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Development of manganese ferrite/graphene oxide nanocomposites for magnetorheological fluid with enhanced sedimentation stability

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ABSTRACT

Novel nanocomposites consisting of manganese ferrite nanoparticles and graphene oxide nanosheets ($MnFe_2O_4$/GO) have been synthesized as a promising candidate for magnetorheological (MR) fluid. The morphology, microstructure, composition and magnetic properties of the obtained $MnFe_2O_4$/GO were studied in detail. It was found that the $MnFe_2O_4$ nanoparticles with diameter of 8–12 nm were densely decorated on the surface of GO nanosheets. The magnetization investigation revealed that as-prepared $MnFe_2O_4$/GO had superparamagnetic behavior with saturation magnetization of 36.2 emu/g. The MR fluid was prepared by the obtained $MnFe_2O_4$/GO and the corresponding MR properties were investigated using a Physica MCR301 rheometer fitted with a magneto-rheological module. The $MnFe_2O_4$/GO-based MR fluid exhibited typical MR effect with increasing shear stress, yield stress and dynamic shear modulus depending on magnetic fields. More importantly, the sedimentation stability of the prepared MR fluid was found to be improved due to the unique sheet-like structure and the reduced density mismatch between the dispersed particles and the carrier medium. The $MnFe_2O_4$/GO-based fluid with typical MR effect and excellent sedimentation stability would provide a feasible candidate for practical applications.

Introduction

Magnetorheological (MR) fluids are composed of magnetically polarizable particles dispersed in nonmagnetic liquid medium, have attracted much attention in recent years due to their low driving magnetic fields, controllable mechanical properties and broad operating temperatures [1]. The MR fluids are smart materials with the ability to change from a fluid-like to a solid-like structure under an external magnetic field [2–6]. In the absence of a magnetic field, the magnetizable particles are randomly dispersed in carrier liquid and the suspensions exhibit a Newtonian-like fluid behavior. After the external magnetic field is applied, the particles are formed chain-like structures in the direction of magnetic field.

Recently, MR fluids as smart materials have been utilized in a broad potential applications including electronic controls, haptic devices, optical fishing and mechanical systems [7–9]. Besides the established commercial devices of MR fluids, their increasing importance derives from potential utilizations in biomedicine for artificial muscles, high intelligence prosthesis and local embolization of blood vessels [10,11]. Although MR fluids have made great progress towards commercialization, there are still several disadvantages limiting their broad utility in engineering applications. The long-term stability of MR fluids is threatened by the sedimentation problem along with re-dispersibility, which is considered as one of the most important factors influencing feasibility and effectivity of MR fluids in real-life applications [12,13]. Many research groups have focused on dealing with these crucial restriction factors, and a critical strategy has been proved to be effective that the bigger micro-sized particles were replaced by smaller magnetic nanoparticles as dispersed phase, because nanoparticles are able to suspend more stably in the carrier liquid [14].

Manganese ferrite ($MnFe_2O_4$) nanoparticles have captured considerable attention in recent years due to unique properties and have been explored in a wide range of applications, such as biomedicine, catalysis, adsorbent, water treatment and lithium ion batteries [15–19]. Due to high surface area and strong dipole–dipole interactions, the bare $MnFe_2O_4$ nanoparticles appear to suffer from irreversible and severe aggregation, which seriously affects the magnetorheological properties and sedimentation stability of MR fluids. Although extensive efforts have been paid to avoid or reduce aggregation and settling, such as the application of surfactants, additives, inorganic/organic coating and employing

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viscoelastic carrier, it is still a major problem to improve long-term sedimentation stability in carrier media [2,12,20–23]. Graphene oxide (GO), a two-dimensional honeycomb material has received a great deal of attention in various fields [24–27]. Due to their unique properties including low density, special planar structure and large specific surface area, the emerging GO nanosheets are considered as a promising candidate to handle the present problems of dispersion and sedimentation for MR fluids. In our previous study, cobalt ferrite ($CoFe_2O_4$) nanoparticles were deposited on the surface of GO nanosheets to synthesize $CoFe_2O_4$/GO nanocomposites, and the obtained composite particles as dispersed phase to prepare MR fluid [20]. However, the $CoFe_2O_4$/GO-based MR fluid did not show enhanced sedimentation stability compared with the carbonyl iron (CI) particles. Considering the unique properties of $MnFe_2O_4$ including high magnetic susceptibility, high initial permeability, high resistivity and low losses compared to the other ferrites, such as Fe_3O_4, $CoFe_2O_4$ and $NiFe_2O_4$ [28–30], the $MnFe_2O_4$/GO nanocomposites are expected to acquire excellent sedimentation stability.

Herein, we reported a controllable and facile sonochemical method to synthesize $MnFe_2O_4$/GO nanocomposites, where the $MnFe_2O_4$ nanoparticles were homogeneously anchored on the surface of GO nanosheets. The obtained $MnFe_2O_4$/GO nanocomposites were chosen as dispersed particles to prepare MR fluid, and the magnetorheological properties of as-prepared MR fluid were investigated by a Physica MCR301 rheometer. In addition, the sedimentation experiments of the MR fluid were performed and compared with that of commercial carbonyl iron particles.

