*Full Paper*

# Dextran Capped Gd$^{3+}$-doped Fe$_3$O$_4$ Nanoparticles: Electrochemical Synthesis and Characterization

**Mohammad Reza Ganjali[1,2,*] Eslam Pourbasheer,[3] and Morteza Rezapour[4]**

[1]*Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran*

[2]*Biosensor Research Center, Endocrinology and Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran*

[3]*Department of Chemistry, Payame Noor University (PNU), Tehran, Iran*

[4]*IP Department, Research Institute of the Petroleum Industry (RIPI), P.O. Box 14665-137, Tehran, Iran*

*Corresponding Author, Tel.: +982188356138

E-Mail: ganjali@khayam.ut.ac.ir

**Abstract**- In this work, we report dextran capped Gd$^{3+}$-doped Fe$_3$O$_4$ nanoparticles prepared through a novel and facile electrodeposition method. The properties of the nanoparticles such as size, percentage of dextran capped layer, crystallinity, and magnetic properties were evaluated through XRD, IR, FE-SEM, VSM and DSC-TGA techniques. The electrodeposited IONs showed saturation magnetization of 18.02 emu g$^{-1}$, remanent magnetization of 0.063 emu g$^{-1}$ and coercivity of 2.59 G, and have superparamagnetic nature. Based on the obtained results, the developed electrochemical synthesis method is proposed as an easy route for the fabrication of superparamagnetic polymer-grafted and metal-ion doped iron oxide nanoparticles.

**Keywords-** Magnetic materials, Gd doping, Nanoparticles, Electrochemical synthesis, Dextran

## 1. INTRODUCTION

Magnetic nano-particles (MNPs) with suitable surface characteristics have potential applications both *in vitro* and *in vivo* [1,2]. In almost all bio-medical uses, the fabrication and surface engineering of MNPs is major step, which determine the particle size, shape and distribution, the surface chemistry and consequently the magnetic characteristics of NPs, all important for use in biomedicine [3]. The synthesis and fabrication of iron oxide nanoparticles (IONs) could be performed through physical (like as electron beam lithography, laser ablation and gas phase deposition) [4-8], wet chemical (co-precipitation, sole-gel, thermal decomposition and hydrothermal) [9-16] and electrochemical [17-23] methods. The wet chemical methods (i.e. thermal decomposition and precipitation procedures) are widely used due to their straightforward nature and ease of control over size, composition and even the shape of the nanoparticles [10-15]. Beside these methods, electrochemical method has been also advantages of simplicity, feasibility, controllability on the reaction rate and product phase, size and shape [17-21]. This method has been also confirmed as a facile technique for the preparation of metal oxides/hydroxide NPs [24-34].

Dextran is an abundant, inexpensive polymer that composed of alpha-D-glucopyranosyl monomers. The polysaccharide has a large number of hydroxyl groups that foster chelation and hydrogen bonding interactions with IONs surfaces as well as provide local sites for surface capping [35]. Dextran capped layer could provide biological compatibility and stability to the IONs, thereby making them suitable candidate for biomedical application like as hyperthermia and MRI contrast agent [36-40]. It was reported that dextran interacts with metals and covers its surface yielding aggregates with hydrodynamic diameters between 20 and 150nm [36,37]. Up now, Dextran capped iron oxide nanoparticles (DEX IONs) have been fabricated through various techniques of co-precipitation, hydrothermal, sol-gel, thermal-decomposition and so on [38-45]. Furthermore, it was reported that DEX IONs are a powerful platform for the special applications, where they support diagnostic optical, and positron emission tomography (PET) modalities, also imaging by magnetic resonance (MRI), and constitute a versatile platform for conjugation to targeting ligands [44-52].

