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Nanosystems and magnetism

Abstract

Magnetism in nanomaterials (popularly known as nanomagnetism) is one of the fast emerging scientific disciplines of nanoscience and nanotechnology. Magnetic particles are special class of nanoparticles whose properties can be tailored by the magnetic field. Being nanoparticles, their chemical reactivity along with chemical stability plus superparamagnetism character have made them useful for various biomedical applications. In this short description, we would like to highlight the basic features of magnetic nanoparticles and their potential use in various technological areas.

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Introduction

Magnetic Nanoparticles (MNPs) generally consist of two components a magnetic material, most often iron, nickel and cobalt, (ferromagnetic one) and the other a chemical component having wide functionality, reactivity and stability.[1–5] The typical size of such nanoparticles lies between 1–100 nanometer and may display superparamagnetism.[6,7] In Figure 1, we schematically show the multifunctional character of various nanoparticles. In a common paramagnentic material, spins are not subjected to any exchange interaction and they do not show any hysterisis or domain like a ferromagnet. In the presence of an external magnetic field, the spins tend to align to it generating a weak attractive interaction. However, in a superparamagnetic material, spins are substituted by small ferromagnetic domains characterized by positive exchange interaction. In the presence of an external magnetic field, these domains tend to align to it generating a strong attractive interaction. Thus, superparamagnetism is another characteristic form of magnetism that does appear in small ferromagnetic or ferrimagnetic nanoparticles. Besides their magnetic response is significantly higher than paramagnetism. Moreover, magnetization in such smaller sized nanopartciles can randomly ip direction under the influence of temperature. Another significant characteristic feature is that it occurs below the Curie temperature of the material. Note that generally any ferromagnet or ferrimagnet material transforms to a paramagnet only above the unique Curie temperature dependent on the strength of exchange interaction and the underlying lattice structure. This particular magnetism occurs in those nanoparticles composed of single domain. Further due to the magnetic anisotropy of the nanoparticles, the relevant magnetic moment possesses two stable orientations antiparallel to each other separated by an energy barrier (KV). The competition between this energy barrier and thermal energy ($KV\sim25k_BT$) gives rise to a characteristic relaxation time ($T=T_0$ $exp(KV=k_BT$)) in this nanometerial. The exchange bias between ferromagnetic/ferrmagnetic and antiferromagnetic interface is the key parameter in controlling the magnetization and other related phenomena in these systems.[8–10] In fact, the particles can invert their magnetization by tunneling without the help of thermal energy. Under the application of an external magnetic field, these materials develop magnetization and as a function of the external field, the magnetization looks like reversible S-shaped increasing curve ($L(x) = \coth(x) - 1/x$). The AC susceptibility measurements of these nanoparticles can identify the various time scales and frequency dependent susceptibility.

Discussion

The chemical and physical features of such particles essentially depend on the synthesis route and chemical structure. A closer look reveals that natural magnetic nanoparticles are everywhere in human brain, in bacteria, algae, birds, ants, bees,[11] etc, in soils and lacustrine sediments, in meteorites and even in interstellar space. It is interestig to note that the homing pigeon have clusters of magnetic nanoparticles (2–4 nm in the pigeon) in their beak area, which help them with their homing ability.[12] Even magnetotactic bacteria possess nanometer-sized magnets, which they use for alignment with the earth's magnetic field. In Figure 2, we sketch some biosensors based on magnetic nanoparticles.

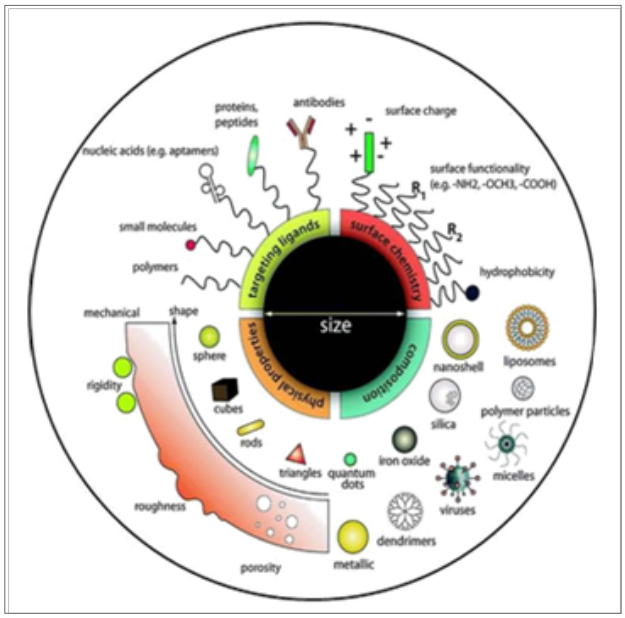

Figure 1 Size and Morphology of nanoparticles.

