Magnetophoresis of iron oxide nanoparticles at low field gradient: The role of shape anisotropy

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A B S T R A C T

Magnetophoresis of iron oxide magnetic nanoparticle (IOMNP) under low magnetic field gradient (<100 T/m) is significantly enhanced by particle shape anisotropy. This unique feature of magnetophoresis is influenced by the particle concentration and applied magnetic field gradient. By comparing the nanosphere and nanorod magnetophoresis at different concentration, we revealed the ability for these two species of particles to achieve the same separation rate by adjusting the field gradient. Under cooperative magnetophoresis, the nanorods would first go through self- and magnetic field induced aggregation followed by the alignment of the particle clusters formed with magnetic field. Time scale associated to these two processes is investigated to understand the kinetic behavior of nanorod separation under low field gradient. Surface functionalization of nanoparticles can be employed as an effective strategy to vary the temporal evolution of these two aggregation processes which subsequently influence the magnetophoretic separation time and rate.

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1. Introduction

Iron oxide magnetic nanoparticles (IOMNPs) have been used extensively in processes ranging from biomedical [1–3] to environmental waste and pollutant removal [4–6]. There are several advantages exhibited by IOMNP which make them a unique nano-agent for aforementioned applications, such as high specific surface area [7], catalytically active [8], magnetically responsive [9], optically tunable [10], and can be easily synthesized by a large selection of chemical and physical methods [2,6]. Out from all these features of IOMNP, the ability of this particle to response to an externally applied magnetic field is crucial for its application in separation processes [11,12]. Here, IOMNPs are typically being employed to imparting a paramagnetic dipole moment to the targeted non-magnetic compounds. These IOMNPs tagged compounds become magnetically susceptible and can be separated out from solution through magnetophoretic collection.

Under the influence of a magnetic field, the IOMNPs would migrate toward the region where the field gradient is the highest [13]. This motion of particles relative to their surrounding fluid is

known as magnetophoresis. The ability to capture the IOMNPs from suspension media sets the foundation for various magnetic separation technologies and its core working principles under high gradient (∇B > 1000 T/m) [14] and low gradient (∇B < 100 T/m) [15] magnetic field have been actively studied. Traditionally, the removal of magnetic nanoparticles (plus all the magnetically tagged compounds) in solution is carried out through high gradient magnetic separation (HGMS). This HGMS technology has been successfully employed for various applications and is capable to capture particles with sizes from microns to tens of nanometers [16]. However, two major drawbacks of HGMS are (1) high initial investment cost to setup automated separator [17], and (2) inhomogeneous magnetic field associated to the operational of HGMS make it difficult to develop numerical and/or analytical solutions to aid the design of a separation process used for specific applications [18].

On the other hand, low gradient magnetic separation (LGMS) does not involve the use of loading matrix. A nice review article on this topic is recently published by Faraudo and coworkers with detail descriptions on fundamental physics involved [19]. In short, under LGMS the separation of magnetic nanoparticles is first driven by aggregation of particles by an externally applied magnetic field, and later the particle clusters formed can be easily collected through cooperative magnetophoresis [15,20,21]. Since LGMS of IOMNPs is relying on the formation of particle clusters, hence, this

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process is highly concentration dependent [20]. It is anticipated that the increment of particles concentration will lead to higher collision frequency between the particles, and eventually, higher change for the formation of particle clusters. Furthermore, the chaining of particles due to magnetic dipole–dipole and hydrodynamic interactions also play a significant role in LGMS as enhancement factors to accelerate the collection of IOMNPs [21]. Besides, our group has recently demonstrated the important of surface modification in dictating the magnetophoretic separation rate [22]. From our experimental results, the more colloidal stable the IOMNP is, the harder it is to be magnetophoretically collected. This observation can also be generalized to HGMS process [23].

In previous research on magnetic separation of IOMNPs, by using either HGMS or LGMS, almost all the efforts were dedicated to the understanding of magnetophoretic behavior of spherical particles. Even though rod-like magnetic nanoparticles have been used for various interesting applications [24,25], there are very limited works have been done on the magnetophoresis of nanorod that exhibit magneto-shape anisotropy [26]. Despite its interesting and added benefits in rapid magnetic separation [12], numbers of uncertainties and issues remain unexplored related to the use of magnetic nanorod for separation process. In addition, it is also equally unclear about the contributing factors that would influence the performance of magnetic nanorod in magnetophoretic separation. It is our interest in this paper to show the comparison of cooperative magnetophoresis for spherical and rod-like IOMNPs under low gradient magnetic separation. By monitoring the migration of iron oxide nanorod with respect to an externally applied magnetic field in two and three dimensional space, we investigate the underlying mechanisms and time scale involved within each stage of nanorod magnetophoresis. In addition, we also evaluate the effects of particle concentration and magnetic field gradient on the separation kinetics of nanorod. All these studies are important to establish design rule for LGMS by using rod-like particles as a magnetic tagging agent.

