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A comparative study of magnetic transferability of superparamagnetic nanoparticles

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ABSTRACT

The aspect of magnetic transferability was established using an automated magnetic particle transfer workstation. Maghemite (γ-Fe_2O_3) nanoparticles were synthesized via conventional co-precipitation procedure. Their transferability was determined in addition to several commercial nanoparticles that ranged in diameter, surface functionality, and composition. Transmission and scanning electron micrographs and infrared spectrum, respectively, provided size and surface information on the synthesized particles for comparison to commercially available magnetic nanoparticles.

1. Introduction

Magnetic nanoparticles have crossed the boarders of many disciplines currently thriving in biotechnology and biomedicine [1–3]. They have also spawned into the realms of magnetic fluids [4], catalysis [5], magnetic resonance imagining [6], and environmental remediation [7]. The assortment of commercially available magnetic nanoparticles attests to the wide range of applications that benefit from the ease of magnetic separation. The most common material used to provide magnetism is iron oxide in either magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) form. The popularity of these oxide crystals is found in their unique response to an external magnetic force and subsequent lack of residual magnetism once the force is removed, deeming them with paramagnetic behavior. If the particle magnetic moment reverses at times shorter than the experimental time scales, the system is in a superparamagnetic state [8]. In the wide spread development of magnetic nanotechnology, many effects must be taken into account to improve the architecture of the final product before its applications.

The difficulty with such particles is their significantly small size range that makes them inherently unstable for long periods of time. The high chemical activity causes vulnerability to oxidation, agglomeration, and inevitable loss in magnetism [8]. Protective strategies to overcome these hindrances can be easily achieved by the incorporation of either an organic material, such as a polymer [9], surfactant [10], or inorganic coating of silica [11]. The presence of protective material can also be regulated to introduce further functionality that provides desirable physical and chemical properties.

The surface modification of magnetic nanoparticles is typically approached by the core–shell method in the post-functionalization of synthesized particles. Alternatively, the embedded method, where many magnetic nanoparticles reside in a guest matrix, has also been achieved. Matrix-dispersed magnetic nanoparticles can be created in a variety of different states: (1) they can be dispersed in a continuous matrix, (2) they can be presently dispersed in a coating on other larger particles (e.g. layer-by-layer method), or (3) they can form agglomerates of individual nanoparticles which are connected through their protective shells [8]. As a consequence, there are a great number of published literatures related to the properties of well-characterized iron oxide nanoparticles and their coated counterparts [12–15].

In the broad range of magnetic nanoparticle compositions available, finite size effects and surface effects govern consequential magnetic properties. Finite size effects can be considered to be those that are originated by the discontinuity of some characteristic length due to the purely geometric constraint of finite volume. In contrast, surface effects arise from the lack of translational symmetry at the boundaries of the particle as a result of lower coordination number and the existence of broken magnetic exchange bonds which lead to surface spin disorder [16]. Amongst the extensive scope of approaches to evaluate different parameters of magnetic properties, the most commonly used techniques are vibrating sample magnetometry (VSM) and superconducting quantum interface device magnetometry (SQUID magnetometer) [17–20]. Despite the sophisticated methods available, different and unique means of characterizing magnetic

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properties would provide greater insight to the continual development of the synthetic mechanisms involved.

In this paper, we present a new aspect of magnetic characterization of nanoparticles: magnetic transferability. Magnetic transferability can be defined as the susceptibility of superparamagnetic nanoparticles toward magnetic-field-assisted separation. The magnetic transferability of synthesized and commercial magnetic materials was characterized by an automated magnetic particle transfer device, BioSprint 15. It was important to compare their transferability due to the wide accessibility of commercial sources and, therefore, resultant magnetic particles. Magnetic γ-Fe_2O_3 nanoparticles were prepared by conventional co-precipitation of ferrous and ferric salts in basic solution. In addition, the physical properties of the resulting material were investigated for comparison with a number of commercially obtained magnetic particles.

2. Experimental

2.1. Materials

Ferrous chloride ($FeCl_2 \cdot 4\,H_2O$) with 99% purity and anhydrous ferric chloride ($FeCl_3$) with 98% purity were obtained from Sigma-Aldrich (St. Louis, MO, USA) and Honeywell Riedel de Haen (Seelze, Germany), respectively. Sodium hydroxide (NaOH) pellets of 97% purity were provided by Caledon Laboratory Chemicals (Georgetown, ON, Canada). Hydrochloric acid (38%) was purchased from Allied Chemical (Mississauga, ON, Canada). Methanol (MeOH) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Distilled and deionized water (DDW) produced by a Millipore (Milli Q, Ottawa, Canada) system was used throughout the experiment. All chemicals and reagents were used as received.

