Silica-coated gadolinium-doped lanthanum strontium manganite nanoparticles for self-controlled hyperthermia applications

Ashfaq Ahmad, Hongsub Bae, and Ilsu Rhee

Department of Physics, Kyungpook National University, Daegu 702-701, Korea

(Received 2 November 2017; accepted 28 December 2017; published online 9 January 2018)

Gadolinium-doped lanthanum strontium manganite (LSM) nanoparticles were synthesized by using a citrate-gel technique. The particles were then annealed at 850 °C to remove defects for good crystallinity, followed by coating with silica for biomedical application to magnetic hyperthermia. The chemical composition was determined to be La$_{0.54}$Sr$_{0.27}$Gd$_{0.19}$MnO$_3$ using an inductively coupled plasma mass spectrometer. The nanoparticles were characterized by X-ray diffraction, transmission electron microscope, and Fourier transform infrared spectrometer to check perovskite crystalline structure and to observe particles size and coating status of silica on the surface of the particles. The Curie temperature of the particles was found to be about 280 K. The saturation temperature of the aqueous solution of the particles remained at the hyperthermia target temperature of 42 °C with increasing concentration of particles from 6 to 60 mg/mL in the dispersion. This saturation temperature for a highly concentrated 120-mg/mL-sample increased further, but less than the dangerous temperature of 47 °C for normal tissues. The saturation temperature of the powder sample reached only up to 53 °C. These results showed that the gadolinium-doped LSM nanoparticles can be used for self-controlled hyperthermia in which the temperature does not exceed the target temperature of hyperthermia even at the tissue site of highly accumulated nanoparticles. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5011717

I. INTRODUCTION

Magnetic nanoparticles have been widely explored for the variety of applications including information devices, data storage, and biomedical applications such as in the drug delivery, MRI, and magnetic hyperthermia.

Magnetic hyperthermia treatment of cancer is a therapeutic concept based on killing cancer by using magnetic nanoparticles as heat generators. Gilchrist et al. first reported the application of the maghemite nanoparticle to magnetic hyperthermia. The magnetic nanoparticles generate heat when subjected to RF magnetic field due to loss mechanisms. In the magnetic hyperthermia treatment of cancer the nanoparticles are injected into the tumor site, and these particles generate heat in the presence of RF magnetic field to increase the temperature of the cancerous tissue to the target temperature of 42 °C to eliminate them. The magnetic hyperthermia is a noninvasive technique and can be used for the localized killing of the cancerous tissue.

Two types of heat loss mechanism are associated with heating effect of magnetic nanoparticles in RF field. The hysteresis power losses occur in the ferromagnetic magnetic nanoparticles due to the domain wall motion. Relaxational losses are of two types: Neel relaxation in superparamagnetic nanoparticles due to rotation of their magnetic moment in the presence of external alternating magnetic field, and Brownian relaxational losses due to friction of rotating particles inside the medium.
The specific absorption rate (SAR), which is the amount of heat dissipated per unit mass of the magnetic particles in RF magnetic field is an important parameter for the magnetic nanoparticles used in magnetic hyperthermia. High SAR not only reduces the dosage of nanoparticles to be injected, but also lowers the magnetic field strength and frequency. Additionally for the self-controlled hyperthermia, magnetic nanoparticles with lower Curie temperature are required. The self-controlled hyperthermia minimizes the risk of overheating that would harm the healthy tissue in the surroundings. This can be attained by using magnetic nanoparticles with lower Curie temperature to prevent heating the tissue above this temperature. One of the candidate materials for this is lanthanum strontium manganite. Several studies have been carried out on these nanoparticles with different chemical composition and coating materials. Sadia et al. demonstrated the influence of the chemical composition and particles size on the magneto-thermal properties and Curie temperature of these manganite nanoparticles. These results showed that Curie temperature could be tuned both by changing the chemical composition and size of the particles.

Nontoxic suspensions of magnetic nanoparticles are required to be used in magnetic hyperthermia. This can be done by coating the magnetic nanoparticles with biocompatible materials such as silica, dextran, polyethylene glycol etc. The toxic magnetic nanoparticle core separated by the biocompatible shell can minimize the unwanted toxic effects on surrounding biological systems.

