



## Research articles

# The influence of bias magnetization of nanoparticles on GMR sensor signal and sensitivity for the ultra-low concentration detection



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## ABSTRACT

In the broad research of the GMR bio-sensing technology, it is vital to explore appropriate magnetic labels and its influences on the detection signal. In this work, four kinds of ferrite particles of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and NiZnFe<sub>2</sub>O<sub>4</sub> were prepared through calcining the Dimethyl Formamide (DMF) solution of the transition metal nitrates [Fe(NO<sub>3</sub>)<sub>3</sub> and X(NO<sub>3</sub>)<sub>2</sub>, X = Co, Ni, Zn] to study the effect of magnetic properties on detection signals using a DC in-plane measuring method. It was revealed that for four particles, the output voltage differences  $|\Delta V|$  between with and without magnetic particles exhibit log-linear functions of the particles concentrations  $x$  in the range from 0.1 to 10 ng/mL. A very low limitation of detection (LOD) of 0.1 ng/mL for all the samples was obtained, which is two orders smaller than that in the previous work. Moreover, the change of output voltage difference at the LOD ( $|\Delta V_{lim}|$ ) is proportional to the magnetization at bias field (bias magnetization,  $M_{bias}$ ), which indicates that larger  $M_{bias}$  leads to a lower LOD. This work provides a useful guidance in selecting or preparing magnetic labels to enhance the sensitivity of GMR biosensors.

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## 1. Introduction

Over the past two decades, giant magnetoresistance (GMR) based magnetic biodetection technology has received increasing research and development efforts [1–9]. The magnetic particles used in labeling biomolecules are an important part of the research field of GMR biosensing technology. The GMR sensor determines the number of biomolecules through capturing the magnetic fringing fields introduced by the magnetic particles attached on the sensor surface. Therefore, the size and magnetic property of the particles will directly affect the detection result. In earlier studies, the commercial magnetic microbeads were a very popular choice of the labels for the GMR biodetection [10–13]. These microbeads usually consist of superparamagnetic magnetic nanoparticles dispersed in a silica or polymer matrix [14–16]. As a GMR biodetection label, the biggest problem of these microbeads is the silica or polymer components in the microbeads reduce the average magnetism of the composite particles greatly. With the development of the nanotechnology, more and more magnetic nanoparticles with grain sizes from 5 to 150 nm are used for biological

labelling, because the composition, size, morphology and surface chemistry of particles can all be tailored in combination with their nanoscale magnetic phenomena [17]. However, these nanoparticles aggregate easily due to magnetic interaction each other in the magnetic field which limits their applications [18]. So the superparamagnetic nanoparticles gets a lot of attention because of the excellent dispersion without magnetic field [5,13,19–22]. Usually, superparamagnetic nanoparticles are too small (usually <20 nm) to generate enough dispersion magnetic field, hard to obtain a low LOD. In order to improve the sensitivity of GMR biodetection, the self-assembly superparamagnetic particles were used as the magnetic labels because those particles possess both higher magnetization and superparamagnetism simultaneously [8,18,21–24].

In brief, researchers attempted to choose different particles as the labels to improve the detection performances, such as LOD, linear range and signal-to-noise ratio. In this work, we synthesized four kinds of ferrite particles by calcination, which were used to prepare a series of magnetic particles-alcohol solutions for biodetection. Although these ferrite particles have the relative higher coercivity and remanence which may lead to the aggregation of particles in the external magnetic field, our samples showed excellent performances for the ultra-low concentration biodetections.

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This can be explained that, there may be one or a few nanoparticles attached on the sensor surface in an ultra-low concentration biodection, and nanoparticles are far from each other, which can avoid aggregation of particles. What is more important, the magnetic characteristics of ferrite particles are even more favourable [15], the large bias magnetization of nanoparticles will introduce the large diffusion field which is beneficial to improve the LOD. We found that an ultra-low LOD of 0.1 ng/mL can be obtained for all samples, which is two orders smaller than that in the previous work [7,8]. Moreover the output voltage differences at the LOD concentration  $|\Delta V_{\text{lim}}|$  were related to the bias magnetization of particles.

