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Magnesium ferrite nanocrystal clusters for magnetorheological fluid with enhanced sedimentation stability

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ABSTRACT

In this study, magnesium ferrite ($MgFe_2O_4$) nanocrystal clusters were synthesized using an ascorbic acid-assistant solvothermal method and evaluated as a candidate for magnetorheological (MR) fluid. The morphology, microstructure and magnetic properties of the $MgFe_2O_4$ nanocrystal clusters were investigated in detail by field emission scanning electron microscopy (FESEM), transmission electron microscope (TEM), thermogravimetric analyzer (TGA), X-ray diffraction (XRD) and superconducting quantum interference device (SQUID). The $MgFe_2O_4$ nanocrystal clusters were suspended in silicone oil to prepare MR fluid and the MR properties were tested using a Physica MCR301 rheometer fitted with a magnetorheological module. The prepared MR fluid showed typical Bingham plastic behavior, changing from a liquid-like to a solid-like structure under an external magnetic field. Compared with the conventional carbonyl iron particles, $MgFe_2O_4$ nanocrystal clusters-based MR fluid demonstrated enhanced sedimentation stability due to the reduced mismatch in density between the particles and the carrier medium. In summary, the as-prepared $MgFe_2O_4$ nanocrystal clusters are regarded as a promising candidate for MR fluid with enhanced sedimentation stability.

1. Introduction

Magnetorheological (MR) fluid is a suspension composed of solid magnetizable particles dispersed in a non-magnetizable carrier liquid [1–3]. The important and interesting feature of MR fluid is the fast and reversible transition from a liquid to solid-like structure with the application of magnetic field. Without a magnetic field, the magnetizable particles are randomly dispersed in a hydraulic- or oil-based medium, and the MR fluid behaves as like a Newtonian or quasi-Newtonian fluid. When a magnetic field is applied, the magnetizable particles create a chain-like structure along the applied magnetic field due to induced magnetic dipole-dipole interactions, which is quite similar to the behavior of electrorheological (ER) fluids [4–7]. Due to these merits of MR fluids, they have recently received a great deal of attention in broad potential applications including dynamic seals, cooling liquid, active bearing devices and directional transportation. In particular, a number of MR fluids have been commercialized, such as a brake used in the exercise industry, a damper in truck seat suspensions and a shock absorber for oval track automobile racing [8–11].

In general, soft-magnetic carbonyl iron (CI) particles are commonly used as the dispersing phase for MR fluids due to their high saturation magnetization, favorable magnetic permeability and suitable particle size. Although these materials have plenty of advantages, there are still some disadvantages limiting their broad applications. The main existing problem is that the density of CI particles (7.86 g/cm^3) is greatly higher than that of liquid phase, and consequently results in weak colloidal stability and long-standing sedimentation matter. In recent years, many research groups have focused on altering the sedimentation, for instance the methods of adding dispersion stabilizers or additives, adapting magnetic particles with polymers and introducing carbon materials [12–15]. Instead of the complicated process of modifying CI particles, spinel ferrites have been shown as good candidates for MR fluids, due to their much lower density (4.3–4.8 g/cm^3) and sufficient magnetic behavior [16–18]. In principle, the magnetic properties of the ferrites can be systematically varied by changing the identity of the

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divalent cation or by partial substitution while maintaining the basic crystal structure.

Among these spinel ferrites, magnesium ferrite ($MgFe_2O_4$) has received increasing interest in recent years, due to high magnetic susceptibility and moderate saturation magnetization [19–21]. Relatively little attention has been paid to synthesis and application of $MgFe_2O_4$ nanocrystal clusters, especially for MR fluids using $MgFe_2O_4$ nanocrystal clusters as dispersing phase, which are expected to acquire high dispersion stability. Herein, $MgFe_2O_4$ nanocrystal clusters with uniform size and well-defined shape were prepared through an ascorbic acid-assistant solvothermal method. And then, the magnetoresponsive behavior of the obtained MR fluid based on $MgFe_2O_4$ nanocrystal clusters under different magnetic fields was examined. The results showed that the prepared $MgFe_2O_4$-based MR fluid exhibited typical MR properties and excellent sedimentation stability.

2. Experimental

2.1. Materials

Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 98%), ascorbic acid (AA), sodium hydroxide (NaOH) and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade and used without further purification.

2.2. Preparation of $MgFe_2O_4$ nanocrystal clusters

The $MgFe_2O_4$ nanocrystal clusters were synthesized with a surfactant-assistant solvothermal method. In brief, 1.35 g $FeCl_3 \cdot 6H_2O$ and 0.51 g $MgCl_2 \cdot 6H_2O$ were dissolved in 50 mL EG until a homogeneous solution was formed. Then 1.00 g AA and 3.20 g NaOH were added slowly into the above solution under strongly agitation. The mixture was stirred for 45 min and then transferred into a Teflon-lined stainless-steel autoclave, which was sealed tightly and maintained at 200 °C for 12 h. The black products were separated with a magnet and washed several times with absolute ethanol and deionized water. The resulting magnetic materials were then dried in vacuum for 24 h.