Here, we report an electrochemical platform for fabrication of dextran capped $Gd^{3+}$ doped iron oxide nanoparticles (DEX Gd-IONs). This platform is based on the cathodic deposition of Gd-IONs in the presence of dextran as capping agent. Notably, it was reported that the metal ion doped IONs could be easily fabricated through cathodic electrochemical deposition route [53-57]. In this work, we applied a similar strategy for the fabrication of DEX Gd-IONs. The prepared NPs are characterized through the techniques of XRD, FE-SEM, DSC-TGA and the superparamagnetic nature of the electrosynthesized DEX Gd-IONs is also specified using VSM.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Electrochemical synthesis of DEX GD-IONs

All chemicals including iron(II) chloride ($FeCl_2.4H_2O$, 99%), iron(III) nitrate ($Fe(NO_3)_2.9H_2O$, 99.95%), gadolinium chloride ($GdCl_3 .6H2O$, 99.8%) and dextran ($M_w=70000$) were purchased from the Sigma Aldrich Company and used as received. The deposition electrolyte includes $FeCl_2.4H_2O$ (1.6 g), $Fe(NO_3)_3.9H_2O$ (3.4 g), $GdCl_3 .6H_2O$ (0.7 g) and 1 g/L dextran as additive. First, the mentioned metal salts were dissolved in 1 litter deionized aqueous solution and then dextran was added in to the solution and stirred for 1 h. A two-electrode system including a stainless-steel cathode centered between two graphite anodes was used as the electrodeposition set-up, as mentioned in Refs. [53,54]. The deposition experiment was ran by applying a current density of 10 mA cm$^{-2}$. The deposition time and bath temperature were 30 min and 25 °C, respectively. At the end of deposition, black film was clearly observed on the steel surface. The steel cathode was removed from the deposition bath and washed several times with deionized water. The deposited film were scraped from the steel sheet and dispersed in water. The solution was centrifuged at 6000 rpm for 20 min in order to removal of weekly bounded dextran attached to the Gd-IONs surface. After that, the IONs was collected from the solution and separated by magnet. The obtained wet-powder was dried in a vacuum oven at 70 °C for 1h, and the resulted dry black powder was labeled DEX Gd-IONs.

### 2.2. Sample characterization

The morphology of the prepared DEX Gd-IONs powder was observed by field-emission scanning electron microscopy (FE-SEM, Mira 3-XMU with accelerating voltage of 100 kV). The crystal structure of the prepared powder was studied by X-ray diffraction (XRD, Phillips PW-1800) using a Co Kα radiation. Thermal behavior (DCS-TG) analysis was carried out in N2 atmosphere between room temperature and 500 °C at a heating rate of 5°C min$^{-1}$ using a thermoanalyzer (STA-1500). The FTIR analysis was done at a resolution of 4 cm$^{-1}$ from 400 to 4000 cm$^{-1}$ using a Bruker Vector 22 Fourier transformed infrared spectroscope. The magnetic properties of the prepared DEX Gd-IONs were specified in the range of $-20000$ to 20000 Oe at room temperature using vibrating sample magnetometer (VSM, model: Meghnatis Daghigh Kavir Co., Iran).

## 3. RESULTS AND DISCUSSION

Fig. 1 presets the XRD patterns of pristine and dextran capped Gd-IONs. The observed diffraction peaks in these patterns are completely matched with magnetite phase of iron oxide with spinal structure (JCPDS card No. 01-088-0315). Using the Debye–Sherrer equation

(D=Kλ/βcosθ), the average crystallite sizes of pristine and dextran capped Gd-IONs were calculated to be about 9.7 and 9.1 nm, respectively.
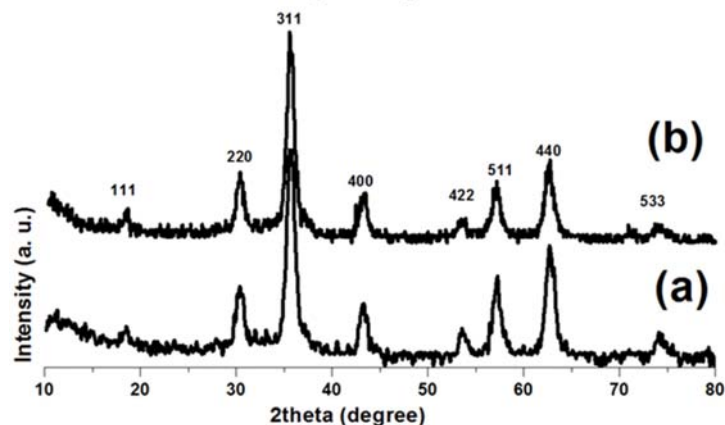


