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Research paper

# Anomalous room temperature magnetorheological behavior of colloidal graphene nanogels

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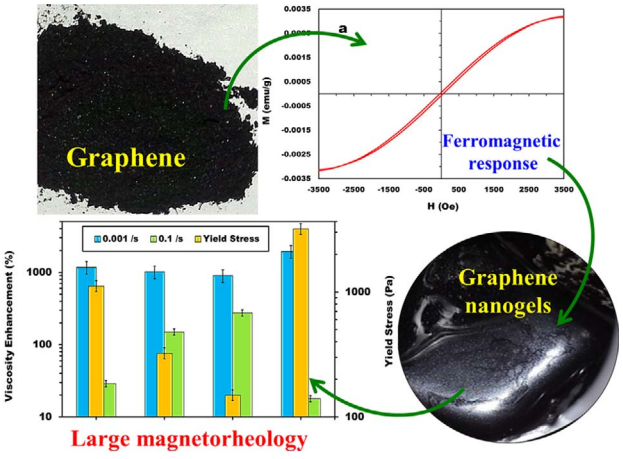
## GRAPHICAL ABSTRACT

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## ABSTRACT

Weak magnetism is known to exist in graphene systems, yet, as of now, it remains unharnessed for bulk scale applications. Weak ferromagnetic response from chemically exfoliated graphene samples has been employed to harness appreciable magnetorheological effects via the use of novel graphene nanogels. Chemically exfoliated graphene samples have been synthesized and ferromagnetic response has been registered (in tune with scarce reports in literature). Characterizations reveal that presence of magnetic impurities would be unable to yield magnetic moments as obtained and hence the response is innate to the vacancy and defects in the graphenic structure. Polymer based nanogels with infused graphene nanoplatelets has been synthesized and the colloidal gel phase enables harnessing of magnetorheology from such weak moment systems. Strong magnetorheological response is obtained from the colloidal gel phase due to the compact texture which aids in fibrillation of the nanoplatelets. Largely enhanced magnetoviscosity and yield stress have been observed from the gels in similitude to conventional magnetorheological nanocolloids. The presence of dispersed phase with platelet morphology as well as surface lubrication behavior of graphene has been found responsible for certain anomalous behavior such as magnetic shear thickening in the gels which has been explained based on order to disorder transitions under field influence. Transient response of the gels show good modulation caliber in field actuated viscous control as well as minute magnetoviscous hysteresis. The present colloids show novel promise in use of

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graphene as potential magnetic material in magnetic field governed actuation, control and tuning MEMS/NEMS and allied devices.

## 1. Introduction

The emergence of graphene as the next generation wonder–material, owing to its unique transport properties [1,2] has opened up several avenues of promise. Among the more prominent ones are utilities such as nanoelectronics [3], smart materials [4,5], thermal management fluids [6], targeted drug delivery and biomaterials [7,8] and so on. The nanomaterial has led to multifaceted research and development, both on the fundamental as well as application fronts. One such area of fundamental study is the occurrence of magnetism in graphene systems. While electronic transport in graphene has been unraveled to a large extent, moderate to large magnetic response from organic systems, especially graphene is an area with limited understanding as of today. Studies have been reported where graphene's magnetic response has been predicted employing theoretical calculations. Several studies have conclusively shown through DFT (density functional theory) simulations that net magnetic spin is possible in graphene members and defect induced vacancy in the graphene nanostructures is responsible for such magnetism [9–11]. Likewise, ab-initio quantum computations have revealed that existence of certain electron rich or starved covalent functional groups on the graphene sheets can also lead to magnetic moment due to electron sharing and exchange [12,13]. This leads to the possibility of ferromagnetic or antiferromagnetic response from graphene oxide as well [14].

Studies have also inferred that magnetism in graphene systems is also a function of the states of edges in the graphene flakes. Quantum DSMC (direct simulation Monte Carlo) studies [15] reveal that short ranged static edge magnetism can stably exist in graphene nanoribbons. The study also reported that increase in width of the ribbon structures leads to the magnetic behavior tending towards ferromagnetic. However, stability studies [16] have shown that under several conditions, the different edge states can either amplify the intrinsic magnetism in graphene or even reduce it to such extent that the intrinsic magnetism might not be strong enough at room temperature. Also, studies have shown that magnetism in graphene family can be explained based on several other molecular mechanisms behind magnetism, such as orbital state magnetism [17], magnetism due to concentrated or localized pseudospin [18] within the flakes, etc. In spite of several theoretical inferences regarding possible existence of magnetism in graphene structures, only few studies have reported the same from experimental data [19,20] and it has been further concluded that not all samples of graphene, even if from the same parent sample, may exhibit magnetic moment. This essentially illustrates that the source of magnetism in graphene is highly based on defect induced vacancies and spin concentration, which due to its non–uniform distribution leads to differences in values of magnetic moment.

