. It is insoluble in water or alkali solution, but soluble in acid solution and ammonia water. The crystal structure of NiO is cubic,

similar to sodium chloride (NaCl), named the rock salt structure. Nano-NiO has high activity, high selectivity and some other outstanding features which made it became an important raw material for preparing the catalyst. Because the crystal size is largely affected the performance of the material the material has high strength and high toughness, high specific heat and high cost, high electrical conductivity and magnetic susceptibility [2], and a strong absorption properties of the electromagnetic wave [3], could improve the sensitivity of the sensor and so on [4-6]. In materials, electronic and chemical industry, it is often used in the manufacture of chemical sensors, super capacitors, etc. Because of its processing performance in a other materials [7], it also widely used in battery electrodes, ceramic coloring materials, optoelectronic materials and so on [8-11]. If according to the different states of the raw material, the preparation method of nano-nickel (II) oxide can be divided into solid phase method [12, 13], liquid phase method and gas phase method. In the early 1960s, the interaction between laser and matter has been discovered. The pulsed laser ablation technique is based on this physical basis. It uses a bunch of high-energy pulsed laser irradiate the target surface, making the surface rapidly heated, melted and evaporate, then has the cooling crystallization. When a high brightness laser beam focused by a lens, it can produce thousands even millions of degrees high temperature in the vicinity of the focal point. This high temperature can almost melt away all the material. When a laser irradiated to the target surface, a part of

*Corresponding author:
Tel : +82-2-2290-0501
Fax: +82-2-2299-2884
E-mail: kbshim@hanyang.ac.kr

the incident light is reflected while a part of the incident light is absorbed. Once the energy of the absorbed laser comes over the surface evaporation temperature, the target will melt and evaporation from a large number of atoms, electrons and ions, thereby forming a plasma on the target surface. After the pulsed laser was removed, the plasma first expanded and then rapidly cooled. So the atoms curdled on the collector which is on the opposite side of the target. And the wanted nanoparticle can be obtained. According to the experimental conditions, there are two kinds of the preparation methods, gas phase and liquid phase methods. Because the gas phase preparation has certain requirements to the vacuum and temperature, more complex and costly, the liquid phase pulsed laser ablation (LP-PLA) have received more attention [14-16]. PLA has been used to prepared metal nanoparticles for a long time. It is a convenient, effective and broad applicability material preparation method [17-20]. It uses a pulsed laser to bombardment the metal target which immersed in the liquid (water or other solvents), making the thermal melting and (or) vaporization occur on its surface [21, 22]. The resulting metal atoms or clusters condensed with each other and formed into nanoparticles [23-25]. These metal nanoparticles suspended and dispersed in the solution that formed a nano-colloidal [26]. Since the preparation process does not involve a chemical reaction, this method can prepare the pure metal nanoparticles, avoid the influence of other substances. Due to the local high temperature and high pressure and non-equilibrium process, this method is a new capable synthesis method of the nano materials which cannot be prepared by conventional ways, such as the high melting point metal nanoparticles [27, 28]. In recent years, liquid phase pulsed laser ablation (LP-PLA) method has received great attention and increasingly used for producing NiO nanoparticles [29]. The parameters of the processing are easy to control. It also has advantages of simple equipment, low-cost and fast preparation. There have some studies on the preparation of NiO nanoparticles by LP-PLA. Laser parameters, such as the laser wavelength, the laser influence and the pulse duration, ablating time and type of surrounding liquid media are the effects to the structural morphology, particle size, compositional phase and other properties of the final nanoparticles products. Lui et al. and Khan et al. reported on the effect of surfactant on particle size of NiO nanoparticles that synthesized by LP-PLA [30, 31]. The average size of NiO nanoparticles was decreased by the addition of sodium dodecyl sulfate (SDS) which used as the surfactant. Mahfouz et al. presented the effect of ablating time on the particles size and the size distribution of NiO nanoparticles produced from laser irradiation of nickel metal target [32]. They found that the size distribution and the average size of nanoparticles decrease with the increasing of the ablation time. There are a few reports of laser ablation syntheses of NiO

nanoparticles in organic solvents such as ethanol and acetone. It is very challenging to investigate the effect of inorganic and organic liquid media on properties of the final product nanoparticles produced by laser irradiation of NiO target. In this report we studied the pulsed laser ablation of NiO target in different solvents, D.I. water, ethanol and acetone, and discussed the effect of liquid media on the particle size distribution, the particle size, the particle shape and the compositional phase of the nanoparticles product. And also we inferred the reason of these. In final part, the magnetic characters of the nanoparticles are also been discussed.