It is interesting to point out that the magnetism phenomenon occurring in solid is a unique one which can be understood from the quantum theory only.[13] Again, the intriguing features of nanomaterials[14] as compared to bulk are due to the emergence of quantum effects so called quantum confinement effect. Thus, to comprehend the properties of the magnetic nanoparticles, it is essential to apply the quantum mechanics at the nanoscale. The conventional

spin magnetism originates from the partial d or filled bands. The governing exchange interactions between the electrons in this band are resposible for the typical magnetic order.[15] However, in the magnetic nanomaterials, it happens that they originate from either completely empty or fulld and f shells. Even magnetic order can be observed without the participation of d shells known as d0 ferromagnetism. The bulk ZnO is diamagnetic however below the size of 30 nm or so, the material becomes ferromagnetism.[16–18] Magnetism in ZnO can be explained via the unbalanced 3d holes with appropriate exchange interactions. Ferromagnetism has been regarded as a universal of these nanoparticles where their bulk structure is non-magnetic in nature.[19,20] The orgin of such unexpected magnetism can be routed back to the effects of reduced dimensions and of course the dominating quantum effects occurring at low dimensions. In fact, the reduction in one or more dimensions typically results in the reduction of coordination number of atoms which on the other hand reduce the hopping tendency of electrons from site to site. As a result, the necessary kinetic energy (band-width) of electrons is reduced and Coulomb interactions/bandwidth ratio is enhanced.[2–4] The combined effect of these two gives rise to a non-zero magnetism in nanomaterials. Also, the range of this interaction/exchange correlation length is limited to nanometers. Besides, the appearance of surface and interface states due to the reduced symmetry and changed boundary conditions plays a key important role in inducing the magnetism in these materials. The localized defect states due to dopants and/or vacancies can also induce ferromagnetism by localizing the electrons.

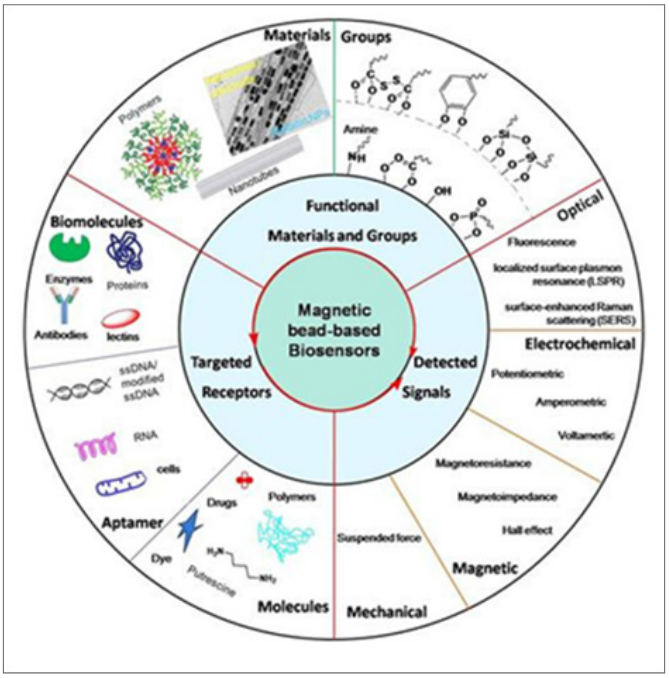

Figure 2 Magnetic nanoparticles based various biosensors.