**Fig. 1.** XRD patterns of the prepared (a) pristine and (b) dextran capped $Gd^{3+}$ doped IONs

FT-IR is suitable route for specifying the chemically adsorbed spices on the surface of IONs [36-44]. Hence, FT-IR analysis of the prepared powder was carried out to determine the presence of dextran on the fabricated DEX Gd-IONs. The FT-IR spectrum of the DEX capped $Gd^{3+}$ doped IONs is given in Fig. 2. The IR peaks located at the wavenumbers below 750 cm$^{-1}$ are related to the Fe-O-Fe and Gd-O-Fe bonds in Gd-IONs [22,23,55,56].
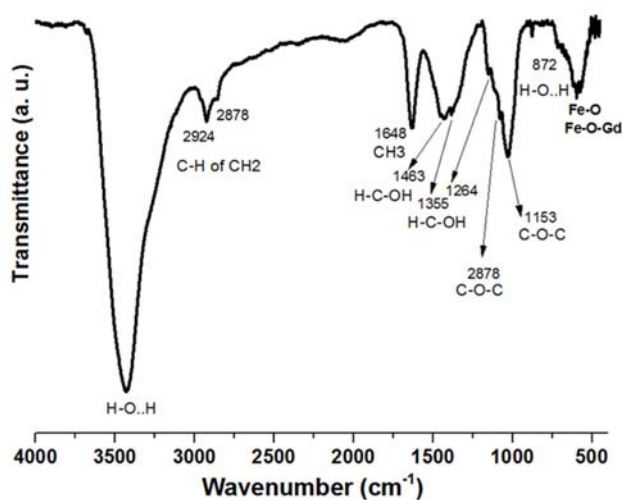


**Fig. 2.** IR spectrum of the fabricated dextran capped $Gd^{3+}$ doped IONs

Furthermore, there are some distinctive IR bands, which are due to the presence of Dextran on the surface of the fabricated Gd-IONs. For instance, these IR bands are (i) a broad band located at 3300-3500 cm$^{-1}$ (due to the structural OH in the dextran backbone) [45,56],

(ii) the two bands at 1152 and 846 cm$^{-1}$ (relating to the vas and vs vibrations of C-O-C respectively) (iii) the bands located at 1468, 1355 and 1264 cm$^{-1}$ (due to the deformation vibrations of H-C-OH in the dextran chains) (iv) the band of O-H vibration modes are placed at 872 and 1016 cm$^{-1}$, (v) the band at 1648 cm$^{-1}$ (resulting from the bending vibration of C–H bond in CH$_3$ group), and (vi) the bands at 2924 and 2878 cm$^{-1}$ (due to vas and vs vibrations of C-H in CH$_2$ group, respectively), [19-25,45,59,60]. These findings completely specified the dextran capped layer onto the Gd-IONs.
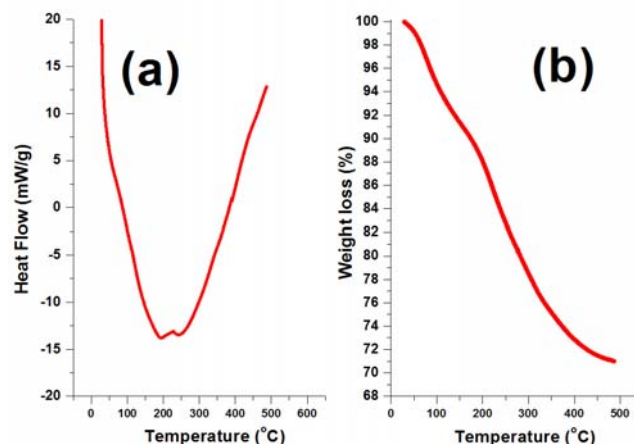


