Journal of Magnetism and Magnetic Materials 402 (2016) 150–155

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Optical detection of magnetic nanoparticles in colloidal suspensions

Alejandro J. Gimenez [a], Diana G. Ramirez-Wong [a], Sarai E. Favela-Camacho [a],
Isaac C. Sanchez [b], J.M. Yáñez-Limón [a], Gabriel Luna-Bárcenas [a,*]

[a] *Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional Unidad Querétaro, Querétaro, México*
[b] *Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form
11 November 2015
Accepted 21 November 2015
Available online 22 November 2015

Keywords:
Light scattering
Magnetic nanowires
Light transmission
Nanoparticle detection
Colloidal magnetic nanoparticles

ABSTRACT

This study reports the change of light transmittance and light scattering dispersion by colloidal suspensions of magnetic nanoparticles. Optical changes were observed during the application of transversal magnetic fields to magnetic nanoparticles and nanowires at concentrations spanning from 20 μg/mL to 2 ng/mL. Results show that light scattering modulation is a simple, fast and inexpensive method for detection of magnetic nanoparticles at low concentrations. Frequency and time response of the optical modulation strongly depends on the geometry of the particles. In this regard, light transmittance and scattering measurements may prove useful in characterizing the morphology of suspended nanoparticles.

1. Introduction

One of the main challenges related to working with nanoparticles is the inherently difficult manipulation due to their size, which can complicate the separation, cleaning, functionalization, and other synthesis steps. However, the use of magnetic nanoparticles seems to minimize the problem of working at the nanoscale since magnetic fields can be applied and removed to handle the particles. Consequently, there is an increase in the study of magnetic nanoparticles for their application in ferrofluids [1,2], cancer treatments by hyperthermia [3], magnetic immunoassay [4], water remediation [5], immobilization of proteins and enzymes [6], among others [7,8].

Along with the growth in the use and development of magnetic nanoparticles, the ability to detect of such materials gains relevance. For instance, detection and quantification of a specific analyte is crucial for immunoassays [4,9] which could be improved thanks to the use of magnetic nanoparticles. Another novel application may include mineral prospecting detection of magnetite leading to valuable ores [10].

Previous studies have demonstrated that magnetometers can be used to detect magnetic nanoparticles in liquid suspensions; for instance Knappe et al. [11] used a superconducting magnetometer to detect samples down to 20 μg/mL (4 μg in 140 μL). Similarly, Nikitin et al. [12] detected concentrations down to 30 ng/mL (3 ng per 0.1 cm^3) of magnetite beads with a non-lineal magnetization method. Dynamic Light scattering methods have already been used to detect gold nanoparticles at 20 fM concentrations [13]. In this study we adopted two methods to detect nanoparticles. The first method is based upon the change of transmissibility of colloidal suspensions when a magnetic field is applied; this method yields an important signal related to the magnetic particle content on a colloidal suspension [14,15]. The second method measures the intensity of the light scattered in the colloidal suspension by the suspended nanoparticles. This method was originally proposed by Tyndall [16]; since then it has been broadly used to detect and measure particles in colloidal suspensions [17,18]. Indeed, a previous work of our group reported a large light scattering change response of nanowire colloidal suspensions [19].

The use of Quantum Dots (QD) as fluorescent labels [20,21] has been successfully used for biomedical sensing applications in a detection range of a few ng/mL; this concentration range detection is comparable with the detection threshold using QD fluorescence immunoassays [22]. QD detection usually requires complex and expensive spectrofluorometer equipment. In this regard, methods using magnetic nanoparticles offer the advantage of easier manipulation of the nanoparticles by using magnetic fields. Methods used in this article use a simple and inexpensive experimental setup.

Herein we present a comparison of the optical response given by 0D magnetite nanoparticles and 1D nickel nanowires. Magnetic nanoparticles are synthesized by fast injection coprecipitation method [23], and the nanowires are fabricated by electrodeposition over anodized alumina pores [24–26]. Both techniques of synthesis have already proven their ability to produce magnetic

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.jmmm.2015.11.058
0304-8853/

nanosized materials in a reliable fashion. Based upon the above, the spirit of our work is to advance nanomaterial's detection and characterization by comparing light transmittance and scattering by 0D and 1D magnetic nanomaterials.

2. Methodology

2.1. Synthesis of nanomaterials

Ni nanowires are fabricated by electrodeposition using anodized aluminum as a template in a procedure described by Nielsch et al. [25]. To fabricate nanowires of different sizes the alumina template is grown under two different conditions: for thin and small nanowires (snw), 30 V for 1 h at 15 °C, and for wider and longer nanowires (lnw), 50 V for 6 h at 6 °C. Magnetite nanoparticles were synthetized by fast injection coprecipitation method, which is based on a modification of Terrazas coprecipitation method [23]. Iron (III) chloride hexahydrate (6.7 g, $FeCl_3 \cdot 6H_2O$) and Iron (III) sulfate heptahydrate (3.4 g, $FeSO_4 \cdot 7H_2O$) were dissolved in 50 mL of distilled water through an ultrasonic bath for 10 min and subsequently, ammonium hydroxide (20 mL, NH_4OH) was fast-injected. The precipitate was separated using magnetic field and washed with deionized water until neutral pH was achieved. Obtained magnetite was dried at 30 ± 5 °C for 24 h, and magnetic nanoparticles were imaged with a Transmission Electron Microscope (TEM), JEOL model JEM-1010 by implementing a digital camera model Gatan-ORIUS.

