



# Magnetic nanomaterials and sensors for biological detection

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## Abstract

It is becoming progressively more understandable that sensitivity and versatility of magnetic biosensors provides unique platform for high performance diagnostics in clinical settings. Confluence of information suggested that magnetic biosensors required well-tailored magnetic particles as probes for detection that generate large and specific biological signal with minimum possible nonspecific binding. However, there are visible knowledge gaps in our understanding of the strategies to overcome existing challenges related to even smaller size of intracellular targets and lower signal-to-noise ratio than that in whole-cell studies, therefore tool designing and development for intracellular measurement and manipulation is problematic. In this review we describe magnetic nanoparticles, synthesis and sensing principles of magnetic nanoparticles as well as surface functionalization and modification and finally magnetic nanoparticles for medical diagnostics. This review gathers important and up-to-date information and may help to develop the method of obtaining magnetic materials especially for medical application.

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**Key words:** Magnetic nanoparticles; Synthesis; Sensing principles of magnetic nanoparticles; Surface functionalization and modification; Magnetic nanoparticles for medical diagnostics

Biosensors comprise a number of different components among which the most important part constitutes magnetic particles. Recently, Koh and Josephson<sup>1</sup> reported that, “magnetic nanoparticles constitute a significant replacements of commonly available labels in biosensing because of their magnetic properties not present in biological systems”. The implication of magnetic particles in biosensors means that it is important to have a better understanding of the properties of magnetic particles. Recently, great attention has been devoted to syntheses of various magnetic

nanoparticles due to their widespread applications in many fields such as biomedicine, biotechnology, materials science and environmental areas.<sup>2,3</sup> The synthesis of monodispersed and shape controlled nanoparticles is significant because the properties of the nanostructures depend strictly on their dimensions. Moreover, synthesis of nanoparticles focused in particular on formation of the proper dimensions is crucial to determine physicochemical properties of nanocrystals. The magnetic nanoparticles attain their particular properties when their size decreases reaching the value below critical dimensions. The low dimensional structures are characterized by an enhanced magnetic moment and thus exhibit properties similar to paramagnetic structure, able to respond immediately to magnetic field applied. Such properties result in wide applications of superparamagnetic NPs in biomedicine due to their properties which are able not to form the aggregates at ambient temperature.<sup>4</sup> It is well recognized that therapy based on application of magnetic nanoparticles seems to

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minimize side effects of therapy in comparison with conventional drug delivery treatments such as radiation, chemotherapy or immunotherapy.<sup>5–9</sup> In turn, magnetic hyperthermia is another experimental method of tumors treatment, based on the heat generation by the magnetic nanoparticles under the alternating magnetic field.<sup>4,10–12</sup> Notably, hyperthermia utilized alone to treat the cancer cells is not sufficient enough, thus it must be followed by additional therapy such as irradiation or chemotherapy.<sup>13–15</sup> Recently ferrofluids consisting of superparamagnetic or ferrimagnetic particles of  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$  have been widely utilized for hyperthermia applications.<sup>14,16–18</sup> Magnetic nanoparticles of various compositions and phases such as oxides ( $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ), pure metals (Fe, Co) and ferromagnets ( $\text{MgFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ ) have been described.<sup>3,4,19–22</sup> Great attention has been devoted to develop synthetic routes that led to the formation of well monodispersed and shape controlled magnetic nanoparticles.<sup>4</sup> Nowadays, numerous chemical and green synthesis methods such as: co-precipitation,<sup>23,24</sup> thermal decomposition,<sup>25</sup> microemulsions,<sup>26,27</sup> hydrothermal synthesis,<sup>28</sup> flame spray pyrolysis,<sup>29</sup> and green approaches<sup>30</sup> can be employed to attain magnetic nanoparticles.

## Magnetic nanoparticles

To understand a behavior of magnetic particles it is necessary to determine their physicochemical parameters such as size, shape and magnetic properties. Three types of magnetic particles can be distinguished and they are as follows: oxides, metallic metals and alloys. They exhibit various magnetic properties. The oxides tended to possess antiferromagnetic or fluctuating magnetic properties. Metals are magnetic, however, the nature of their magnetic properties depends on size and morphology of their particles. Alloys on the other hand tend to have characteristics that are a combination of the magnetic properties of the metals they are composed of.