Magnetic hyperthermia treatment of cancer is not yet generally applied clinically. Some limited cases of clinical applications have been reported. On the other hand, various magnetic nanoparticles and coating materials have been researched for the clinical application of these particles in near future. Spinal ferrites especially magnetite nanoparticles are widely believed to be promising heat generators for magnetic hyperthermia due to their easy synthetic process, high magnetic moment, and versatility. However, the magnetite particles have some drawbacks due to their high Curie temperature. In the magnetic hyperthermia treatment the suspension of the magnetite particles should be injected to the human body, and the particles can be accumulated at the cancerous site by some targeting techniques. However, in this targeting process, the particles can be located at unwanted healthy tissue site. The overheating of the particles can damage the nearby healthy tissues around cancer, and also the particles happen to be densely located at the healthy tissue site and in that case the tissues can be killed by overheating. This kind of catastrophe can be prevented by using particles with low Curie temperature. Doped perovskite manganite nanoparticles are of interest due to their low Curie temperature, high magnetic moment, and tunable magnetic properties. Manganite nanoparticles with different chemical compositions possibly satisfy most of the requirements for self-controlled hyperthermia.

Doped manganite have been extensively studied due to their low Curie temperature and relatively high magnetization. Efforts have been made to increase the saturation magnetization and for tuning the Curie temperature by means of changing doping elements such as Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$, doping level, different synthesis techniques, and coating materials. It has been reported that the radius of the doping cationic element tunes the magnetic properties of manganite. The differing cationic radius leads to the distortion in the lattice structure resulting in the change of the magnetic properties. Due to this, the doping level of cationic elements influences on the magnetic properties of the manganite. For instance, increasing the doping level of Ca$^{2+}$ from x=0.1 to 0.2 resulted in the increase of the Curie temperature from 260 K to 350 K.

The aim of this work is to synthesize the gadolinium-doped lanthanum strontium manganite nanoparticles with low Curie temperature to be applied to the self-controlled magnetic hyperthermia. The nanoparticles with chemical composition of $La_{0.54}Sr_{0.27}Gd_{0.19}MnO_3$ were synthesized by using the citrate-gel auto-combustion technique, and then coated with silica. The Curie temperature of these particles were determined to be in the range of 280K suitable for the controlled hyperthermia applications. The highly concentrated suspension of these nanoparticles showed low saturation temperature less than 47 °C. Thus, overheating will be prevented by using these particles in the magnetic hyperthermia. The saturation temperature of the powder sample in the RF field reached only to 53 °C confirming that these particles are suitable for the controlled magnetic hyperthermia applications. The SAR of the 9-mg/mL-sample of low particle concentration was 46 W/mg which is also sufficiently high for magnetic hyperthermia application.
II. EXPERIMENTAL

Gadolinium-doped LSM nanoparticles were synthesized by using the citrate gel combustion method reported previously.\textsuperscript{13,24} Stoichiometric amounts of analytical grade La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$, Gd(NO$_3$)$_3$, and Mn(NO$_3$)$_2$ were dissolved in 60 ml distilled water. While pH was adjusted to 9 using ammonium hydroxide, the citric acid and 2 ml of ethylene glycol were added to the solution as a fuel and gel forming agent, respectively. The mixture was then kept at 120 °C on a hotplate for 1 h while stirring. After yellow gel was formed, the temperature was increased to 160 °C to obtain dry powder. The powder was then self-ignited in a microwave oven and the black fluffy powder was obtained. This powder sample was calcined for 4 h at 450 °C to complete the formation of manganite’s phase. The synthesized gadolinium-doped LSM powders were annealed at 850 °C for 3 h to improve the crystallinity and also to remove the impurity residue.

The gadolinium-doped LSM nanoparticles were encapsulated by silica using the method reported by Kaman et al.\textsuperscript{14} The particles were dispersed in the nitric acid using ultrasonic bath, and then the particles were washed and redispersed in 1 M citric acid. These nanoparticles were separated using a centrifuge, and then alkalized by ammonia. Then, the suspension was added to a mixture of ethanol (150 ml), water (35 ml), and ammonia (10 ml) followed by addition of tetra-orthosilicate while stirring, and kept at 40 °C for 4 h with continuous stirring. The silica-coated particles were then magnetically separated from solution and washed several times using water, and then dispersed in water for further characterization.