**Fig. 3.** DSC-TGA of the electrodeposited dextran coated Gd$^{3+}$ doped IONs

Thermogravimetric behavior of the DEX Gd-IONs was recorded in the temperature range of 25–500 °C, which are presented in Fig. 3. For our sample, in the temperature range of 150 to 300 °C, DSC curve exhibits two-step exothermic peak (Fig. 3a), which is completely in agreement with the reported ones in literature [19-22,61-63]. Also, TGA curve has a sharp weight loss at 150- 300 °C. Beside these peaks, a small weigh loss (about 4.5%) is also observed at the temperature up to 150°C, because of removal of the adsorbed water and OH groups in dextran chain [62,63]. the breakdown of organic skeleton in dextran (i.e. two-step degradation [61-63]) is occurred at 185-270 °C, as clearly seen in Fig. 3a. For this process, a total weight loss of 19.5% is observed on the TG curve (Fig. 3b). Furthermore, 5% weight loss is taken at the temperatures of 300-500 °C indicating the complete dextran dissociation from the surface of Gd-IONs [26,61-63]. The total weight loss of DEX Gd-IONs is observed to be 29%.

FE-SEM observations of DEX Gd-IONs sample are provided in Fig. 4. As seen in Figs. 4a and b, spherical particles are observed for this sample. The size of particles is in the range of 15-25 nm. For our sample, the composition of 63.36% Fe, 9.71% Mn and 26.93% O elements were detected (Fig. 2b). Energy-dispersive X-ray spectroscopy (EDAX) graph with the related elemental data are also provided in Fig. 4c. The sample has composition of

31.18% Fe, 13.65% Gd, 37.31% O, 14.43% C and 2.80% N. The presence of Gd in sample composition proved the $Gd^{3+}$ doping into iron oxide structure. The presence of C and O elements in composition is also confirmed the dextran capped layer.
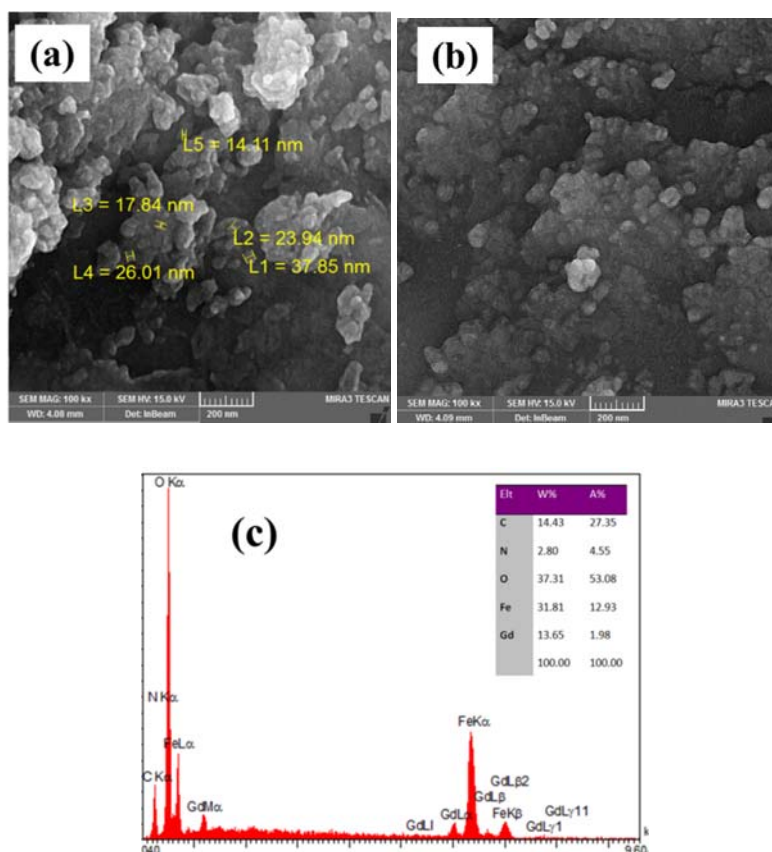