## Oxides

The first type of magnetic particles that needs to be considered is oxides. He and Shi<sup>31</sup> stated that, “CoO in bulk is regarded as an insulating antiferromagnet with rocksalt cubic structure and Neel temperature of 298 K”. There are two important magnetic particles that are in oxide form, FeO and  $\text{Co}_3\text{O}_4$ . One of the most important characteristics of  $\text{Co}_3\text{O}_4$  is that its magnetic properties are changing under different conditions. Gawali et al<sup>32</sup> found that, the vibration sample magnetometer (VSM) data of nanoparticles exhibit weak ferromagnetic properties with magnetic saturation of about 0.02 emu/g at the maximum magnetic field of 10 kOe, whereas material in bulk shows antiferromagnetic properties. When cobalt (II,III) oxide is exposed to a magnetic field it acts like a typical magnet and displays weak ferromagnetic behavior. However, a sample of  $\text{Co}_3\text{O}_4$  not exposed to magnetic field will display antiferromagnetic behavior. Also, CoO seems to possess variable magnetic properties. He and Shi<sup>31</sup> found that, the CoO nanoparticles possess anomalous magnetic properties, such as large movements, coercivities and loop shifts. These features determine the formation of spin compensation of random system in CoO. These findings are important because they suggest that the magnetic properties of

CoO are highly variable. However, it must be noted that it did not seem to develop the antiferromagnetic characteristics of  $\text{Co}_3\text{O}_4$ . However, it seemed to display a greater range of magnetic properties.

## Metallic

There are a number of metallic particles that have magnetic properties. Considering the properties of nickel (Ni), He et al<sup>33</sup> explained that: “The transition metal such as nickel exhibits particular magnetic and catalytic properties”. This suggests that Ni is a metal that have a unique magnetic and catalytic properties. Size and organization mode of Ni particles affect their magnetic properties. Deraz<sup>34</sup> found, that high value of magnetization of the studied materials can be correlated with a finite-size and surface effect. Particularly, the magnetization is correlated with the microstructure of the interface (roughness and crystallinity degree) that determines the configuration of the spin. These findings suggest that morphology of the Ni, Ni lattices and compounds that contain Ni particles determines their magnetic properties. Various morphological structures of materials containing Ni affect their behavior and even result in changes of the surface area of Ni particles. Many reports state that the size of the particle affects properties of Ni. According to He et al<sup>33</sup> “...the Curie temperature, saturation magnetization, and remanent magnetization increase whereas the coercivity decreases monotonously with the increase of particle size”. This may suggest that the larger Ni may be characterized by higher levels of saturation and remanent magnetization.

## Alloys

Alloys are combinations of atoms of different metals. When discussing the process of making  $\text{Fe}_{56}\text{Co}_7\text{Ni}_7\text{B}_{20}\text{Nb}_{10}$  alloy Lesz et al<sup>35</sup> explain that the Fe-based master alloy ingots can be formed by melting the mixtures of Fe–B and Fe–Nb as starting alloys and accordingly Fe, Co, or Ni are added metals under protective atmosphere of inert gas such as argon. Such synthetic route leads to the formation of  $\text{Fe}_{56}\text{Co}_7\text{Ni}_7\text{B}_{20}\text{Nb}_{10}$  and a large number alloys that exhibit the complex nature with wide range of properties. The combination of metals in  $\text{Fe}_{56}\text{Co}_7\text{Ni}_7\text{B}_{20}\text{Nb}_{10}$  results in a combination of morphological, chemical and physical characteristics of the material. Lesz et al<sup>35</sup> reported, that the XRD and TEM structural and morphological analyses showed that the ribbons obtained were amorphous. SEM micrographs depicted some structural differences in the ribbons (smooth fracture inside with few grains network on the surface freely solidified). Consequently, the material exhibits various physical and chemical properties at different locations. Also, the magnetic properties of such alloy exhibit its heterogeneous nature. Analyzing such structure Lutz et al<sup>36</sup> reported that Ni was always superparamagnetic, while Co possessed superparamagnetism only at low temperatures.  $\text{Fe}_{56}\text{Co}_7\text{Ni}_7\text{B}_{20}\text{Nb}_{10}$  seems to possess the magnetic properties derived from all the metals that form such structure. The formed alloys possess soft magnetic properties instead of the supermagnetic ones, observed in metals such as Ni. This suggests that  $\text{Fe}_{56}\text{Co}_7\text{Ni}_7\text{B}_{20}\text{Nb}_{10}$  as an alloy has magnetic properties that are a combination of the magnetic properties of the various metals that form such structure. In the

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