In recent years, the magnetism has been observed in two-dimensional system[21,22] by doping, applying strain or creating vacancy or a combinations of them. The size and morphology of graphene quantum dot can influence the electronic and magnetic properties.[23]The magnetic properties can be controlled by introducing double vacancy into the pristine planar silicene[24] (2B) and silicene/graphene hybrid[25] (~4μB). The importance of shape dependence in calculating the density of states (DOS) in silicene nanodisks has been understood by realizing that a zigzag trigonal (ZT) possesses the maximum magnetic moment.[26] Although tetragonal graphene (TG) is non-magnetic character, but the transition metal can induce a magnetic moment upto 2.82μB in the TG network.[27] Trilayer structures (single-layer graphene sandwiched between two boron nitride monolayers) have shown interesting magnetic properties[28] relevant for future nano-electronic devices. The site dependent adatoms arsenic and gallium,[29] beryllium[30] and carbonsilicon decoration[31] in the germenene network can create appreciable magnetic moment in the system. Thus, several 2D systems have been shown to possess significant magnetic moment by chemical functionalization or creating vacancy.[32] Pristine SnO_2 is nonmagnetic, however experimental as well as theoretical studies have established[33] that room temperature ferromagnetism in SnO_2 is due to Sn vacancies not the oxygen vacancies.

The most explored MNPs in the research is the ferrite nanoparticles or iron oxide nanopartcles. It is interesting to note that when the average size of particles becomes less than 128 nm, then they show superparamagnetism[3,34] instead of bulk ferromagnetism. Due to the inertness of the surface of these nanoparticles, they cannot form a promising covalent bond with functionalized molecules. However, the essential reactivity required for the practical utility can be significantly enhanced by coating a layer of silica onto their surface.[35] The magnetic moment of such core-shell structure can be controlled by the cluster size of the nanoparticles. But their retained super-paramagnetic properties are independent of the cluster size. The functional modification of magnetic nanoparticle by protein is shown in Figure 3.

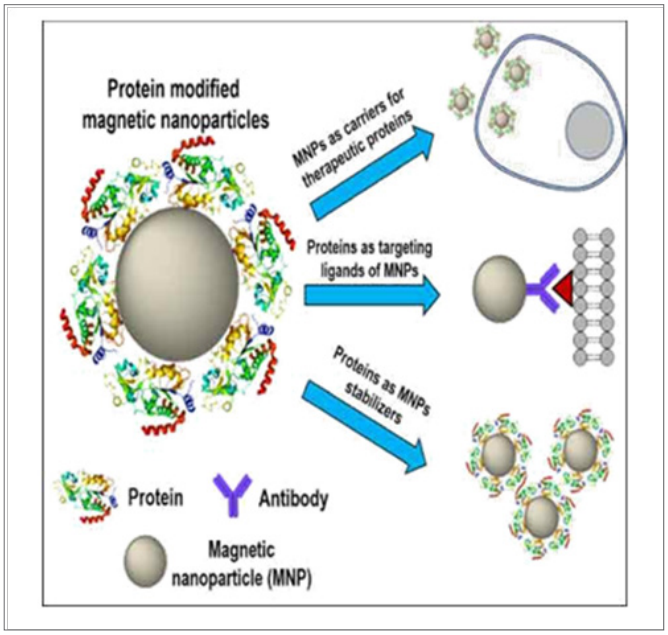

Figure 3 Protein modified magnetic nanoparticles.

There are three important aspects[36] of MNPs which facilitate them for improved diagnosis, targeting and treatment of diseases. First of all, it is the superparamagnetism, secondly their essential ability to respond to an external magnetic field and finally, most importantly, the surface functionalization. In fact through this functionalization, not only the stability (both physical and chemical) of these MNPs is ensured but also it provides a path for targeting specific tissues and the disease sites. The superparamagnetism property of these MNPs hinder

the aggregation of particles. Because of their nanodimension sizes, MNPs aided devices can readily interact with biomolecules on both the surface of cells and inside of cells. By gaining access to so many areas of the body, they have the potential to detect disease and the deliver treatment.[37] MNPs apart from the basic science research have found applications in cancer therapy.[38] In particular, in magnetic fluid hyperthermia, different types of iron oxides or even gold are injected to the tumor and then a high radio-frequency magnetic field is applied to produce a temperature of the order of 40-46oC. This temperature is enough to kill the majority of the cancer cells.[39–43] Another potential application of this typical nanoparticle lies in their ability to combine the heat and direct drug delivery[44,45] in a cancer treatment. Although this treatment is still under its development condition, but is expected that this approach is likely to cure tumor better than other options available at the stage.