**Fig. 4.** (a,b) FE-SEM images and (c) EDS data of DEX coated $Gd^{3+}$ doped IONs

The superparamagnetic behavior of the fabricated IONs was investigated using VSM and its profile is shown in Fig. 5. This profile has no hysteresis loop and exhibits S form. These characteristics indicate the superparamagnetic nature of the fabricated DEX Gd-IONs sample. The magnetic data of sample is also listed in Fig. 5, which are obtained to be $Ms$=18.02 emu $g^{-1}$, $Mr$=0.063 emu $g^{-1}$ and $H_{Ci}$=2.59 G. The low saturation magnetization of sample is related to the presence of $Gd^{3+}$ ions [64,65]. In fact, $Gd^{3+}$ in the iron oxide particles is responsible for a decrease in the $Ms$ value, which can be related to change in the magneto-crystalline structure of the magnetite lattice and change in the magneto-crystalline anisotropy, as has been proved by SQUID analysis in Refs. [64,65]. Furthermore, low saturation magnetization could be result from the nano-magnetic dextran layer (29% of total mass, as confirmed by TGA) on the composition of the fabricated Gd-IONs sample. However, the prepared sample exhibit a negligible $Mr$ and $H_{Ci}$ values when the magnetic field is vanished, confirming its proper magnetic behavior for biomedical applications like as hyperthermia.
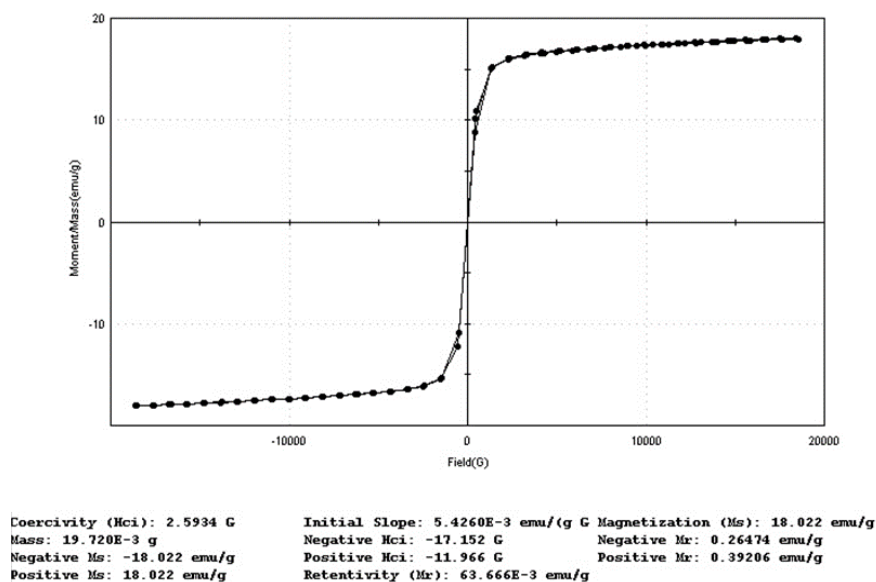
**Fig. 5.** Hysteresis loops for the electrodeposited dextran capped Gd-IONs

## 4. CONCLUSION

A facile electrochemical synthesis procedure was developed for fabrication of polymer capped gadolinium doped iron oxide nanoparticles. The magnetic properties was determined through VSM analysis, where the fabricated Gd-IONs exhibited proper magnetic values of $Ms$=18.02 emu g$^{-1}$, $Mr$=0.063 emu g$^{-1}$ and $H_{Ci}$=2.59 G. The XRD and FE-SEM analyses proved the magnetite crystal structure and nanometer size (~20 nm) of the prepared IONs. The observed characters for the dextran capped Gd-IONs proved that they have all required structural and magnetic criteria for biomedical applications.

