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Magnetoresponsive conductive colloidal suspensions with magnetized carbon nanotubes

Ahmed M. Abdalla^a, Abdel Rahman Abdel Fattah^b, Suvojit Ghosh^a, Ishwar K. Puri^{a,b,*}^a Department of Engineering Physics, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7^b Department of Mechanical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7

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ABSTRACT

We synthesize a novel and hitherto unreported class of colloidal suspensions for which the dispersed phase, which consists of multiwall carbon nanotubes (MWNTs) decorated with magnetic nanoparticles (MNPs), is both magnetoresponsive and electrically conductive. Synthesis of the dispersed phase merges processes for producing ferrofluids and magnetic MWNTs (mMWNTs). We explore means to tune the properties of these magnetic conductive colloids (MCCs) by varying the (1) MNP material composition, and (2) MNP:MWNT (w/w) magnetization weight ratio (γ). The mMWNTs are examined using XRD, TEM, EDX and SQUID and MCCs are by measuring their zeta potential and electric conductivity. Magnetite (Fe_3O_4) MNPs, which possess a high Curie temperature, produce mMWNTs with high saturation magnetization that respond relatively weakly to temperature variations. $\text{Mn}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ and $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ MNPs with lower Curie temperatures are more sensitive to changing temperature. Increasing the MNP Cu content improves the electric conductivity of the corresponding MCC while increasing γ enhances its magnetic response. After γ is raised above a threshold value, mMWNT decoration on the CNT surface becomes nonuniform since the MNPs now agglomerate perpendicular to the nanotube surface. These colloidal suspensions are a promising new class of material that can be manipulated with a magnetic field to tune their electrical conductivity.

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1. Introduction

Nanofluids are colloidal suspensions that contain nanoparticles dispersed in a liquid [1]. Due to their superior electric conductivity, carbon nanotubes (CNTs) have been introduced as the dispersed phase in a nanofluid. When dispersed in an aqueous medium, as little as 0.5% (w/w) of CNTs can increase its electric conductivity by an order of magnitude [2]. However, CNTs tend to flocculate rapidly in an aqueous medium, yielding clusters of randomly oriented nanotubes that settle under gravity [3]. Since flocculation is typically caused by inter-CNT attractions due to surface charges [4,5], temporary dispersions can be achieved by enhancing inter-CNT distances, e.g., through ultrasonication [6,7]. However, to achieve long term stability, chemical peptization methods are required, such as providing CNTs with a surface coating to counterbalance the surface interactions [8]. Peptization is hard to achieve for CNTs due to their high molecular weight, hydrophobicity and inertness of their outer surfaces [9].

Ferrofluids are nanofluids that respond to a magnetic field [10–13] since the dispersed phase consists of magnetic nanoparticles (MNPs) [14–16]. Several methods have been developed to peptize MNPs in aqueous media to enable their colloidal stability for extended periods [17–19]. Typically, MNPs are coated with a surfactant that produces interparticle repulsion [5,20]. These MNPs can chaperone other nonmagnetic materials, such as MWNTs, to orient and organize them [21,22], and print spatial heterogeneities in materials [23,24]. However, the MNPs in most ferrofluids are ferrites that possess poor intrinsic electrical conductivity. A ferrofluid containing an electrically conductive dispersed phase has promising applications. Since its MNPs can be manipulated by a magnetic field, the local electrical conductivity of a conductive ferrofluid can be tuned. Magnetic manipulation also allows the printing of an electronic circuit with a conductive ink.

Conductive nanofluid inks are typically dispersions of gold, silver, and copper nanoparticles, but these are expensive, require nanoparticle sintering and have only fair dispersion and oxidation resistance [25]. While use of graphene and CNTs has been reported, their agglomeration and dispersion are problematic [1,26,27]. Our solution is to decorate multiwall carbon nanotubes (MWNTs, the electrically conductive dispersed phase) with magnetically responsive MNPs.

* Corresponding author at: Department of Engineering Physics, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7.

E-mail address: ikpuri@mcmaster.ca (I.K. Puri).

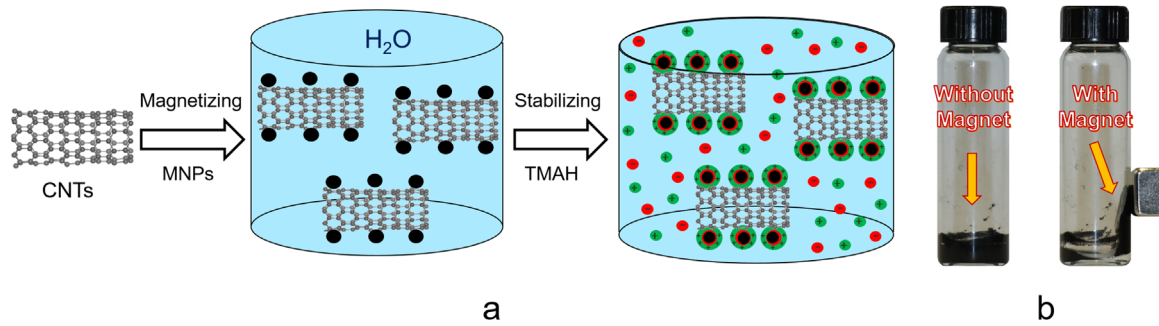


Fig. 1. Synthesis of magneto-responsive conductive colloids (MCCs). (a) MWNTs are first dispersed in water and then covalently functionalized with MNPs that are coprecipitated in situ. The resulting mMWNTs are peptized using tetramethylammonium hydroxide (TMAH) as a surfactant, yielding magneto-responsive conductive colloids (MCCs). (b) Upon visual inspection, an aqueous dispersion of MCCs rests in the absence of a magnet (left) whereas it is attracted towards a magnet when it is present (right). In either situation, the dispersion remains stable, i.e., coagulation is not observed.