2.3. Characterization

The morphology and particle size was observed by field emission scanning electron microscopy (FESEM) (S-4800, Hitachi) and transmission electron microscope (TEM) (G2 F20, Tecnai). Thermal stability was performed by NETZSCH209 thermogravimetric analyzer (TGA) (Netzsch, Germany) 25 °C–700 °C under nitrogen flow, and weight retention/temperature curve was recorded. The crystalline structure was examined by X-ray diffraction (XRD) (Dmax-Ultima+, Rigaku) with Ni-filtered Cu/K-α radiation. The magnetic properties were investigated in a superconducting quantum interference device (SQUID) (MPMS-XL-7, Quantum Design) at room temperature.

2.4. Magnetorheological measurements

Carbonyl iron (CI) particles were purchased from Jiangyou Hebao Nanomaterial Co., Ltd. and used to prepare CI particles-based magnetorheological (MR) fluid. Silicon oil with dynamic viscosity of 0.5 Pa s was used as the carrier liquid. CI particles and $MgFe_2O_4$ nanocrystal clusters were mixed with silicone oil to prepare two different MR fluids, respectively, and the particle mass fraction was 25%. The additional silicone oil was dried at 80 °C for 24 h to remove the moisture. The density of CI particles and $MgFe_2O_4$ nanocrystal clusters was determined by a pycnometer method, and the values were measured to be 7.86 g/cm^3 and 4.57 g/cm^3, respectively.

The MR fluids were stirred mechanically and then placed in an ultrasonic bath for 60 s prior to measurement. The curves of shear viscosity-shear rate, shear stress-shear rate and shear stress-time at different applied magnetic fields were recorded using a Physica MCR301 rheometer fitted with a magneto-rheological module. The module could produce different magnetic fields by changing direct current. The diameter and gap of the parallel-plate system were 20 mm and 1 mm, respectively. All the MR measurements were carried out at room temperature. The sedimentation experiments were performed at room temperature by using cuvettes. The sedimentation stability of MR fluids was evaluated by sedimentation ratio, defined by the height percentage of the particle-rich phase relative to the total suspension height.

3. Results and discussions

Uniform $MgFe_2O_4$ clusters were synthesized by a surfactant-assistant hydrothermal method, in which ascorbic acid (AA) was used to control the nucleation and clustering-base growth of the colloidal spheres. The morphology and size of the $MgFe_2O_4$ clusters were examined by both FESEM and TEM. It is observed from Fig. 1a that spherical nanocrystal clusters of $MgFe_2O_4$ are formed. The synthesized $MgFe_2O_4$ nanocrystal clusters have sizes ranging from 284 nm to 487 nm with an average diameter of about 376 nm, as shown in TEM images of Fig. 1b–c. The enlarged TEM image (Fig. 1d) reveals that these sub-micrometer sized clusters are formed by the aggregation and assembly of a number of small nanocrystals with grain sizes of 5–8 nm. In addition, thermal stability of the $MgFe_2O_4$ nanocrystal clusters was performed by a thermogravimetric analyzer, as shown in Fig. S1. From the TGA curve, the initial weight loss from $MgFe_2O_4$ clusters up to 145 °C is probably due to the removal of surface hydroxyls and/or surface adsorbed water, while the slower and steady mass loss is observed over the whole temperature range, which can be attributed mainly to the decomposition of the ascorbic acid.

The XRD pattern of as-prepared $MgFe_2O_4$ nanocrystal clusters is shown in Fig. 2. It is found that the XRD pattern consists of well-resolved diffraction peaks, which confirms the polycrystalline and monophasic nature of the prepared $MgFe_2O_4$. The peak positions and relative intensities match well with the standard XRD data for cubic spinel structure of magnesium ferrite (JCPDS card No. 73-2410) [22]. The main peaks are located at $2\theta = 18.5°$, 30.2°, 35.6°, 37.3°, 43.4°, 53.6°, 57.2° and 62.8° corresponding to (200), (220), (311), (222), (400), (422), (511) and (440) crystal reflections of $MgFe_2O_4$, respectively. The broadening of the diffraction peaks suggests that the products are composed of many undersized grains. The average crystallite size of primary nanocrystals in the $MgFe_2O_4$ clusters is about 6.3 nm, which is calculated by Scherrer equation using the strongest (311) peak of XRD pattern.

The magnetic properties of the $MgFe_2O_4$ nanocrystal clusters were investigated by SQUID from −25000 Oe to 25000 Oe at room temperature (Fig. 3). The field-dependent magnetization curve shows that the remanence (M_r) and the coercivity (H_c) are negligible. It indicates that the $MgFe_2O_4$ nanocrystal clusters are considered as a superparamagnetic material for MR applications. In addition, the saturation magnetization (M_s) of $MgFe_2O_4$ nanocrystal clusters is found to be 54.3 emu/g, which is higher than the reported value of bulk $MgFe_2O_4$ (33.4 emu/g) [23,24]. Even though the M_s value of $MgFe_2O_4$ nanocrystal clusters in this study is much lower than that of CI particles (193 emu/g) [14,25], the value of M_s for the $MgFe_2O_4$ nanocrystal clusters is similar or even higher compared with other MR materials such as poly (glycidyl methacrylate)-coated CI micropheres [26], spherical Fe_3O_4 particles