## REFERENCES

[1]   E. Y. Yu, M. Bishop, B. Zheng, R. M. Ferguson, A. P. Khandhar, S. J. Kemp, K. M. Krishnan, P. W. Goodwill, and S. M. Conolly, Nano Lett.  17 (2017) 1648.

[2]   R. Mansell, T. Vemulkar, D. C. M. C. Petit, Y. Cheng, J. Murphy, M. S. Lesniak, and R. P. Cowburn, Scientific Reports 7 (2017) Article number: 4257.

[3]   Z. Wang, R. Qiao, N. Tang, Z. Lu, H. Wang, Z. Zhang, X. Xue, Z. Huang, S. Zhang, G. Zhang, and Y. Li, Biomaterials 127 (2017) 25.

[4]   Z. Ma, and H. Liu, China Particuol. 5 (2007) 1.

[5]  E. Fazio, M. Santoro, G. Lentini, D. Franco, S. Pietro, P. Guglielmino, and F. Neri, Colloids Surf. A 490 (2016) 98.

[6]  K. S. Khashan, G. M. Sulaiman, and R. A. Mahdi, Cells Nanomed. Biotechnol. 45 (2017) 1699.

[7]  Q. Guo, X. Teng, S. Rahman, and H. Yang, J. Am. Chem. Soc. 125 (2003) 630.

[8]  I. Morjana, R. AlexandrescuaI Soare, F. DumitracheaI, S. Voicu, A. Crunteanu, E. Vasile, V. Ciupina, and S. Martelli, Mater. Sci. Eng. C 23 (2003) 211.

[9]  S. Gyergyek, D. M. Marko Jagodič, M. Drofenik, K. Schenk, O. Jordan, J. Kovač, G. Dražič, and H. Hofmann, J. Alloys Compd. 694 (2017) 261.

[10]  J. Zhang, Y. Shao, C. T. Hsieh, Y. F. Chen, T. C. Su, J. P. Hsu, and R. S. Juang, Separation Purification Technol. 174 (2017) 312.

[11]  P. Bhavani, C. H. Rajababu, M. D. Arif, I. V. Subba Reddy, and N. R. Reddy, J. Magn. Magn. Mater. 426 (2017) 459.

[12]  O. A. Attallah, and E. Girgis, J. Magn. Magn. Mater. 397 (2016) 164.

[13]  B. Park, B. HyoKim, and T. Yu, J. Colloid Interface Sci. 518 (2018) 27.

[14]  F. B. Effenberger, R. A. Couto, P. K. Kiyohara, G. Machado, S. H. Masunaga, R. Jardim, and L. M. Rossi, Nanotechnol. 28 (2017) 1215.

[15]  N. Jović Orsini, B. Babić-Stojić, V. Spasojević, M. P. Calatayud, N. Cvjetićanin, and G. F. Goya, J. Magn. Magn. Mater. 449 (2018) 286.

[16]  O. Gerber, B. P. Pichon, D. Ihiawakrim, I. Florea, S. Moldovan, O. Ersen, D. Begin, J. M. Grenèche, S. Lemonnier, E. Barraud, and S. Begin-Colin, Nanoscale 9 (2017) 305.

[17]  M. Aghazadeh, I. Karimzadeh, M. R. Ganjali, and M. Mohebi Morad, Mater. Lett. 196 (2017) 392.

[18]  I. Karimzadeh, M. Aghazadeh, M. R. Ganjali, P. Norouzi, S. Shirvani-Arani, T. Doroudi, P.H. kolivand, S. A. Marashi, and D. Gharailou, Mater. Lett. 179 (2016) 5.

[19]  I. Karimzadeh, M. Aghazadeh, M. R. Ganjali, P. Norouzi, and T. Doroudi, Mater. Lett. 189 (2017) 290.

[20]  M. Aghazadeh, and I. Karimzadeh, Curr. Nanosci. 14 (2018) 42.