Experimental

Materials

Natural flake graphite with average particle size of 40 mesh (NFG, 99%) was obtained from Qingdao Tianhe Graphite Co., Ltd. Potassium permanganate ($KMnO_4$, AR), sulfuric acid (H_2SO_4, AR), sodium nitrate ($NaNO_3$, AR), hydrogen peroxide (H_2O_2, 30% aq.), sodium hydroxide (NaOH, AR), polyvinylpyrrolidone (PVP K30, $M_n = 30{,}000$), iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%) and manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used directly without further purification.

Preparation of $MnFe_2O_4$/GO nanocomposites

$MnFe_2O_4$/GO nanocomposites were synthesized by a sonochemical method with the assistance of ultrasonic vibration. In brief, graphene oxide (GO, 100 mg) (self-made), according to our previous report [20], was added to deionized water (150 mL) with sonication to obtain a uniform solution. Then, PVP (0.67 g), $FeCl_3 \cdot 6H_2O$ (1.61 g) and $MnCl_2 \cdot 4H_2O$ (0.59 g) were added to the above suspension under mechanical stirring, followed by the dropwise addition of NaOH solution (3.5 M, 20 mL). The mixed dispersion was transferred to an ultrasonic bath and allowed to sonicate for 1 h. The power and frequency of the ultrasonic bath were 100 W and 20 kHz, respectively. During the reaction, pH value was adjusted to 11 and the temperature was maintained at 60 °C. The resulting products were magnetically separated, washed with deionized water and absolute ethanol for three times and dried at 40 °C under vacuum for 24 h.

Characterization

The morphology of GO, $MnFe_2O_4$ and $MnFe_2O_4$/GO was observed by a G2 F20 transmission electron microscope (TEM). The particle size distribution of $MnFe_2O_4$/GO was also measured by using a Malvern Zetasizer Nano particle size analyzer. The powder X-ray diffraction (XRD) analysis of GO, $MnFe_2O_4$ and $MnFe_2O_4$/GO was conducted on a D8 Advance X-ray diffractometer equipped with Ni-filtered Cu/K-α source ($\lambda = 0.15{,}418$ nm). The Fourier transform infrared spectroscopy (FTIR) spectra of GO, $MnFe_2O_4$ and $MnFe_2O_4$/GO were performed using a Magna 750 spectrometer at room temperature. The X-ray photoelectron spectroscopy (XPS) spectra of $MnFe_2O_4$/GO were performed on an Escalab 250Xi imaging electron spectrometer. The Raman spectra of GO, $MnFe_2O_4$ and $MnFe_2O_4$/GO were recorded on a LabRAM HR800 laser confocal micro-Raman spectroscopy with 532 nm laser excitation. The magnetic properties of $MnFe_2O_4$ and $MnFe_2O_4$/GO were investigated in a MPMS-XL-7 superconducting quantum interference device (SQUID) magnetometer from −20,000 Oe to 20,000 Oe at room temperature.

Magnetorheological measurements

Commercial carbonyl iron (CI) particles with particle size of 3–5 μm were supplied by Jiangyou Hebao Nanomaterial Co., Ltd. Two different MR fluids were prepared by dispersing the CI particles and the $MnFe_2O_4$/GO nanocomposites in silicone oil, respectively. The particle mass fraction of two MR fluids was set to be 25%. The densities of CI and $MnFe_2O_4$/GO were determined by using a pycnometer method, and the values were measured to be $7.81\,g\,cm^{-3}$ and $4.58\,g\,cm^{-3}$, respectively. The curves of shear stress-shear rate and shear stress-time at different magnetic fields, and dynamic shear moduli under different strain amplitudes and angular frequencies were recorded by a Physica MCR301 rheometer (Fig. 1) at room temperature. The sedimentation stability of the two MR fluids was performed by using cuvettes and evaluated by sedimentation ratio, which was expressed as the height percentage of the particle-rich phase relative to the total fluid height.

Results and discussion

It has been recognized that ultrasonic irradiation in liquid and liquid–solid systems are able to induce unique physical and chemical effects. The ultrasonic irradiations propagate through a liquid medium, the powers not only drive the mass to transfer, but also initiate an interesting phenomenon known as cavitation. In other words, the nucleation, growth and collapse of bubbles occur as a result of transition of acoustic waves in the liquid [31]. The technical advantages of this sonochemical method in the synthesis of metal oxide nanostructures, such as faster reaction time, higher specific surface area and more uniform size distribution, have been well recognized by many scientists [32,33]. The preparation process of the $MnFe_2O_4$/GO nanocomposites is schematically

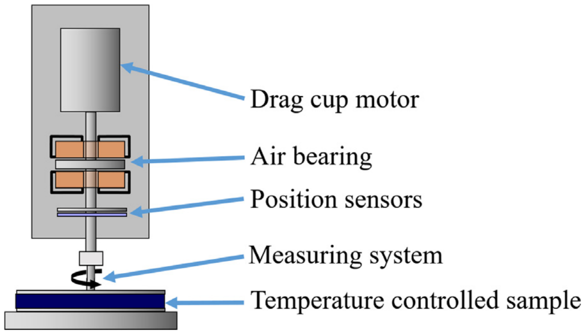

Fig. 1. Schematic image of Physica MCR301 rheometer.

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