Experimental

Commercially available NiO powders were used as a starting material. About 7 g of NiO powder was fabricated by spark plasma sintering (SPS) method at 1400 for 5 min. The fabricated NiO target was fixed in the bottom of a glass vessel containing high purity D.I. water, ethanol and acetone respectively. Three different liquids of D.I. water, ethanol and acetone were used as a media. In case of ethanol and acetone, their volume fraction in aqueous solution was fixed with 40%. The targets were ablated to each liquid media by a laser beam with a 2 mm-diameter focal spot size (Dye Nanosecond Laser, Continuum SLIII-10, USA) for 1 hr with the repetition rate of 10 Hz. The pulse duration is 5 ns. The wavelength and energy were 532 nm and 40 mJ/pulse, respectively. The obtained colloidal solutions with NiO nanoparticles were processed for the characterization using a variety of processing equipment such as a low speed centrifuge, electric drying oven and ultrasonic cleaner. The crystallinity and structural features of the as-processed NiO nanoparticles were examined using a X-ray diffractometer (XRD, Cu, 40kV, 40mA, XRD-7000, Shimadzu Limited, Japan). The structural morphology and chemical composition were characterized by a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) equipped with X-ray energy dispersive spectrometry (EDX). Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, VersaLab, Quantum Design, USA) at room temperature (300K) by saturating the sample in a field of 4000 Oe. sintered at 1100 for 4 hrs under an ambient atmosphere with a conventional electric furnace. The sintered NiO targets exhibited 99.5% of theoretical density ($TD_{NiO} = 6.67 \text{ g/cm}^3$) and their size were typically 20mm in diameter and 3mm in thickness. Fig. 1 shows the image and X-ray diffraction pattern of the sintered NiO target.

Three different liquids of D.I. water, ethanol and acetone were used as a media. In case of ethanol and acetone, their volume fraction in aqueous solution was fixed with 40%. The targets were ablated to each liquid media by a laser beam with a 2 mm-diameter focal spot size (Dye Nanosecond Laser, Continuum SLIII-10,

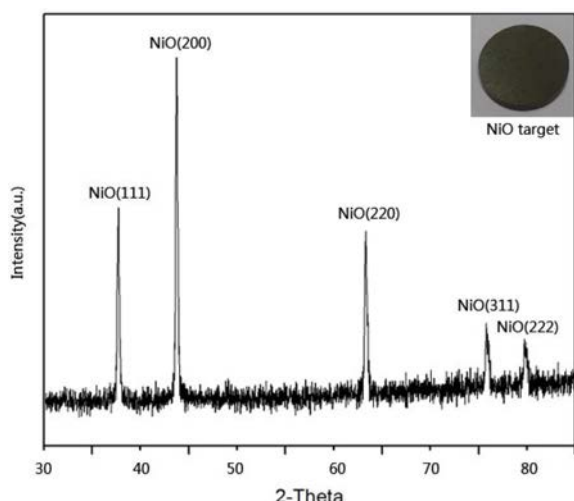


Fig. 1. The image and XRD patterns of the sintered NiO target.

USA) for 1 hr with the repetition rate of 10 Hz. The pulse duration is 5 ns. The wavelength and energy were 532 nm and 40 mJ/pulse, respectively. The obtained colloidal solutions with NiO nanoparticles were processed for the characterization using a variety of processing equipment such as a low speed centrifuge, electric drying oven and ultrasonic cleaner.

The crystallinity and structural features of the as-processed NiO nanoparticles were examined using a X-ray diffractometer (XRD, Cu, 40 kV, 40 mA, XRD-7000, Shimadzu Limited, Japan). The structural morphology and chemical composition were characterized by a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) equipped with X-ray energy dispersive spectrometry (EDX). Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, VersaLab, Quantum Design, USA) at room temperature (300K) by saturating the sample in a field of 4000 Oe.