[21]  I. Karimzadeh, M. Aghazadeh, M. R. Ganjali, and T. Dourudi, Curr. Nanosci. 13 (2017) 167.

[22]  M. Aghazadeh, P. Kolivand, I. Karimzadeh, M. R. Ganjali, and D. Gharailou, Curr. Nanosci. 13 (2017) 274.

[23]  I. Karimzadeh, H. Rezagholipour Dizaji, and M. Aghazadeh, Mater. Res. Express 3 (2016) 095022.

[24]  M. Aghazadeh, Mater. Lett. 211 (2018) 225.

[25]  F. Khosrow-pour, M. Aghazadeh, B. Sabour, and S. Dalvand, Ceram. Int. 39 (2013) 9491

[26] M. Aghazadeh, M. G. Maragheh, M. R. Ganjali, and P. Norouzi, RSC Adv. 6 (2016) 10442.

[27] J. Tizfahm, B. Safibonab, M. Aghazadeh, A. Majdabadi, B. Sabour, and S. Dalvand, Colloids Surf. A 443 (2014) 544.

[28] M. Aghazadeh, A. N. Golikand, and M. Ghaemi, Int. J. Hydrogen. Energy 36 (20118674.

[29] M. Aghazadeh, A. A. M. Barmi, and D. Gharailou, Appl. Surf. Sci. 283 (2013) 871.

[30] M. Aghazadeh, T. Yousefi, Emamalizadeh M. Ghaemi, J. Rare. Earths 30 (2012) 236.

[31] M. Aghazadeh, M. Asadi, M. R. Ganjali, P. Norouzi, B. Sabour, and M. Emamalizadeh, Thin Solid Films 634 (2017) 24.

[32] M. Aghazadeh, B. Sabour, M. R. Ganjali, and S. Dalvand, Appl. Surf. Sci. 313 (2014) 581.

[33] M. Aghazadeh, M. Hosseinifard, B. Sabour, and S. Dalvand, Appl. Surf. Sci. 287 (2013) 187.

[34] A. Barani, M. Aghazadeh, and M. R. Ganjali, Mater. Sci. Semicond. Process 23 (2014) 85.

[35] E. A. Osborne, T. M. Atkins, D. A. Gilbert, S. M. Kauzlarich, K. Liu, and A. Y. Louie, Nanotechnol. 23 (2012) 215602.

[36] T. Shen, R. Weissleder, M. Papisov, A. Jr Bogdanov, and T. J. Brady, Magn. Reson. Med. 29 (1993) 599.

[37] M. C. Bautista, O. Bomati-Miguel, M. P. Morales, C. J. Serna, and S. Veintemillas-Verdaguer, J. Magn. Magn. Mater. 293 (2005) 20.

[38] Z. Shaterabadi, G. Nabiyouni, and M. Soleymani, Mater. Sci. Eng. C 75 (2017) 947.

[39] A. K. Hauser, R. Mathias, K. W. Anderson, and J. Zach Hilt, Mater. Chem. Phys. 160 (2015) 177.

[40] G. B. da Silva, M. Marciello, M. Morales, C. J. Serna, M. D. Vargas, and C. M. Ronconi, J. Braz. Chem. Soc. 28 (2017) 731.

[41] N. S. Remya, S. Syama, A. Sabareeswaran, and P. V. Mohanan, Int. J. Pharmaceut. 511 (2016) 586.

[42] D. G. You, G. Saravanakumar, S. Son, H. S. Han, R. Heo, K. Kim, I. C. Kwon, J. Y. Lee, and J. H. Park, Carbohydrate Polym. 101 (2014) 1225.

[43] R. Y. Hong, J. H. Li, J. M. Qu, L. L. Chen, and H. Z. Li, Chem. Eng. J. 150 (2009) 572.

[44] M. Khalkhali, S. Sadighian, K. Rostamizadeh, F. Khoeini, M. Naghibi, N. Bayat, M. Habibizadeh, and M. Hamidi, Bioimpacts 5 (2015) 141.