We probe ways to influence the electrical and magnetic properties of the MWNTs by altering the material content of the MNPs as well as the MNP:MWNT magnetization weight ratios γ . The synthesized mMWNTs are dispersed in an aqueous medium to prepare novel magneto-responsive conductive colloidal suspensions (MCCs). An ionic dispersant (tetramethylammonium hydroxide, or TMAH), commonly used to peptize ferrite MNPs, is used to ensure colloidal stability. These MCCs are a hitherto unreported type of colloidal suspension that responds to an external magnetic field, is electrically conductive and can be stably dispersed.

2. Materials and methods

2.1. Materials and reagents

Multiwall carbon nanotubes (MWNTs) produced by CVD with purity > 95%, outside diameter of 20–30 nm, inside diameter of 5–10 nm and length between 0.5 and 2.0 μm , were purchased from US Research Nanomaterials. Other reagents used were ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%, Alfa Aesar), ferrous chloride hexahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 98%, Alfa Aesar), copper II chloride (CuCl_2 , 98%, Alfa Aesar), tetramethyl ammonium hydroxide ($\text{C}_4\text{H}_{13}\text{NO} \cdot 5\text{H}_2\text{O}$, 98%, Alfa Aesar), manganese II chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 99%, Sigma Aldrich), zinc chloride (ZnCl_2 , 99%, Sigma Aldrich), sodium hydroxide (NaOH, 97%, Caledon Laboratory Chemicals), nitric acid (HNO_3 , 68–70%, Caledon), and ammonium hydroxide (NH_4OH , 28–30%, Caledon). All reagents were used as received without further purification.

2.2. Synthesis of magnetic MWNTs (mMWNTs)

MWNTs were initially activated with 200 ml of concentrated nitric acid for each g of MWNTs used [28]. This acid treatment was performed in a sonication bath (VWR International, Model: 97043–936) for 4 h. Then, samples were washed with deionized (DI) water, decanted, filtered, and finally dried in a vacuum oven at 70 $^\circ\text{C}$ for 1 h.

Activated MWNTs (aMWNTs) were functionalized with coprecipitated magnetite nanoparticles based on stoichiometric calculations for a Fe_3O_4 :MWNT (w/w) magnetization weight ratio (γ) of unity. 1 g of MWNTs was dispersed in a solution of $\text{Fe}^{+2}/\text{Fe}^{+3}$ ions (2.3 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.9 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 400 ml DI water) [28]. To prevent the formation of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) due to oxidation by dissolved oxygen [29,30] in the DI water, prior to dissolving the salts or dispersing the aMWNTs, the water was carefully degassed by boiling and sonication. The mixture was sonicated for 10 min with a probe sonicator (Qsonica, Model:Q500 with $\frac{1}{4}$ " micro-tip at 35% power) and

a subsequent 50 min in a sonication bath at 50 $^\circ\text{C}$ (VWR International, Model: 97,043–936). Ammonium hydroxide solution was slowly introduced as a precipitant during the latter sonication process until the pH reached 9–10. After co-precipitation, the samples were settled by magnetic sedimentation, washed with DI water, filtered and dried in a vacuum oven at 70 $^\circ\text{C}$ for 1 h.

2.3. Influence of MNPs concentration and chemical composition

Employing the process described in Section 2.2, stoichiometric calculations for different samples (S1, S1.2, S1.3, S1.4, and S1.5) were conducted to obtain $\gamma=1, 1.25, 1.5, 1.75$ and 2. The effect of changing magnetization weight ratio γ on the uniformity and density of decoration was observed through transmission electron microscopy (TEM) images.

For the magnetization weight ratio γ of unity, the magnetite nanoparticles in S1 with a relatively high Curie temperature [31] were replaced with $\text{Mn}_{0.2}\text{Cu}_{0.20.6}\text{Fe}_2\text{O}_4$ to produce sample S2 and with $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ to make S3, since both of the latter MNPs have lower Curie temperatures [32,33]. For S2 and S3, we used Mn^{+2} , Cu^{+2} , and Zn^{+2} chloride salts for co-precipitation and NaOH as the precipitant [34,35], and the MWNTs and salt solution were dropped into the precipitant instead of vice versa [34]. SQUID magnetometry provided changes in the magnetic properties of the mMWNTs, X-Ray diffraction (XRD) revealed the material phases and MNP crystal sizes. TEM and energy-dispersive X-Ray spectroscopy (EDX) were used to visualize the mMWNTs, the uniformity and density of their decoration with MNPs, and to identify their elemental composition.

2.4. Synthesis of magneto-responsive conductive colloids (MCCs)

Three different MCCs (MCC1, MCC2 and MCC3) were synthesized using the mMWNT samples S1, S2, and S3. These preparations followed principles used to synthesize ordinary ionic ferrofluids [36]. As illustrated in Fig. 1, since the MNPs are attached to the outer surface of the MWNTs through covalent bonds, they magnetize the MWNTs and, with assistance of an ionic surfactant and vigorous sonication, carry, suspend, and stabilize the MWNTs in DI water. The mMWNTs therefore have the ability to move along with the whole fluid in response to an applied magnetic field. The ionic surfactant facilitates whole fluid electric conductivity since the electrical discontinuity due to separate suspended mMWNTs is now overcome.

Although the mMWNT suspensions were not filtered or dried, the co-precipitation by-products were removed from the three samples by decanting and washing them. The pH was concurrently stabilized between 9 and 10 using precipitant drops during washing. The resulting dilute suspensions settled over 24 h under

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