These novel functionalized nanoparticle systems have been used for in vitro and in vivo biomedical applications[46–49] such as magnetic separation of cells, proteins and DNA fragments, bio-imaging, magnetic resonance imaging (MRI) enhancement. In MRI enhancement, superparamagnetic iron oxide particles are invoked in order to increase the typical relaxation process of the proton nuclear spins. However, in hyperthermia studies targeted cancerous cells as mentioned above are locally heated by radio-frequency magnetic field. As a result, electromagnetic energy is absorbed by the magnetic nanoparticles and subsequently dissipated in the surrounding tissue to cure the cancerous patient. In Figure 4, the various uses of MNPs have been shown schematically in medical diagnosis and proper treatment. As a concrete example, iron oxide nanoparticles (core coated with–cyclodextrin (CD)and pluronic polymer (F68)) with curcumin loading have shown enhanced MRI properties compared to conventional nanoparticles and enough promise for breast cancer therapeutics.[50,51] MNPs can also be used for genetics applications such as the rapid isolation of mRNA.[52] In fact, due to their large surface to volume ratio, magnetic nanoparticles can be used for treatment of contaminated water by applying a magnetic field.[53] Fluorescence microscopy study has established the ability of the MNPs for active brain targeting of water-soluble P-glycoprotein (P-gp) substrate rhodamine 123 (Rh123).[54]

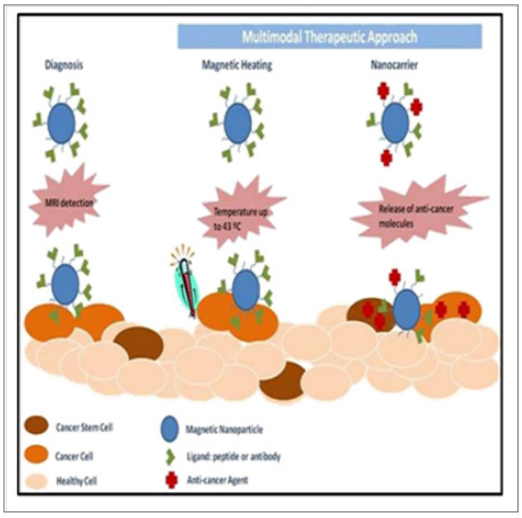

Figure 4 Use of MNP in medical diagnosis and treatment.

Conclusion

To conclude, the unconventional magnetism associated with these nanosystems will trigger further research and will hopefully overcome the constraints appeared along with for their practical application. Since, the dynamics of spins through various interactions in these systems are the key ingredients, theoretical effort is currently been pursued in understanding some novel non-equilibrium scaling phenomena in such systems. The origin of the nanomagnetism lies in the following six parameters:

a. Dimensions must be comparable to characteristic lengths (limiting size of the magnetic domain)

b. There should be break in translation symmetry due to exchange bonds and/or frustration,

c. Reduced coordination number is necessary,

d. Higher proportion of surface atoms are required,

e. There must be a change in electronic density of states and finally

f. The magnetic anisotropy energy should be comparable to thermal energy. We have also indicated some possible uses of MNPs in biomedical applications such as nanocarriers for drugs, contrast imaging agents in MRI, in local hyperthermia, magnetic targeting and cancer treatment.

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Conflicts of interest

The authors declare there is no conflict of interest.

References

1. Bader SD. Colloquium: Opportunities in nanomagnetism. *Rev Mod Phys*. 2006;78:1.
2. Singh R. Unexpected magnetism in nanomaterials. *Journal of Magnetism and Magnetic Materials*. 2013;346:58.
3. Petracic O. Superparamagnetic nanoparticle ensembles. *Super-lattices and Microstructures*. 2010;47:569.
4. Papaefthymiou Georgia C. Nanoparticle magnetism. *Nano Today*. 2009;4(5): 438.
5. Koksharov YA. *Magnetism of Nanoparticles: Effects of Size, Shape, and Interactions in Magnetic Nanoparticles*. In: Sergey P Gubin, editor. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; 2007. 198 p.
6. Lu A-H, Salabas EL, Schth F. Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application. *Angew Chem Int Ed*. 2007;46:1222.
7. Peddis D, Cannas C, Musinu A, et al. Magnetism in Nanoparticles: Beyond the Effect of Particle Size. *Chem Eur J*. 2009;15:7822
8. Battle X, abarta A. Finite size effects infinite particles: magnetic and transport properties. *J Phys D: Appl Phys*. 2002;35:R15.
9. Nogues J, Schuller IK. Exchange bias. *J Magn Magn Material*. 1999;192:203.