However, despite the fact that magnetism in graphene has been a topic of widespread interest, potential applications of the same at the bulk scale is yet to be reported. One of the most important and novel applications of magnetism in nanomaterials for bulk scale usage is magnetic fluids such as ferrofluids, magnetocolloids [21], etc. Since graphene nanostructures are mesoscale in distribution (ranging from 10 nm–1000 nm in flake sizes, in case of wet synthesized systems), the magnetism can be harnessed for magnetorheology from formulated colloids. Magnetic response in graphene is known to be weak in nature and hence it is not feasible to obtain proper magnetorheological response from graphene based magnetic fluids due to the predominantly liquid nature of the colloid. It has been reported by present authors that carefully synthesized gel phase colloids [22] can lead to very complex conglomeration of the nanostructures with respect to the fluid phase and hence even weak transport properties can be harnessed as smart effects. The present article reports such a novel polymer gel employing graphene samples (those where appreciable magnetic moment is observed after synthesis) and discusses the magnetorheological characteristics of such gels. Both static and dynamic rheological characteristics of the gels have been discussed and interesting features such as enhanced magnetic field induced viscosity and yield stress have been observed. Furthermore, novel effects such as magnetic shear thickening have been observed in some cases of the gels under specific field and shear conditions. The present gels and their magnetorheological behavior is an important example of usage of carbon based magnetism for bulk scale smart effects. The gels could find potential implications in micro-nanoscale actuation, vibration isolation, sensing and damping using magnetic stimuli.

## 2. Materials and methodologies

The graphene (G) nanoflakes employed in the present study have been synthesized via chemical route from natural graphite (Gr) powder. The methodology involves a twin-step protocol [23] along the lines of the modified Hummers' method followed by reduction of the formed G-oxide [24,25]. The final reduced G-oxide or G nanoflakes obtained are rendered hydrophilic by employing sulphonation [26] and this ensures stability of the aqueous colloids. The synthesized samples have been characterized by Raman spectroscopy and High Resolution Scanning Electron Microscopy to ensure that G has been obtained. The size distribution of G flakes has been characterized using Dynamic Light Scattering (DLS) technique. The Raman spectra, SEM image and DLS spectra for representative synthesized samples have been illustrated in Fig. 1. Analysis of the Raman spectrum (Fig. 1(b)) reveals the presence of sharp, high intensity peaks at $\sim 1350\ cm^{-1}$ and $\sim 1560\ cm^{-1}$, which are the characteristic D and G bands of graphene systems [27]. The G band is a manifestation of the planar stretching of the $sp^2$ hybridized carbon atoms in the graphene flakes whereas the D band arises due to the surface defects and wrinkles inherent to the exfoliation process. Also, the broadly distributed peaks at $\sim 2800\ cm^{-1}$ (the 2D band) are also characteristic of such systems and conclusively indicate the presence of G. The ratio of the intensities of 2D and G bands has been utilized to estimate the number of layers in the synthesized G samples. In the present samples, this ratio has been observed to be in the vicinity of 0.3–0.6, which implies that the population of G flakes are on average 2–5 sheets thick [28].

The G sample has also been characterized though HRSEM imaging which provides conclusive evidence in favor of the formation of G structures based on the surface imperfections observed. The imperfections and wrinkles appear due to stretching of the $sp^2$ hybrid carbon atoms, leading to nanoscale faults and crests, as indicated by arrows in Fig. 1(a). The strong oxidizers used in the chemical synthesis exfoliate the Gr to form G and due to non–uniform localized gradients and reaction kinetics, the exfoliation is seldom uniform spatially and leads to presence of voluminous amounts of surface wrinkles and sheet defects, features in general absent on Gr flakes. The surface wrinkling in the SEM images in fact confirms the presence of exfoliated G structures. The flake size distributions for two representative G populations have been obtained using DLS analysis and have been illustrated in Fig. 1(c). It reveals that major fraction of the flakes of one sample lie around the peak size of 100 nm, with minor populations around 25 nm and 30 nm. In the other sample the major population is distributed around 300 nm, with minor populations around 70 nm, 800 nm and 3000 nm. Therefore, the total population of G flake sizes lies within the meso–nanoscale regime. A visual representation of the nanogels has been presented in Fig. 1(d).