The crystallinity and phase purity were investigated by X-ray diffraction (XRD; X’pert PRO, PANalytical) to confirm the perovskite structure of the nanoparticles. The chemical composition analysis was performed by using the inductively coupled plasma spectroscopy (ICP; IRISAP, Thermo Jarrell Ash). The shape and size of the nanoparticles were investigated by using a transmission electron microscope (TEM; HT 7700, Hitachi Ltd). The Fourier transform infra-red spectroscopy (FTIR; Nicolet 380, Thermo Scientific USA) measurements was performed for both bare and silica-coated nanoparticles to check the status of silica coating. The hysteresis curve and Curie temperature were obtained by using a vibrating sample magnetometer (VSM; MPMS, Quantum Design). The magnetic heating of the powder sample and nanoparticles dispersed in water was measured using an induction heating system (Osung High Tech, OSH-120-B). The temperature of the solution was measured using a CALEX infrared thermometer (PyroUSB CF, Calex Electronics Limited).

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of the gadolinium-doped LSM nanoparticles are shown in Fig. 1. The patterns show the perovskite structure with homogenous phase formation. ICP results also confirmed the pure phase and stoichiometry. All XRD peaks correspond to the presence of a unique cubic perovskite structure matching the crystal planes of (012), (110), (202), (024), (116), (018), (208), and (128).

The calcination temperature effect on the structural and magnetic properties of manganite has been reported.\textsuperscript{24,25} It is evident from this report that lower calcination temperature produces smaller nanoparticles size, while higher calcination temperature leads to larger particle size and wider particle size distribution. Therefore, the two-step synthesis technique for calcination and annealing is better for obtaining good crystallinity, small particle size, narrow particle size distribution, as well as homogeneity.

The TEM images of the silica encapsulated nanoparticles are shown in Fig. 2. We can clearly see that the particles are well coated with silica showing the typical core-shell structure. Highly stable suspension could be obtained due to the coating of the nanoparticles with silica. The layer of the silica on the nanoparticles surface acted as a shielding shell from surrounding environments making nanoparticles biocompatible and reducing unwanted toxic chemical effects. The average core size was about 35 nm, and the shell thickness of the silica is about 60 nm. Thus, the size of the coated particles was in the range of 150 nm. Thickness of silica shell can be controlled by changing reaction parameters, such as amount of ammonia, TEOS, and reaction time as reported in previous literatures.\textsuperscript{26} It should be noted increase in silica shell thickness results in decrease
FIG. 1. X-ray diffraction patterns of the $\text{La}_{0.54}\text{Sr}_{0.27}\text{Gd}_{0.19}\text{MnO}_3$ nanoparticles. The indices are identical to those of the perovskite crystal structure.

of magnetization due to surface bonding. On the other hand, decrease in shell thickness can lead to conglomeration of particles. Therefore, it is best to optimize shell thickness to the size and purpose of the nanoparticles.

FT-IR spectra of the bare and silica-coated gadolinium-doped LSM nanoparticles are shown in Fig. 3. Comparison of two spectra clearly indicates the presence of the silica shells in the coated particles. The band at 565 cm$^{-1}$ corresponds to the metal-oxygen vibration of Gd-O indicating the formation of the manganite oxide. The bands at 1,050, 950, and 800 cm$^{-1}$ represent typical amorphous silica vibrations due to silanol groups. On the other hand, the bands at 1,050 and 800 cm$^{-1}$ can be ascribed to symmetric and antisymmetric vibrations of Si-O-Si and Si-OH, respectively. The band of the bare particle at 400 cm$^{-1}$ corresponds to the Mn-O bonding, while the band of the coated particle at around 800 cm$^{-1}$ can be assigned to the C-O bonding. The band at 2,970 cm$^{-1}$ represents the asymmetric C-H stretching derived from CH$_2$ in TEOS. The band of the coated particle at 445 cm$^{-1}$ corresponds to the O-Si-O bending. The bands at 1,626 cm$^{-1}$ can be assigned to the stretching vibrations of C-H bonds.

From these spectra we can confirm that the nanoparticles are coated with silica as already seen in TEM images.

The perovskite has the chemical formula of ABO$_3$, where A and B represent metal cations and O is an oxygen (anion) that bonds to both. Each A cation (Ca, Sr, Ba, La, etc.) is octahedrally
coordinated with six oxygen atoms, with B cation (Mn, Fe, etc.) in the center. LaMnO$_3$ has the perovskite structure and is antiferromagnetic insulator in bulk form, however it becomes weakly paramagnetic in nanoparticle form. Due to John-Teller effect, LaMnO$_3$ is an antiferromagnetic insulator. But, doping with divalent cations, for example, Sr$^{2+}$, transforms it from antiferromagnetic to ferromagnetic ordering due to double exchange interaction. In the same token, gadolinium-doped LSM nanoparticles (La$_{0.54}$Sr$_{0.27}$Gd$_{0.19}$MnO$_3$) also show the ferromagnetic ordering. Fig. 4 shows the hysteresis curve of the gadolinium-doped LSM nanoparticles at room temperature. It shows negligible coercivity (8 Oe) showing that the particles are superparamagnetic. The core size of the particles was about 35 nm, which results in the single domain particles showing the superparamagnetic behavior. Reports on effects of silica coating on the magnetic properties of nanoparticles showed that magnetization decreased with increasing silica shell thickness. This decrease in saturation magnetization is attributed to the surface spin disorder and silica bonding with metal ions on the particle surface.