## 2. Experimental details

Four kinds of ferrite particles of  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and  $\text{NiZnFe}_2\text{O}_4$  have been prepared by calcination [25]. For simplicity, we took  $\text{CoFe}_2\text{O}_4$  as an example. The typically synthetic procedure as follows: firstly, 1.45 g Ferric nitrate ( $\text{Fe}(\text{NO}_3)_3$ ) and 0.72 g cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ ) were dissolved respectively in 15 mL Dimethyl Formamide (DMF) solution; secondly, the mixed solution was transferred to a crucible and calcined at the heating rate of  $1^\circ\text{C}/\text{min}$  until  $680^\circ\text{C}$ , then retaining for 2 h; finally, the samples were cooled to room temperature naturally, all of the processes were under the air. For the other three samples, calcination process was the same as  $\text{CoFe}_2\text{O}_4$  except the mass ratio of reactants (more details for the mass ratio of reactants showed in Table 1).

The exchange-biased GMR sensor chip (GF708, manufactured by Sensitec GmbH, Germany) was employed in the home-made detection system which using a DC in-plane measuring method. The GMR sensor chip used in our detection system is a Wheatstone bridge consisted of four same artificial antiferromagnet pinned spin-valve elements. The DC power is connected to the Helmholtz coil to provide an in-plane static magnetic field  $H$  along the sensitive direction of the sensor, two ports of the Wheatstone bridge are provided a constant current (10  $\mu\text{A}$ ) by Keithley 2400 source meter and the output voltage  $V_{\text{out}}$  from the other two ports are measured by the Keithley 2182 digital nanovoltmeter. The detailed detection procedure was described in our previous work [7,8].

Four kinds of ferrite samples were prepared to the particles-alcohol solutions with various concentrations (0.01, 0.1, 1, 10, 100 and 1000 ng/mL) to explore the effect of magnetic properties on detection signals. The concentration  $x$  and detection time  $t$  dependence of the output voltage of the sensor  $V_{\text{out}}$  were recorded by computer via GPIB connection for further analysis.

## 3. Results and discussion

The XRD patterns of the powder shows in Fig. 1, four kinds of ferrite particles were all spinel ferrite crystal structure. The peak positions and relative intensity of all diffraction peaks for the four ferrite samples match well with the standard diffraction data of  $\text{NiZnFe}_2\text{O}_4$  (JCPDS 08-0234),  $\text{CoFe}_2\text{O}_4$  (JCPDS 22-1086),  $\text{NiFe}_2\text{O}_4$  (JCPDS 10-0325), and  $\gamma\text{-Fe}_2\text{O}_3$  (JCPDS 39-1346) respectively, and no distinct peak attributed from impurities can be found for all

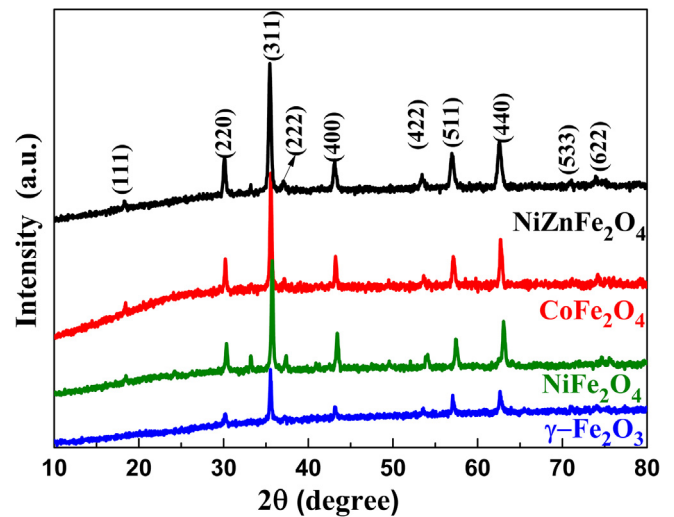


Fig. 1. The XRD patterns for four kinds of ferrite particles.

of the samples. The average crystallite sizes of those particles calculated by Scherrer's formula are 22, 24, 23, 27 nm for  $\text{NiZnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , respectively, indicating a similar primary crystal size.