Results and Discussion

The NiO colloidal suspensions, which were obtained by laser ablation of NiO target, in three different liquid media (Fig 2(a)). In case of D.I. water and ethanol solution, much shallow black substances were suspended in the colorless solutions. However, in acetone solution, the shallow black substance were suspended in light yellow solution. This maybe because of the presence of carbonyl nickel, possibly $\text{Ni}(\text{CO})_4$, which were made from the reaction of the part of Ni from the NiO target and the carbonyls. After standing for 72 hours, most of the suspended substances have been dispersed into the solutions without color change of solutions (Fig. 2(b)).

Fig. 3 shows TEM images of the NiO nanoparticles extracted from three solutions. Spherical shape with a little of nearly cubical shape mixed are seen in all three solvents. Khan *et al.* reported that shape of nanoparticles depended on the favorable growth plane during the

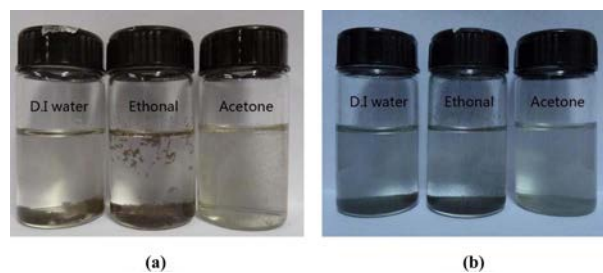


Fig. 2. The colloidal suspensions prepared by laser irradiation in different liquid media; (a) as-irradiated and (b) after standing for 72 hrs.

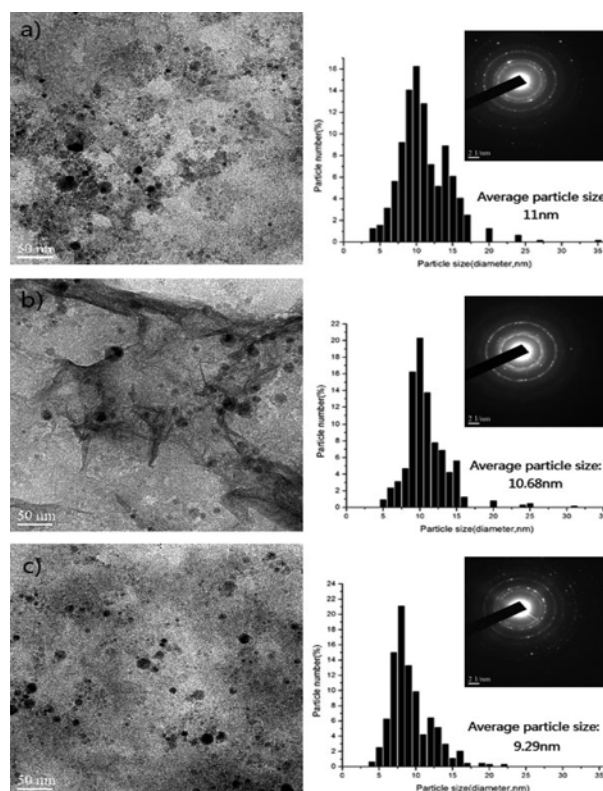


Fig. 3. TEM image of nanoparticles extracted from the three solutions by laser irradiation of NiO target in (a) D.I. water, (b) ethanol and (c) acetone, with the relative particle size distribution and SAED patterns of the corresponding nanoparticles (inset).

formation. In D.I. water, the diameter of the particles is in the range of 4 to 35 nm with an average size of 11 nm (Fig. 3(a)). The diameter of the particles in ethanol is in the range of 5 to 31 nm with an average size of 10.68 nm (Fig. 3(b)). The particles obtained in acetone were ranged in diameter of 4 to 22 nm with an average size of 9.29 nm (Fig. 3(c)). The average sizes of the nanoparticles in all the three solvents are similar. Compared with the nanoparticles obtained in D.I. water and ethanol, those in acetone have the small range of particle size which is 4 to 22 nm. This might because of the molecular polarizability of the liquid media. The acetone has higher dipole moment than other solvents. It can bond stronger and more packed to the nanoparticle surface. Tilaki *et al.* reported that the electrostatic