2. Experimental section

2.1. Materials

Iron oxide nanosphere, Fe_3O_4 (APS, 98 + % purity) (Fig. 1a), was purchased from Nanostructured & Amorphous Materials, Inc. Iron oxide nanorods (Fig. 1b) employed in this work were generously supply by TODA American, Inc. (refer to Fig. SI of supporting information for size distribution of these particles). The saturation magnetization M_s for these two species of IOMNPs was measured previously with value at ∼90 emu/g and 74.61 emu/g for nanorod and nanosphere, respectively [12]. Water soluble cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) with average molecular weight ∼100,000–200,000 Da (20 wt.% in H_2O) was supplied by Sigma–Aldrich. Sodium chloride, NaCl used in zeta potential measurement was purchased from Merck Sdn.Bhd. Cylindrical shaped N50-graded Neodymium Boron Ferrite (NdBFe) and Aluminium Nickel Cobalt (Alnico) permanent magnet with 14 mm in diameter and 15 mm in length were purchased from Ningbo YuXiang E&M Int'l Co., Ltd. The remanence B_r for these two magnets is 1.20 Tesla and 1.45 Tesla for Alnico and NdFeB, respectively. All the chemicals were used as received without further modification or purification.

2.2. Preparation of PDDA-coated IOMNPs

Suspension of IOMNPs at 1000 mg/L in deionized water was prepared by ultrasonication to disperse the black powder obtained commercially. At the same time, PDDA solution with concentration at ∼0.005 g/mL was prepared by addition of 1.25 mL of as accepted PDDA solution into 48.75 mL of deionized water. This mixture was immediately subjected to intermittent ultrasonication for at least 30 min to promote their dissolution and left overnight on an end-to-end rotator with mixing rate of 40 rpm. This concentration of PDDA is chosen to ensure the available PDDA molecules are at least 500 times more than the estimated amount needed to form monolayer on the particles surface [23]. Before mixing, the IOMNPs solution was subjected to intense sonication for 2 min. Drop wise addition of IOMNPs suspension into PDDA solution was carried under intense sonicafication within a sonicator bath. Successful attachment of PDDA onto IOMNPs was verified by monitoring the electrophoretic mobility changes before and after the PDDA adsorption with Malvern Instruments Nanosizer ZS. By using the same analytical equipment, the particles size distribution before and after the PDDA attachment was measured through dynamic light scattering method (see Fig. SI in supporting information).

2.3. Monitoring magnetophoresis of IOMNPs

A custom built optical sensing system was employed to obtain the kinetic profile of IOMNPs under magnetophoresis [22]. Depends on the extent of light transmitted through the IOMNP suspension, by using a light dependent resistor (LDR), we monitored the voltage changes associate to the changes in intensity of detected light from a light-emitting diode (LED). The wavelength of the LED employed is at around 620 nm and the suspension
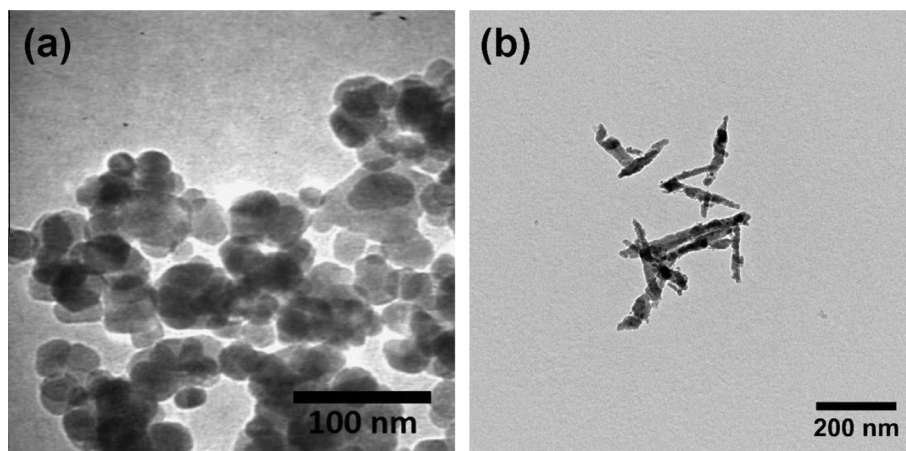

Fig. 1. Transmission electron micrographs of iron oxide (a) nanosphere and (b) nanorod used in this work.