10. Nogues J, Sort J. Exchange bias in nanostructures. *Phys Reports*. 2005;422:65.

11. Wiltschko R, Wiltschko W. Magnetic Orientation in Animals. Springer, Berlin; 1995.

12. Fleissner G, Stahl B, Thalau P, et al. A novel concept of Fe-mineral-based magnetoreception: histological and physicochemical data from the upper beak of homing pigeons. *Natur-wissenschaften*. 2007;94(8):631.

13. Jana D. *On Study of Universal Diamagnetism of Spinless Bosons: From N Finite particles to Field Theory, in Astrophysics and Condensed Matter (Horizons in World Physics)*. In: Thomas G. Hardwell, editor. Nova Science Publishers, NY; USA. 73 p.

14. Das D, Nandi K, Jana D. Nanostructures: Physics and Technology. *Physics Education*. 2002;19(3):155.

15. Hochella MF, Lower SK, Maurice PA, et al. Nanominerals, mineral nanoparticles, and earth systems. *Science*. 2008;319:1631.

16. Ghose S, Chattopadhaya S, Sarkar A, et al. Surface defects induced Ferromagnetism in nano crystalline ZnO. *J Appl Phys*. 2013;114:073516.

17. Ghose S, Rakshit T, Ranganathan R, et al. Role of Zn-interstitial defect states on d0 ferromagnetism of mechanically milled ZnO nanoparticles. *RSC Adv*. 2015;5:99766.

18. Ghose S, Gogurla N, Ranganathan R, et al. Strong Free Exciton Emission for Undoped ZnO Nanoparticles with d0 Ferromagnetism: Effective Exciton-Phonon Coupling at Surfaces. *RSC Adv*. 2016;6:83909.

19. Shipra, Gomathi A, Sundaresan A, et al. Room temperature ferromagnetism in nanoparticles of superconducting materials. *Solid State Communications*. 2007;142:685.

20. Sundarsan A, Bhargavi R, Rangarajan N, et al. Ferromagnetism as a universal feature of nanoparticles of otherwise non-magnetic oxide. *Phys Rev B*. 2006;74:161306.

21. Jana D. 2D Materials: Future and Perspectives. *J Nanomed Res*. 2018;7(1):00169.

22. Chowdhury S, Jana D. A theoretical review on electronic and optical properties of silicone. *Rep Prog Phys*. 2016;79:126501.

23. Das R, Dhar N, Bandyopadhyay A, et al. Size dependent magnetic and optical properties in diamond shaped graphene quantum dots: a DFT study. *J Phys Chem Solid*. 2016;99:34.

24. Majumdar A, Chowdhury S, Nath P, et al. Defect induced magnetism in silicene: A first principles study. *RSC Adv*. 2014;4:32221.

25. Chowdhury S, Jana D. Electronic and magnetic property study of modified silicene/graphene hybrid. *Mat Chem Phys*. 2016;183:580.

26. Chowdhury S, Nath P, Jana D. Shape Dependent Anisotropic Optical Property of graphene nanodisk. *J Phys Chem Solid*. 2015;3:32.

27. Chowdhury S, Majumder A, Jana D. Search for magnetism in transition metal atoms doped tetragonal graphene- A DFT Approach. *Jour Magn Magn*. 2017;441:523.

28. Das R, Chowdhury S, Jana D. A first principles approach to magnetic and optical properties in single-layer graphene sandwiched between boron nitride monolayers. *Material Research Express*. 2015;2:075601.

29. Dhar N, Bandyopadhyay A, Jana D. Tuning electronic, magnetic and optical properties of germanene nanosheet with site dependent adatoms arsenic and gallium: A first principles study. *Current Applied Physics*. 2017;17:573.

30. Dhar N, Jana D. Effect of beryllium doping and vacancy in band structure, magnetic and optical properties of free standing germanene. *Current Applied Physics*. 2017;17:1589.

31. Dhar N, Jana D. Magnetic and optical properties of carbon and silicon decorated free standing buckled germanene: A DFT approach. *J Phys Chem Solid*. 2018;115:332.

32. Chowdhury S, Dhar N, Bandyopadhyay A, et al. Optical and magnetic Properties of Free Standing Silicene, Germanene and T-graphene System: A first principles Study. *Physical Sciences Reviews*. 2017;2:20160102.