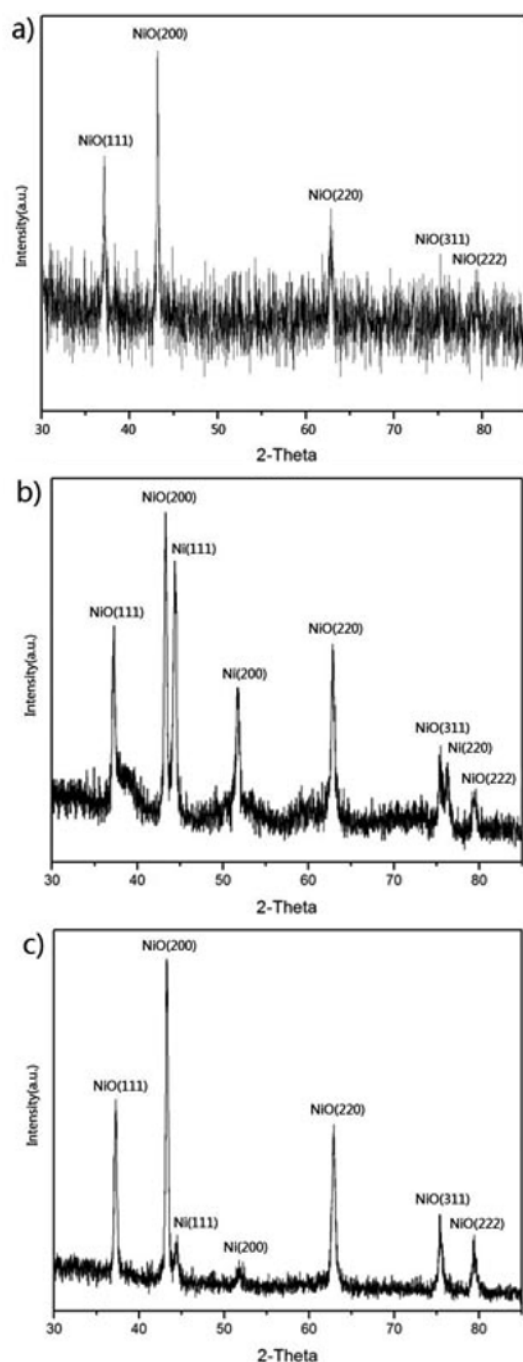


Fig. 4. X-ray diffraction patterns of nanoparticles extracted from the colloidal solutions obtained in (a) D.I. water, (b) ethanol and (c) acetone.

repulsive force resulted the overlapping of the electrical double layer, while the nuclei in the plume prevent further growth and aggregation [33]. Fig. 4 shows the XRD pattern of nanoparticles obtained in three different liquid media. In case of D.I. water, only cubic NiO phase was detected (Fig. 4(a)). However, in ethanol and acetone, cubic NiO phase and metal Ni phase were detected (Figs. 4(b) and 4(c)). The nanoparticles obtained in ethanol contained much Ni phase than in acetone. HR-TEM analysis was performed in order to identify more