[45] M. Peng, H. Li, Z. Luo, J. Kong, Y. Wan, L. Zheng, Q. Zhang, H. Niu, A. Vermorken, W. Van de Ven, C. Chen, X. Zhang, F. Li, L. Guo, and Y. Cui, Nanoscale 7 (2015) 11155.

[46] D. Jinmori, Y. Masubuchi, and S. Kikkawa, Mater. Res. Bulletin 88 (2017) 214.

[47] B. Yang, X. Yang, X. Li, Y. Cao, and R. Yu, J. Magn. Magn. Mater. 405 (2016) 22.

[48] W. J. Hsieh, C. J. Liang, J. J. Chieh, I. R. Lai, J. H. Chen, F. H. Chang, W. K. Tseng, S. Y. Yang, C. C. Wu, and Y. L. Chen, Int. J. Nanomed. 7 (2012) 2833.

[49] C. Tassa, S. Y. Shaw, and R. Weissleder, Acc. Chem. Res. 44 (2011) 842.

[50] M. L. Mojica Pisciotti, E. Lima, M. Vasquez Mansilla, V. E. Tognoli, H. E. Troiani, A. A. Pasa, T. B. Creczynski-Pasa, A. H. Silva, P. Gurman, L. Colombo, G. F. Goya, A. Lamagna, and R. D. Zysler, J. Biomed. Mater. Res. 102 (2014) 860.

[51] Z. Teng, J. Li, F. Yan, R. Zhao, and W. Yang, J. Mater. Chem. 19 (2009) 1811.

[52] J. Xu, H. Yang, W. Fu, K. Du, Y. Sui, J. Chen, Y. Zeng, M. Li, and G. Zou, J. Magn. Magn. Mater. 309 (2007) 307.

[53] M. Aghazadeh, and M. R. Ganjali, Ceram. Int. 44 (2018) 520.

[54] M. Aghazadeh, and M. R. Ganjali, J. Mater. Sci. 53 (2018) 295.

[55] M. Aghazadeh, and M. R. Ganjali, J. Mater. Sci.: Mater. Electron. 29 (2018) 2291.

[56] M. Aghazadeh, and M. R. Ganjali, J. Mater. Sci.: Mater. Electron. 29 (2018) 4981.

[57] M. Aghazadeh, R. Ahmadi, D. Gharailou, M. R. Ganjali, and P. Norouzi, J. Mater. Sci.: Mater. Electron. 27 (2016) 8623.

[58] G. Singh, B. H. McDonagh, S. Hak, D. Peddis, S. Bandopadhyay, I. Sandvig, A. Sandvige, and W. R. Glomm, J. Mater. Chem. B 5 (2017) 418.

[59] G. Liua, R. Y. Honga, L. Guoe, Y. G. Li e, and H. Z. Li, Appl. Surf. Sci. 257 (2011) 6711.

[60] M. Khalkhali, K. Rostamizadeh, S. Sadighian, F. Khoeini, M. Naghibi, and M. Hamidi, Daru J. Pharm. Sci. 23 (2015) 45.

[61] A. K. Hauser, R. Mathias, K. W. Anderson, and J. Zach Hilt, Mater. Chem. Phys. 160 (2015) 177.

[62] O. Carp, L. Patron, D. C. Culita, P. Budrugeac, M. Feder, and L. Diamandescu, J. Thermal. Anal. Calorimet. 101 (2010) 181.

[63] A. Saraswathy, S. S. Nazeer, N. Nimi, S. Arumugam, S. J. Shenoy, and R. S. Jayasree, Carbohydrate Polym. 101 (2014) 760.

[64] F. J. Douglas, D. A. MacLaren, N. Maclean, I. Andreu, F. J. Kettles, F. Tuna, C. C. Berry, M. Castroc, and M. Murrie, RSC Adv. 6 (2016) 74500.

[65] H. Zhang, V. Malik, S. Mallapragada, and M. Akin, J. Magn. Magn. Mater. 423 (2017) 386.