2.2. Detection

An experimental setup device was used to apply transversal magnetic fields to a magnetic nanoparticle suspension inside a 40 mL vial; the magnetic flux measured inside the device is 10 gauss. In this setup, a red laser beam (650 nm at 5 mW) is directed through the magnetic nanoparticle suspension; it is possible to rapidly switch the magnetic field applied to orient the magnetic field either in parallel or perpendicularly to the laser beam. An explanatory drawing of this setup is shown in Fig. 1. This experimental setup allows one to measure the optical transmission and scattering change of colloidal suspensions while aligning the magnetic particles oriented in parallel and perpendicularly to the laser beam. These tests are done at different frequencies to evaluate the alignment capacity of the studied nanoparticle suspensions since the rotation speed of the nanowires is related to their size and magnetic strength; therefore, important information from the nanowires properties could be obtained by performing the measurements at different frequencies.

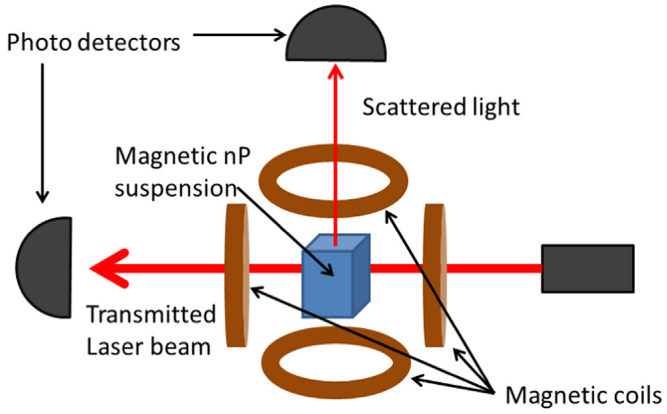

Fig. 1. Apparatus constructed to measure transmitted and scattered light of nanoparticles magnetically aligned in a colloidal suspension.

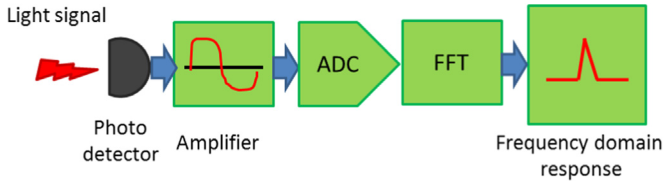

Fig. 2. Signal measurement procedure followed to amplify and digitally filter the signal obtained from samples of suspended magnetic nanoparticles.

Colloidal suspensions samples of 30 mL were prepared using different concentrations (20, 2, 0.2, 0.02 and 0.002 μg/mL) of nanoparticles content. No stabilizer is used.

In our experiments we used magnetite nanoparticles (mnp) and small (snw) and large (lnw) nanowires of nickel for the study of nanomaterial's characterization. Suspensions were subjected to alternated direction of the magnetic fields, while their optical transmissibility and scattered light was measured. Signals from photodetectors were first amplified, and then digitalized with a Digital Storage Oscilloscope (DSO) Velleman PCSGU250, and the digital signal was submitted to a Fast Fourier Transform (FFT) to obtain the frequency domain signal read by the photodetectors. This procedure makes easier to discard power line noise at 60 Hz and by other sources; it also facilitates the identification and measurement of the signal-to-noise ratio (SNR) from the target signal. Our method also improves the signal by nearly three orders of magnitude compared to the measurements performed directly to the signals amplitude [19]. The diagram in Fig. 2 describes the signal data handling procedure.

3. Results and discussion

3.1. Morphology of the nanomaterials

TEM was used to observe the morphology of all the prepared nanomaterials prior to the optical modulation experiments. Fig. 3a shows magnetite nanoparticles with spherical shape and an average diameter of 10–30 nm; Fig. 3b and c shows short and long Ni nanowires. The difference on the characteristic dimensions of the nanowires was achieved growing the alumina template at different temperatures [27]. Nanowires prepared at 15 °C are ca. 600–1000 nm long and have a diameter of ca. 15 nm (also named snw, Fig. 3b). Conversely, nanowires prepared at 6 °C have a broad size distribution with a maximum length of 3 μm and 50 nm diameter (also named lnw, Fig. 3c).

3.2. Detection of magnetic nanomaterials

Prepared materials were suspended in aqueous solutions at different concentrations to detect their resulting light modulation from scattering and transmittance as described on the experimental section. Starting concentration for the suspensions was set at 20 μg/mL; it is noteworthy that the scattered laser beam can be easily observed by the naked eye at concentrations above 2 μg/mL as shown in Fig. 4. The optical modulation from the scattering change on beam intensity can also be easily identified by direct observation; this happens when magnetic fields are applied while operating above the mentioned concentration.

Testing of magnetite nanoparticles allows evaluating the signal-to-noise ratio for light scattering and transmittance experiments and the results are shown in Fig. 5. Plots show the frequency behavior of nanoparticle suspension at different concentrations ranging from 20 μg/mL to 20 ng/mL. Signal intensity decreases as frequency increases in Fig. 5; this effect is caused by nanoparticles moving slower due to medium viscosity and inertial