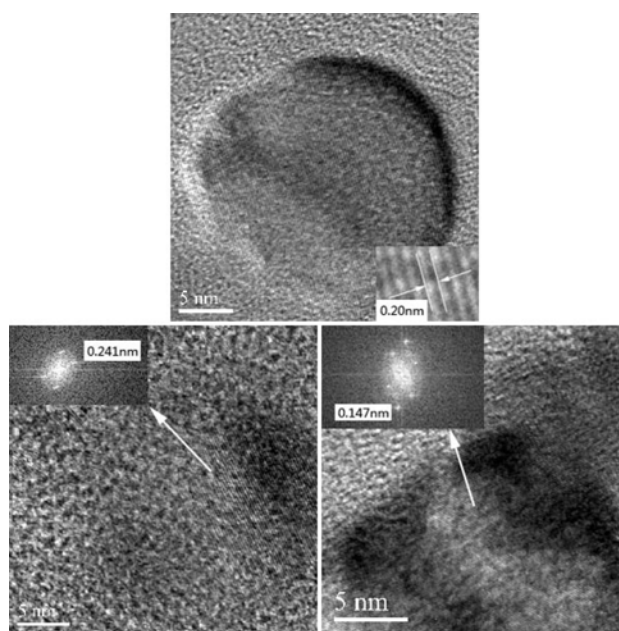


Fig. 5. HR-TEM image of nanoparticles obtained in D.I. water and corresponding 2D-FFTs (inset).

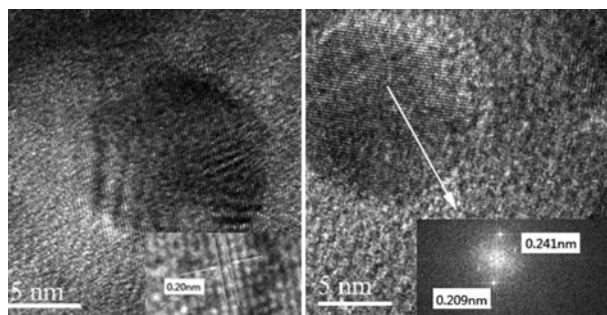


Fig. 6. HR-TEM image of single nanoparticles obtained in ethanol. Nearly cubical shapes was showed on the left. On the right, 10 nm NiO particle and corresponding 2D-FFTs (inset).

accurately the phase of the NiO nanoparticles obtained in all these three solvents. Fig. 5 shows HR-TEM image of the nanoparticles obtained in D.I. water. The particles with various sizes and shapes are seen, which has the interplanar distance of 0.2 nm, 0.241 nm or 0.147 nm in D.I. water. The interplanar distances correspond to NiO (111) plane [$d_{(111)} = 0.241$ nm], NiO (100) plane [$d_{(200)} = 0.209$ nm; owing to an extinction for $d_{(100)}$ in face centered cubic materials] and NiO (220) plane [$d_{(220)} = 0.147$ nm]. The interplanar distance of the particles in ethanol is 0.20 or 0.24 nm, and compatible with NiO composition as shown in Fig. 6 (on the right). On the left of Fig. 6, it might be a Ni particle. The interplanar distances of Ni (111) plane is 0.204 nm which is very close to the interplanar distances of NiO (100) plane [$d_{(200)} = 0.209$ nm]. These results of XRD indicated the nanoparticles in ethanol are composed of NiO phases and Ni phases.

In case of the nanoparticles in acetone, HR-TEM analysis showed that the observed nanoparticles exhibited

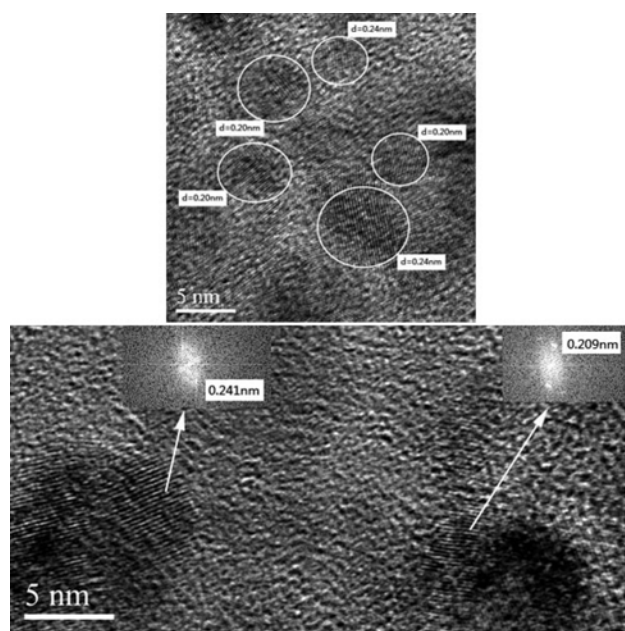


Fig. 7. HR-TEM image of near-spherical nanoparticles obtained in acetone and corresponding 2D-FFTS (inset).

near-spherical shape with the interplanar distances of 0.20 nm or 0.24 nm, corresponding to NiO phase as shown in Fig. 7. After the irradiation of NiO target in acetone, the solution became light yellow, might because of the formation of $\text{Ni}(\text{CO})_4$.