FIG. 3. FT-IR spectra for the bare and silica-coated La$_{0.54}$Sr$_{0.27}$Gd$_{0.19}$MnO$_3$ nanoparticles.

FIG. 4. Hysteresis curve of the silica-coated La$_{0.54}$Sr$_{0.27}$Gd$_{0.19}$MnO$_3$ nanoparticles at room temperature. The particles show the superparamagnetic behavior with negligible coercive force.
The thermal demagnetization was measured in the temperature range of 100 to 400 K under the field of 1,000 Oe, which is shown in Fig. 5. The Curie temperature was estimated from this magnetization versus temperature curve. From the first derivative of the magnetization with respect to the temperature as shown in the inset of Fig. 5, the inflection point (technical Curie point) was observed at 280 K. However, the magnetization becomes negligible at around 330 K. Thus, we can conclude that the particles start to lose their magnetization from 280 K, and most of particles do not show the magnetic behavior above 330 K.

The coercivity and Curie temperature are considerably reduced in our gadolinium-doped LSM nanoparticles comparing with those of un-doped manganite reported for similar composition of strontium concentration of $La_{0.63}Sr_{0.27}MnO_3$. These differences can be attributed to the cation size and lower Curie temperature of gadolinium. Epherre et al. studied the structural variations of doped manganites with respect to their dopant cationic radii. Large Curie temperature change was observed from -13 to 77 °C when the dopant cationic radius was larger than $La^{3+}$. However, for the dopants of smaller radius than $La^{3+}$, the Curie temperature was decreased due to the lattice distortions. The gadolinium cationic radius is smaller than that of $La^{3+}$, and thus the substitution of gadolinium into the lanthanum strontium manganite results in the distortion of the crystal lattice structure. This distortion in the perovskite unit cell leads to the change in bond angles and lengths, leading to the change of the Curie temperature and magnetic properties. Furthermore, the gadolinium’s lower Curie point acts as another factor for the reduction of Curie temperature in the gadolinium-doped LSM nanoparticles.

The magnetic heating experiments were carried out for powder sample and aqueous solution of silica-coated nanoparticles under the field amplitude of 4.4 kA/m with frequency of 216 kHz. The heating curves for the powder sample and dispersion of various particle concentrations are shown in Fig. 6. The temperature rises fast at first, and then saturated in a certain time depending on particle concentration. This saturation of temperature is achieved when the heat generation of particles balances with the heat loss to the surroundings. The magnetization of the particles decreases with increasing temperature near Curie point, resulting in the decrease of the heat generation. Additionally, silica coating on the surface of particles affects heat transfer to the surrounding due to absorption of some heat by silica during heat conduction. The saturation of the temperature reaches when the total heat generated by particles is balanced by the thermal loss. The powder sample has no water, and thus the temperature reached quickly to 52 °C and then stabilized. On the other hand, the saturation temperature of the dispersion samples is reached slower than the powder sample. The dispersion sample with higher particle concentration reached the saturation temperature faster, and also the saturation temperature is higher, which is as expected.

![Fig. 5. Magnetization versus temperature curve for the silica-coated $La_{0.54}Sr_{0.27}Gd_{0.19}MnO_3$ nanoparticles at 1,000 Oe. The inset shows the first derivative of the magnetization with respect to the temperature showing the inflection temperature which can be defined as a technical Curie point.](image)
FIG. 6. Heating curves for the powder sample and aqueous dispersions of the silica-coated $\text{La}_{0.54}\text{Sr}_{0.27}\text{Gd}_{0.19}\text{MnO}_3$ nanoparticles with varying concentration. The powder sample reached the saturation temperature of 52 °C only. The saturation temperature of the dispersion of wide range of the particle concentration (6 to 60 mg/mL) was maintained at 42 °C, the target temperature of the magnetic hyperthermia.