The morphologies of ferrite particles were investigated by SEM as shown in Fig. 2. Four samples have a large quantity of uniform nano-granules and narrow size dispersion. The average particle sizes estimated from SEM of the histograms are about 52, 51, 118, and 130 nm for  $\text{NiFe}_2\text{O}_4$ ,  $\text{NiZnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ , and  $\gamma\text{-Fe}_2\text{O}_3$ , respectively. The sizes of samples are larger than the primary nanocrystal sizes estimated from XRD, which suggest the particles may be composed of some primary nanocrystallites. In addition, the particle sizes of  $\text{CoFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  are larger than the other two samples because  $\text{CoFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  have lower crystallization temperatures [25].

In order to investigate the magnetic properties of four kinds of ferrite particles, the hysteresis loops were measured at 298 K by cycling the field between  $\pm 10$  kOe. As illustrated in Fig. 3,  $M_s$  and  $H_c$  of  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{NiZnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  are 73 emu/g and 100 Oe, 50 emu/g and 120 Oe, 32 emu/g and 500 Oe, 66 emu/g and 2000 Oe, respectively. The magnetic properties of these particles were obviously different by doping the half metallic element in the  $\gamma\text{-Fe}_2\text{O}_3$ , and these results are similar to those reported in other literatures [26,27]. At the operating magnetic field for the sensor chip  $H = 1.5$  Oe, the  $M$  of four ferrite particles are about 29.46, 10.14, 7.78 and 6.6 emu/g for  $\text{CoFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{NiZnFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , respectively. As discussed below, such difference of magnetic performance under bias magnetic field dramatically affect the detection results.

The dependence of  $V_{\text{out}}$  on the external magnetic field for a bare GMR sensor is measured in the range of  $\pm 95$  Oe. Fig. 4 indicates that when the magnetic field from 0 to +3 Oe, the  $V_{\text{out}}$  increases rapidly and linearly with the increase of magnetic field. First order differential shows that there is a maximum value at  $H = 1.5$  Oe where sensitivity of the sensor reaches the maximum. So, we will set the bias field  $H_{\text{bias}}$  as 1.5 Oe in the following detections.

The four kinds of ferrite particles-alcohol solutions with different concentrations were dropped on the GMR sensors, then the dependences of the  $V_{\text{out}}$  with time  $t$  in a stable magnetic field  $H = 1.5$  Oe were measured after the alcohol evaporated. Taking  $\text{NiZnFe}_2\text{O}_4$  as an example, Fig. 5(a) shows that the relation curve of the absolute change values of output voltages  $|\Delta V|$  ( $=|V_{\text{out}} - V_0|$ ,  $V_{\text{out}}$  and  $V_0$  are the output voltages with and without particles respectively) and  $t$  under the different concentrations  $x$ . for

Table 1  
The fabrication condition of ferrite particles.

| Sample                         | $\text{Fe}(\text{NO}_3)_3$<br>(g) | $\text{Ni}(\text{NO}_3)_2$<br>(g) | $\text{Zn}(\text{NO}_3)_2$<br>(g) | $\text{Co}(\text{NO}_3)_2$<br>(g) |
|--------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\gamma\text{-Fe}_2\text{O}_3$ | 1.45                              | 0                                 | 0                                 | 0                                 |
| $\text{NiFe}_2\text{O}_4$      | 1.45                              | 0.72                              | 0                                 | 0                                 |
| $\text{CoFe}_2\text{O}_4$      | 1.45                              | 0                                 | 0                                 | 0.72                              |
| $\text{NiZnFe}_2\text{O}_4$    | 1.45                              | 0.36                              | 0.36                              | 0                                 |

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