Several commercial magnetic particle suspensions of varying sizes and compositions were obtained from Turbobeads (Turbobeads carboxyl coated and amine coated), Chemicell GmbH (fluidMAG-PAD, fluidMAG-UC/A, fluidMAG-UC/C), BioClone (BcMag amine terminated), G. Kisker (PMP-250, PMN-250, PMC-250), and Invitrogen (Dynabeads® MyOne™ carboxylic acid).

2.2. Methods

2.2.1. Synthesis of ferrimagnetic iron oxide nanoparticles

Magnetic material was synthesized by the traditional co-precipitation method of ferrous and ferric chloride in sodium hydroxide as previously reported [21]. Several fractions of supernatant from centrifugation were collected and centrifuged again. Particles collected from the supernatant were tested for magnetic properties by the introduction of a neodymium permanent magnet. Accumulated magnetic precipitates were dispersed in 600 mL of DDW and stored at 4 °C. Portions of isolated precipitates after cleaning were washed with MeOH and dried at room temperature over a period of 24 h for further characterization.

2.2.2. Characterization

The X-ray diffraction pattern was examined using a wide angle X-ray diffractometer with a Statton-type Warhus flat film camera to determine the crystal state of the synthesized magnetic material. Fourier transform infrared spectrum (ABB Bomem MB Series FT-IR) monitoring 4000–400 cm^{-1} in the form of a KBr pellet was obtained to provide further evidence of the most predominant functional groups present in the dried magnetic particles.

The diameter and shape of the synthesized magnetic particles in solution were established using transmission electron microscopy (TEM) and compared with scanning electron microscopy (SEM) images of both fluid and dried particles. A few drops of synthesized magnetic particle suspension were placed on a thin carbon paper and quickly dried. The material was observed with a state of the art JEOL JEM-2100 F field emission transmission electron microscope. A drop of magnetic particle suspension and roughly a milligram of dried particle sample were placed onto respective pieces of black carbon tape. After allowing the solvent to evaporate, both samples were coated in a gold–palladium alloy before analysis using Tescan Vega-II XMU VPSEM.

The magnetic transferability was investigated with the BioSprint 15 automated particle transfer workstation from Quiagen to compare the effects of size, surface functionality and presence of a polymer matrix in an effort to determine the optimal characteristics required of the magnetic material for successful automation of analysis involving magnetic separation.

2.2.3. Method for magnetic particle transfer characterization

The commercially obtained magnetic particle solutions were used directly to prepare standard stock solutions without any pretreatment. Stock solution of synthesized magnetic particles was prepared by weighing out (1 mg) and dispersed in 10 mL of DDW. Solutions of 0.1 mg/mL were prepared in DDW, where 1 mL of the sample solution was placed onto a sample well chamber in the BioSprint 15. The adjacent well contained 1 mL of DDW into which the magnetic particles would be re-dispersed after transfer. The automation of the Biosprint 15 workstation was conducted by an original protocol designed in the laboratory and conducted at room temperature. The amount of particles transferred and remaining were determined by UV/vis absorption (scanning from 800 to 200 nm at 600 nm min^{-1}) through comparison with a calibration curve prepared from known dispersed amounts of magnetic particle in solution. This procedure was then performed 4 more times for each magnetic particle solution.

3. Results and discussion

3.1. Comparison of magnetic particles' properties

The commercially obtained magnetic particle suspensions composed an array of diameters, surface functionality, polymer incorporation, and consequent superparamagnetic properties. An anthology of these properties were compiled to establish the scope of magnetic materials investigated in this study. Turbobeads, which was a more recent product development, was the only provider of magnetic material that was composed of carbon coated cobalt nanoparticles <50 nm in diameter. Compared to other suppliers who utilized the more common nanomagnet iron oxide, Turbobeads were initially created to be a new medium of separation in organic synthesis, achieving the amine and carboxylic acid functionality by the use of diazonium chemistry [22].

The core–shell arrangement of the Turbobeads was also frequented by Chemicell GmbH and BioClone samples. The variety of available terminal functional groups on individual samples of magnetic nanoparticles offered by Chemicell GmbH tributes to their applications in cell separation, MRI-diagnostics, and magnetic drug targeting. For the purpose of this study, however, respective fluidMAG samples from Chemicell GmbH were obtained with uncoated and coated particle surfaces. The bare surface was offered in both cationic (UC/C) and anionic (UC/A) forms manipulating the hydroxyl groups bound to the iron oxide