33. Sarkar A, Sanyal D, Nath P, et al. Defect driven ferromagnetism in SnO_2 : a combined study using density functional theory and positron annihilation spectroscopy. *RSC Adv*. 2015;5:1148.

34. Kralj S, Makovec D. Magnetic Assembly of Superparamagnetic Iron Oxide Nanoparticle Clusters into Nanochains and Nanobundles. *ACS Nano*. 2015;9(10):9700.

35. Kralj S, Makovec D, Campelj S, et al. Producing ultra-thin silica coatings on iron-oxide nanoparticles to improve their surface reactivity. *Journal of Magnetism and Magnetic Materials*. 2010;322(13):1847.

36. Singh D, McMillan JEM, Liu XM, et al. Formulation design facilitates magnetic nanoparticle delivery to diseased cells and tissues. *Nanomedicine (Lond)*. 2014;9(3):469.

37. Singh D, McMillan JM, Kabanov AV, et al. Bench-to-bedside translation of magnetic nanoparticles. *Nanomedicine (Lond)*. 2014;9(4):501–516.

38. Scarberry KE, Dickerson EB, McDonald JF, et al. Magnetic Nanoparticle-Peptide Conjugates for in Vitro and in Vivo Targeting and Extraction of Cancer Cells. *Journal of the American Chemical Society*. 2008;130:10258.

39. Heydari M. Magnetic fluid hyperthermia in a cylindrical gel contains water flow. *J Mech Med Biol*. 2015;15:1550088.

40. Javidi M, Heydari M, Karimi A, et al. Evaluation of the effects of injection velocity and different gel concentrations on nanoparticles in hyperthermia therapy. *J Biomed Phys Eng*. 2014;4(4):151.

41. Obaidat IM, Issa B, Haik Y. Magnetic Properties of Magnetic Nanoparticles for Efficient Hyperthermia. *Nanomaterials*. 2015;5(1):63–89.

42. Javidi M, Heydari M, Attar MM, et al. Cylindrical agar gel with fluid now subjected to an alternating magnetic field during hyperthermia. *Int J Hyperthermia*. 2014;31(1):33–39.

43. Karponis D, Azzawi M, Seifalian A. An arsenal of magnetic nanoparticles; perspectives in the treatment of cancer. *Nanomedicine (Lond)*. 2016;11(16):2215–2232.

44. Kumar CS, Mohammad F. Magnetic nanomaterials for hyperthermia-based therapy and controlled drug delivery. *Adv Drug Deliv Rev*. 2011;63(9):789.

45. Mou X, Ali Z, Li S, et al. Applications of Magnetic Nanoparticles in Targeted Drug Delivery System. *J Nanosci Nanotechnol*. 2015;15(1):54–62.

46. Gupta AK, Gupta M. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterial*s. 2005;26(18):3995.

47. Colombo M, Carregal-Romero S, Casula MF, et al. Biological Applications of Magnetic Nanoparticles. *Chem Soc Rev*. 2012;41(11):4306–4334.

48. Mornet S, Vasseur S, Grasset F, et al. Magnetic nanoparticle design for medical applications. *Progress in Solid State Chemistry*. 2006;34:237.

49. Li X, Wei J, Aifantis KE, et al. Current investigations into magnetic nanoparticles for biomedical applications. *J Biomed Mater Res A*. 2016;104(5):1285–1296.

50. Yallapu MM, Othman SF, Curtis ET, et al. Curcumin loaded magnetic nanoparticles for breast cancer therapeutics and imaging applications. *Int J Nanomedicine*. 2012;7:1761.

51. Ahmed M, Douek M. The role of magnetic nanoparticles in the localization and treatment of breast cancer. *Biomed Res Int*. 2013;1:281230.

52. Elaissari A, Chatterjee J, Hamoudeh N, et al. *Advances in the Preparation and Biomedical Applications of Magnetic Colloids*. In: Roque Hidalgo-lvarez, editor. Structure and Functional Properties of Colloidal Systems. CRC Press; 2010: 315 p.

53. Koehler FM, Fabian M, Rossier M, et al. Magnetic EDTA: Coupling heavy metal chelators to metal nanomagnets for rapid removal of cadmium, lead and copper from contaminated water. *Chem Commun*. 2009;32:4862–4864.

54. Kirthivasan K, Singh D, Bommana MM, et al. Active brain targeting of a fluorescent P-gp substrate using polymeric magnetic nanocarrier system. *Nanotechnology*. 2012;23:255102.