The 2-mg/mL sample reached only 39 °C lower than the target temperature of the hyperthermia, 42 °C. On the other hand, the saturation temperature of the 6-mg/mL sample was close to 42 °C. The saturation temperature for the samples of higher particle concentration up to 60 mg/mL does not increase much with increasing particle concentration in the dispersion. The 60-mg/mL sample reached only 43 °C. The saturation temperature was just one degree increased, while the particle concentration increased ten times from 6 to 60 mg/mL. This behavior can be attributed to low Curie temperature of the particles, reducing the heating capability of the particles due to smaller magnetization of the particles in this temperature range. As the particle concentration increases further, the saturation temperature increases again due to the increase of the number of the particles in the dispersion. The saturation temperature of the 120-mg/mL sample reached 47 °C. The maximum saturation temperature was observed in the powder sample, which was 52 °C. This temperature is close to 330 K at which most of the particles lose their magnetization as seen in Fig. 5. This heating behavior of the particles is suitable for the controlled hyperthermia. The appropriate concentration of the particles at the cancer site for hyperthermia is in between 6 to 9 mg/mL resulting in the temperature increase of that site to 42 °C. Even if the particles are accumulated more than 120 mg/mL locally, the temperature of that site does not increase more than 47 °C at which the normal tissues start to be damaged due to heating. Consequently, we can achieve the controlled hyperthermia by using our silica-coated gadolinium-doped LSM nanoparticles without the risk of overheating.

The specific absorption rate (SAR) is a measure of the heat-generating capability of the magnetic nanoparticles. For the dispersion sample, the specific absorption rate (SAR) can be defined as

$$\text{SAR} = c_w \frac{m_w}{m_p} \frac{\Delta T}{\Delta t}.$$  (1)

The unit of the SAR is W/g. Here, $c_w$ is the specific heat of water (4.18 J/g °C), $\frac{\Delta T}{\Delta t}$ is the slope of the initial heating curve, and $m_p$ is the mass of the particles in the sample. For the expression of Eq. 1, we used the facts that the mass of the water is significantly larger than those of the other components in the dispersion and that the specific heat of water is higher than those of the other constituent components of particles (0.24, 0.19, 0.29, 0.47, and 0.68 J/g °C for Gd, La, Sr, Mn, and silica, respectively). The SAR of the 9-mg/mL sample with the saturation temperature of 42 °C was determined to be 46 W/g, which is comparably higher. If the mass of the magnetic constituents of the particles instead of total mass of the particles is used in calculating the SAR, the higher SAR would be obtained.
IV. CONCLUSION

The silica-coated gadolinium-doped MSM nanoparticles were synthesized by using a citrate-gel combustion technique, followed by silica coating. The morphological characterization of the coated particles confirmed the core-shell structure with an average core size of 35 nm and the shell thickness of 60 nm. The Curie temperature of the particles was found to be reduced due to gadolinium dopants. This low Curie temperature of the particles limited the saturation temperature of the powder sample in the heating measurements only to 52 °C. The target temperature of the hyperthermia, 42 °C, was achieved with the 6-mg/mL sample. Further, this target temperature was maintained for wide range of the particle concentration in the dispersion, at least 6 to 60 mg/mL. This behavior of heating is suitable for the controlled hyperthermia without risk of overheating. Even at high concentration of 120 mg/mL the saturation temperature was 47 °C at which the normal tissues start to be damaged due to heating. Overall results clearly showed that our particles are applicable to the controlled magnetic hyperthermia.

ACKNOWLEDGMENTS

This research was supported by the National Research Foundation of Korea (2016R1A2B1006449).