The experimental results can be discussed like that the local super high temperature and pressure plasma were generated instantly by the interaction of laser and the solid target in the liquid medium. It can be ultrafast cooling by the surrounding liquid medium.

When a beam of laser hit the solid target, it can lead to an immediate material surface melting and evaporation. Because of continued exposure of the laser, there happened a pump produced the ultrahigh pressure and temperature plasma which will be rapid evolution. And then local plasma should be supersonic outwardly adiabatic expansion. At the same time, it has interaction and chemical reaction with the surrounding environment, thereby rapidly cooling, condensation, until the annihilation of plasma. During this process, the plasma will be first to form a small single body, then the nucleation, growth, until form the nanoparticles, and reunited into various nanostructures. This different growth includes the following features. First, the produced plasma has ultra-high temperature and pressure, and contains a high density of free radicals from the highly excited target and liquid medium. Second, the liquid medium will result in the fast annihilation of the high temperature and pressure plasma, and can also cause a chemical reaction for new material and new structure. In our experiment, the liquid phase medium and the target with nickel, oxygen and the carbonyl, has a certain extent on the reaction and the composition of the products. In case of the irradiation of NiO in the D.I. water, Ni species generated from the target were

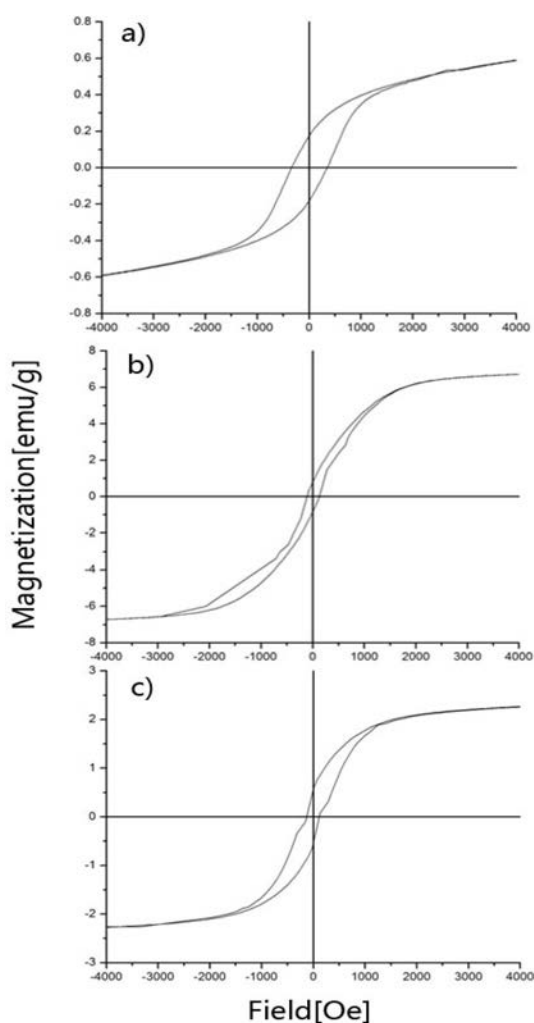


Fig. 8. Magnetic hysteresis curves measured at room temperature (300K) of nanoparticles extracted from colloidal solutions obtained in (a) D.I. water, (b) ethanol and (c) acetone

fully oxidized by oxygen species from target and D.I. water, leading to the only formation of NiO phase in the final product. During the laser ablation in the ethanol, nickel evaporated from the target with the surrounding ethanol was heated decomposition which became a high temperature and high pressure gaseous plume area mainly composed of carbon and nickel. After the laser pulse, the gaseous plume area began to cool and carbon first condensation. When the temperature is lower than the nickel gasification temperature, the formation of nanoscale nickel droplet started and it absorbed and dissolved the carbon. With further decrease of temperature, the solubility of carbon in the nickel droplet decreases. The carbon separated out on the surface of nickel particles and came into the carbon coated nano particles. In case of the irradiation of NiO in the acetone, due to insufficiency in amount of oxygen species, Ni species ejected from specimen were partially oxidized to form nickel oxide phase and some Ni species chemically react each other to form pure nickel phase. But here might be formed to $\text{Ni}(\text{CO})_4$.

