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Synthesis of calcium ferrite nanocrystal clusters for magnetorheological fluid with enhanced sedimentation stability

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ABSTRACT

In this study, we prepared calcium ferrite ($CaFe_2O_4$) nanocrystal clusters by a solvothermal method and evaluated their application potential in magnetorheological (MR) fluid. The morphology, composition, microstructure and magnetic properties of the $CaFe_2O_4$ nanocrystal clusters were investigated in detail. The as-prepared $CaFe_2O_4$-based MR fluid showed typical Bingham fluid behavior, changing from a liquid-like to a solid-like structure under an external magnetic field. Compared with carbonyl iron (CI) particles, the MR fluid based on $CaFe_2O_4$ nanocrystal clusters showed enhanced sedimentation stability, which can be mainly due to the reduced density mismatch between dispersed phase and carrier fluid. In conclusion, the as-prepared $CaFe_2O_4$ nanocrystal clusters are considered as a promising candidate for high-performance MR fluid.

1. Introduction

A magnetorheological (MR) fluid is a suspension of magnetic particles suspended in a carrier liquid [1–3]. Under an external magnetic field, MR fluids can change quickly and reversibly from a liquid-like to a solid-like structure, which is quite similar to the behavior of electrorheological (ER) fluids [4–6]. Compared with ER fluids, MR fluids possess many favorable advantages, such as high yield stress, energy density and power supply [7]. These merits are important for a broad range of applications in dynamic seals, shock absorbers and active bearing devices [1]. In particular, a variety of MR fluids have been commercialized for practical applications, such as a brake in the exercise industry, a damper in truck seat suspensions and a shock absorber for oval track automobile racing [8–11].

Among the vast magnetic particles available, the carbonyl iron (CI) particles are most popular MR materials. However, the major problem is that the high density CI particles usually cause weak sedimentation stability [12]. In the past decades, many efforts have been exerted to deal with the present sedimentation problems, for instance the methods of adding stabilizers, adopting polymeric coatings and introducing graphene-like materials [13–16]. Instead of the complex steps of treating CI particles, spinel ferrites have been considered to be promising candidates for MR fluids due to their unique magnetic behavior and lower density [17–19]. In particular, the magnetic properties of the spinel ferrites can be conveniently adjusted while maintaining the basic crystal structure. Among the diverse types of spinel ferrites, calcium ferrite ($CaFe_2O_4$) has attracted more and more attention in photoelectrodes, sorbents and drug delivery due to their high magnetic susceptibility and moderate saturation magnetization [20–22]. However, the $CaFe_2O_4$ nanocrystal clusters consisting of multiple single-domain magnetic nanocystals are seldom reported. To the best of our knowledge, this is the first report that the $CaFe_2O_4$ nanocrystal clusters were exploited as dispersed phase to prepare MR fluids.

In this study, uniform $CaFe_2O_4$ nanocrystal clusters were synthesized through a solvothermal method using polyethylene glycol (PEG) as a surfactant. The prepared $CaFe_2O_4$ nanocrystal clusters were used as the dispersed particles to prepare MR fluid, and its MR properties were systematically examined under different magnetic field strengths. In addition, the sedimentation experiments were carried out to investigate the anti-sedimentation properties of the prepared MR fluid.

2. Experimental

2.1. Materials

Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$, 98%), sodium hydroxide (NaOH), ethylene glycol (EG) and polyethylene glycol (PEG-1000) were purchased from Sinopharm Chemical Reagent Co., Ltd. Carbonyl iron (CI) particles were purchased from Jiangyou Hebao Nanomaterial Co., Ltd. All the other chemicals were analytical grade and used without further purification.

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2.2. Preparation of $CaFe_2O_4$ nanocrystal clusters

The $CaFe_2O_4$ nanocrystal clusters were synthesized by a modified solvothermal method [23]. $FeCl_3 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ were dissolved in 40 mL EG until a uniform solution was formed. And then PEG-1000 (1.0 g) and NaOH (3.2 g) were slowly added into the above solution under stirring. The mixture was stirred for another 60 min to obtain a homogeneous solution. It was transferred subsequently into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed tightly and maintained at 180 °C for 12 h. Afterward, the black precipitates were collected with magnetic separation and washed with distilled water for three times. The resulting magnetic materials were dried at 60 °C under vacuum for 24 h.

2.3. Characterization

The morphology and composition were investigated with a field emission scanning electron microscopy (FESEM) (S-4800, Hitachi) combined with energy dispersive X-Ray spectroscopy (EDX) microanalysis. The shape and size were confirmed by a transmission electron microscopy (TEM) (G2 F20, Tecnai). The surface analysis was carried out by a X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Scientific) equipped with a hemispherical analyzer. The crystalline phase was identified with a powder X-ray diffractometer (XRD) (Dmax-Ultima$^+$, Rigaku) with Cu/K-α source (1.5418 Å). The magnetic properties were studied in a superconducting quantum interference device (SQUID) (MPMS-XL-7, Quantum Design) at room temperature.

2.4. Magnetorheological measurements

Silicone oil with dynamic viscosity of 0.5 Pa·s was used as the carrier liquid. Two different MR fluids were prepared by dispersing the CI particles and the $CaFe_2O_4$ nanocrystal clusters in silicone oil by sonication for 60 min, respectively. The particle weight fraction of each MR fluid was 25%. The densities of CI particles and $CaFe_2O_4$ nanocrystal clusters were tested by a pycnometer method, and the values were measured to be 7.86 g/cm^3 and 4.67 g/cm^3, respectively.