1 J. Dobson, Drug. Dev. Res. 67, 55 (2006).
2 R. D. K. Misra, Mater. Technol.: Adv. Perform. Mater. 25, 118 (2010).
3 D. Pouliquen, J. J. Le Jeune, R. Perdrisot, A. Ermius, and P. Jallet, Magn. Res. Imaging 9, 275 (1991).
4 T. Ahmad, H. Bae, I. Rhee, Y. Chang, J. Lee, and S. Hong, Curr. Appl. Phys. 12, 969 (2012).
5 T. Ahmad, H. Bae, Y. Iqbal, I. Rhee, S. Hong, Y. Chang, J. Lee, and D. Sohn, J. Magn. Magn. Mater. 381, 151 (2015).
6 H.-S. Huang and J. F. Hainfeld, Int. J. Nanomed. 8, 2521 (2013).
7 Y. Iqbal, H. Bae, I. Rhee, and S. Hong, J. Magn. Magn. Mater. 409, 80 (2016).
8 A. Ahmad, H. Bae, S. Hong, and I. Rhee, J. Magn. Magn. Mater. 447, 42 (2018).
9 R. Gilchrist, R. Medal, W. D. Scortney, R. C. Hanselman, J. C. Parrott, and C. B. Taylor, Ann. Surg. 146, 596 (1957).
10 R. Hergt, R. Hiergeist, M. Zeisberger, G. Glückl, W. Weitschies, L. Ramirez, I. Hilger, and W. A. Kaiser, J. Magn. Magn. Mater. 280, 358 (2004).
11 E. Pollert, K. Knížek, M. Maryško, P. Kašpar, S. Vasseur, and E. Duguet, J. Magn. Magn. Mater. 316, 122 (2007).
12 S. Ahmad and S. Shaheen, J. Appl. Phys. 106, 064701 (2009).
13 S. Manzoor, A. Ahmed, A. Rashid, S. Ahmad, and S. Shaheen, IEEE Trans. Magn. 49, 3504 (2013).
14 Q. Kaman, E. Pollert, P. Veverka, M. Veverka, E. Hadová, K. Knížek, M. Maryško, P. Kašpar, M. Klementová, and V. Grünwaldová, Nanotechnology 20, 275610 (2009).
15 A. Rashid, A. Ahmed, S. Ahmad, S. Shaheen, and S. Manzoor, J. Magn. Magn. Mater. 347, 39 (2013).
16 P. Tartaj, S. Veintemillas-Verdaguer, and C. J. Serna, J. Phys. D: Appl. Phys. 36, R182 (2003).
17 I. Rhee, New Physics: Sae Mulli 65, 411 (2015).
18 R. D. Tucker, C. E. Platz, C. Huidobro, and T. Larson, Urology 60, 166 (2002).
19 B. Thiesen and A. Jordan, Int. J. Hyperthermia 24, 467 (2008).
20 S. Luo, L. F. Wang, W. J. Ding, H. Wang, J. M. Zhou, H. K. Jin, and S. F. Su, OA Cancer 2 (1), 2 (2014).
21 T. Kobayashi, K. Kakimi, E. Nakayama, and K. Jimbow, Nanomedicine 9, 1715 (2014).
22 R. Hergt, R. Hiergeist, I. Hilger, W. A. Kaiser, Y. Lapatnikov, S. Margel, and U. Richter, J. Magn. Magn. Mater. 270, 345 (2004).
23 K. McBride, N. Partridge, S. Bennington-Gray, S. Felton, L. Stella, and D. Poulidi, Mater. Res. Bull. 88, 69 (2017).
24 G. Wang, B. Lu, S. Zhang, L. Zhao, G. Fei, L. Zhang, Y. Ma, and B. Li, Journal of Wuhan University of Technology-Mater. Sci. Ed. 22, 183 (2007).
25 Y. Kobayashi, H. Mitsuura, and M. Komno, J. Phys. Chem. B 107, 14990 (2003).
26 H. L. Ding, Y. X. Zhang, S. Wang, J. M. Xu, S. C. Xu, and G. H. Li, Chem. Mater. 24, 4572 (2012).
27 W. Di, X. Ren, L. Zhang, C. Liu, and S. Lu, Cryst. Eng. Comm. 13, 4831 (2011).
28 P. Rubio, J. Rubio, and I. Oteo, Spectrosc. Lett. 31, 199 (1998).
29 A. A. Rabelo, M. C. de Macedo, D. M. Melo, C. A. Paskocimas, A. E. Martinelli, and R. M. Nascimento, Mater. Res. 14, 91 (2011).
30 J. M. D. Coey, M. Viret, and S. von Molnar, Advances in Physics 48, 167 (1999).
31 D. P. Joshi, G. pant, N. Arora, and S. Nainwal, Heliyon 3, 00253 (2017).
32 C. Vogt, M. S. Toprak, M. Muhammed, S. Laurent, J.-L. Bridot, and R. N. Müller, J. Nanopart. Res. 12, 1137 (2010).
33 O. Kaman, P. Veverka, Z. Jirák, M. Maryško, K. Knížek, M. Veverka, P. Kašpar, M. Burian, V. Šepelák, and E. Pollett, J. Nanopart. Res. 13, 1237 (2011).
34 R. Epherre, C. Pepin, N. Penin, E. Duguet, S. Mornet, E. Pollett, and G. Goglio, J. Mater. Chem. 21, 14990 (2011).