Table 1. The coercive force (H_c), residual magnetization (M_r) and saturation magnetization (M_s) of nanoparticles extracted from colloidal solutions obtained in different liquid media.

	D.I. water	Ethanol	Acetone
H_c (Oe)	414	212	198
M_r (emu g ⁻¹)	0.1657	0.7866	0.5983
M_s (emu g ⁻¹)	0.5914	6.5492	2.2347

Fig. 8 shows the magnetic properties of the nanoparticles obtained in all three solvents. The coercivity, remanent magnetization and magnetization of these nanoparticles are also listed in Table 1. The nanoparticles obtained in all three solvents showed the ferromagnetism. Du *et al.* suggested that the critical size of the NiO coated Ni nanoparticles for super-para magnetism at room temperature is about 15 nm [34]. The results of the nanoparticles obtained in ethanol and acetone are very close while the data of the nanoparticles obtained in D.I. water is obviously different from the other two. That might be because of the mix of the Ni phases in the colloidal suspensions in ethanol and acetone [35, 36]

Conclusions

NiO nanoparticles have been prepared by laser irradiation of NiO target in D. I. water, ethanol and acetone. The composition of the nanoparticles obtained in D. I. water is almost NiO phase, which is different from that of the nanoparticles obtained in ethanol or acetone, NiO phase and Ni phase. This is likely because of the complete oxidation in D. I. water. Also the nanoparticles obtained in ethanol were mixed with lots of Ni phase. And the process mechanism of the LP-PLA method has been discussed.

However, the nanoparticles obtained in acetone have more narrowly range of particle size than that of the nanoparticles obtained in D. I. water or ethanol. The three kinds of nanoparticles was ferromagnetism. This can give more help to the application of NiO nanoparticles. The effect of liquid medium on composition, size and shape of nanoparticles synthesized by pulsed laser ablation has been discussed, which certainly made an important function to the nanoparticle fabrication by liquid phase pulsed laser ablation method.