The MR properties were examined at room temperature using a rotational rheometer (MCR 301, Physica) equipped with a magnetorheological module, which can generate homogeneous magnetic fields by changing direct current. The MR fluid was placed in an ultrasonic bath for 60 s before each measurement. The diameter and the gap distance of the parallel-plate system were 20 mm and 1 mm, respectively. The sedimentation experiments of MR fluids were carried out at room temperature using cuvettes. The sedimentation ratio, defined by the height percentage of the particle-rich phase relative to the total suspension height, was used to evaluate the sedimentation stability of MR fluids.

3. Results and discussions

The surface morphology of the $CaFe_2O_4$ clusters was observed by FESEM and TEM (Fig. 1). Fig. 1a shows the representative FESEM image of the prepared $CaFe_2O_4$ in the presence of PEG, in which uniform spherical clusters are clearly observed. Fig. S1 shows the EDX results, confirming the presence of Ca, Fe and O elements in the sample. It also reveals the stoichoimetric formation of the calcium ferrite during the solvothermal reaction. For comparison, an additional experiment was carried out in the absence of PEG while keeping other parameters constant, as shown in Fig. S2. It is found from FESEM images that the particles have inhomogeneous size distribution and there are a number of particles with small size for the prepared $CaFe_2O_4$ clusters. TEM was further employed to observe the $CaFe_2O_4$ clusters in the presence of PEG. The synthesized $CaFe_2O_4$ particles have sizes ranging from 265 nm to 298 nm with an average diameter of 278 nm, as shown in the TEM images (Fig. 1b and Fig. 1c). The enlarged TEM image (Fig. 1d) reveals that these sub-micrometer sized clusters are composed of a number of small nanocrystals with sizes of 5–8 nm. The morphology observation reveals that uniform $CaFe_2O_4$ clusters were successfully synthesized by a solvothermal method, in which PEG was used as a surfactant to control the nucleation and clustering-base growth of the colloidal spheres.

XPS is generally regarded to be an important and key technique for the surface characterization and analysis of materials. Therefore, the XPS spectra of iron (Fe) and calcium (Ca) were recorded to examine the elemental state in the sample, as shown in Fig. 2. The carbon C 1 s peak at 284.8 eV is used as a reference for charge correction. In Fig. 2a, two binding energy peaks are observed at 710.4 eV and 723.8 eV without no obvious shakeup satellites, which are corresponded to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of Fe^{3+}, respectively [14]. As for the Ca 2p spectrum (Fig. 2b), two binding energy peaks at 349.9 eV and 346.4 eV are assigned to Ca $2p_{3/2}$ and Ca $2p_{1/2}$ of Ca^{2+}, respectively [24]. The XPS results confirm that the $CaFe_2O_4$ clusters have been formed during the solvothermal reaction.

The XRD pattern of as-prepared $CaFe_2O_4$ nanocrystal clusters is shown in Fig. 3. As can be seen, all the diffraction peaks of XRD pattern are in good agreement with the standard data for cubic spinel structure of calcium ferrite (JCPDS No. 78–4321) [25]. The diffraction peaks at $2\theta = 18.4°, 30.3°, 35.7°, 37.4°, 43.3°, 53.7°, 57.2°$ and 62.9° are corresponded to (200), (220), (311), (222), (400), (422), (511) and (440) crystal planes of $CaFe_2O_4$, respectively. No other diffraction peaks are observed, indicating the high purity of $CaFe_2O_4$ nanocrystals obtained by the solvothermal reaction. The broadening of the diffraction peaks suggests that the products are composed of many small sized grains. The average crystallite size of primary nanocrystals in the $CaFe_2O_4$ clusters is estimated using the Williamson-Hall equation. The equation is described as follows:

$$B\cos\theta = \frac{0.9\lambda}{D} + 2\varepsilon\sin\theta \quad (1)$$

where, B = diffraction peak width at half maximum intensity, θ = Bragg diffraction angle, λ = wavelength of the used radiation, D = average crystallite size and ε = average lattice strain. The average crystallite size was estimated from the y-intercept of the line and the value was determined to be 7.8 nm.

The hysteresis loops of as-prepared $CaFe_2O_4$ nanocrystal clusters were measured by SQUID with a maximum magnetic field of 25,000 Oe (Fig. 4). The magnetization curve shows negligible remanent magnetization (M_r) and coercive force (H_c), which is considered as a superparamagnetic material for MR applications. It can be obtained from Fig. 4 that the saturation magnetization (M_s) of $CaFe_2O_4$ nanocrystal clusters value is about 65.7 emu/g, which is lower than the reported value of bulk Fe_3O_4 [26]. The decline of M_s may be attributed to the difference in particle size, crystalline nature and particle arrangement [27,28]. Even though the M_s value of $CaFe_2O_4$ nanocrystal clusters in this study is much lower than that of CI particles (193 emu/g) [2], the value of M_s for the obtained $CaFe_2O_4$ nanocrystal clusters is similar or even higher compared with other reported MR materials, such as polystyrene-coated Fe_2O_3 particles [29] and Fe_3O_4/zinc hydroxysulfate hybrid sheets [30]. Therefore, the magnetic properties indicate that the $CaFe_2O_4$ nanocrystal clusters can be a promising candidate for MR fluids.

The MR properties of $CaFe_2O_4$ nanocrystal clusters-based MR fluid were investigated under different magnetic field strengths. Fig. 5 shows the curves of viscosity as a function of shear rate. The MR fluid exhibits Newtonian behavior without magnetic field, while typical shear thinning behavior is observed under different magnetic fields. When an external magnetic field is applied, it is clear that the viscosity of MR fluid increases with increasing magnetic field intensities. Once the magnetic field intensity is fixed, the viscosity of the MR fluid decreases dramatically with increasing shear rate at low shear rate