References

1. L.D. Zhang, "Nanometer material (1st ed.)", Chemical industry press, Beijing (2000).
2. F. Bodker, M.F. Hansen, K.C. Bender, S. Morup, J. Mag. Mater. 221 (2000) 32-36.
3. R.B. Fahim, A.I. Abu-Shady, J. Catal. 17 (1970) 10-17.
4. C.L. Bai, "Nano-science and nanotechnology", Yunnan science and technology press, Kunming (1995) 44-45.
5. J.T. Richardson, D.I. Yiagas, B. Turk, K. Forster, M.V. Twigg, J. Appl. Phys. 70 (11) (1991) 6977-6982.
6. B.S. Zou, L. Wang, J.G. Lin, Sol. Stat. Comm. 94 [10] (1995) 847-850.
7. C.Y. Zhu, Z.H. Liu, W. Chen, F.Q. He, J. Funct. Mater. 30 [4] (1999) 345.
8. Y.D. Li, C.W. Li, H.G. Zheng, L.Q. Li, X.F. Duan, Y.T. Qian, J. Chem. Chin. Univ. 18 [12] (1997) 1921-1923.
9. P. Tomczyk, H. Sato, K. Yamada, T. Nishina, I. Uchida, J. Elect. Chem. 391 [1-2] (1995) 125.
10. P. Polzot, S. Laruelle, S. Grugeon, L. Dupont, J-M. Tarascon, Nature, London 407 [6803] (2000) 496-499.
11. V. Biju, K. M. Abdul, Mater. Science and Engineering A304-306 (2001) 814-817.
12. L.Q. Zhou, N.H. Yang, L.R. Zhou, et al. J. Chin. Applied Chem. 23 [6] (2006) 682-684.
13. Y.P. Wang, J.W. Zhu, Thermochimica Acta 437 [1-2] (2005) 106-109.
14. J.H. Ryu, J.W. Yoon, K.W. Shim, J.App. Phys. 99 (2006) 086103.
15. J.H. Ryu, J.W. Yoon, K.W. Shim, N. Koshizaki, Appl. Phys. A 84 (2006) 181-185.
16. J.H. Ryu, B.G. Choi, J.W. Yoon, K.B. Shim, K. machi, K. Hamada, J. Lum. 124 (2007) 67-70.
17. J.H. Ryu, S.Y. Bang, W.S. Kim, G.S. Park, K.M. Kim, J.W. Yoon, K.W. Shim, N. Koshizaki, J. Alloy. Com. 441 (2007) 146-151.
18. J.H. Ryu, S.Y. Bang, J.W. Yoon, C.S. Lim, K.B. Shim, J. appl. Sur. Sci. 253 (2007) 8408-8414.
19. J.H. Ryu, G.C. Park, K.M. Kim, C.S. Lim, J.W. Yoon, K.B. Shim, Appl. Phys. A, 88 (2007) 731-736.
20. G.S. Park, K.M. Kim, S.W. Mhin, J.W. Eun, K.B. Shim, J.H. Ryu, N. Koshizaki, Elec. Sol. Lett, 11 (2008) J23-J26.
21. J.H. Ryu, K.M. Kim, S.W. Mhin, G.S. Park, J.W. Eun, K.B. Shim, C.S. Lim, Appl. Phys. A92 (2008) 407-412.
22. S.W. Mhin, J.H. Ryu, K.M. Kim, G.S. Park, H.W. Ryu, K.B. Shim, T. sasaki, N.Koshizaki, Appl. Phys. A96 (2009) 435-440.
23. S.W.Mhin, J.H. Ryu, K.M. Kim, G.S. Park, H.W. Ryu, K.B. Shim, T. sasaki, N. Koshizaki, Nano. Res. Lett. 4 (2009) 888-895.
24. K.M. Kim, J.H. Chung, J.H. Ryu, J. Optic. Soc. Kor. 16 (2012) 76-79.
25. K.M. Kim, J.H. Ryu, J. alloy. Com. 576 (2013) 195-200.
26. D.G. Lee, S.W. Park, Y.S. Yang, H.J. Kim, G.C. Xu, J. Elect. Eng. Tech. 6 (2011) 842-848.
27. D.G. Lee, S.H. Kim, S.W. Park, Y.S. Yang, G.C. Xu, J. Elect. Eng. Tech. 7 (2012) 576-581.
28. S. G. Yoon, A. Safari, Kor. J. Mater. Res. 4 (1994) 401-405.
29. P.S. Liu, H.B. Zeng, W.P. Cai, X.D. Luo, W.P. Jing, J. Electronic components and materials 28 [1] (2009) 68-72.
30. Z. Liu, Y. Yuan, S. Khan, A. Abdolvand, D. Whitehead, M. Schmidt, J. Micromech. Microeng. 19 (2009) 054008.
31. S.Z. Khan, Y. Yuan, A. Abdolvand, M. Schmidt, P. Crouse, L. Li, Z. Liu, M. Sharp, K. G. Watkins, J. Nanopary. Res. 11 (2009) 1421-1427.
32. R. Mahfouz, F.J. Cadete Santos Aires, A. Brenier, B. Jacquier, J. C. Bertolini, Appl. Surf. Sci. 254 (2008) 5181-5190.
33. R.M. Tilaki, A. Irajizad, S.M. Mahdavi, Appl. Phys. A: Mater. Sci. Proc. 84 (2006) 215-219.
34. Y.W. Du, M.X. Xu, J. Wu, Y.B. Shi, H.X. Lu, R.H. Xue, J. Appl. Phys. 70 (1991) 5903-5905.
35. S. Li, M. Lui, H. Bi, W. Zou, Z. Huang, Y. Du, J. Alloys Compd. 425 (2006) 1-3.
36. S. Guo, W. Lui, H. Meng, X.H. Liu, W.J. Gong, Z. Han, Z.D. Zhang, J. Alloys Compd. 497 (2010) 10-13.