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Effect of solvents on the structure and magnetic properties of pyrolysis derived carbon globules embedded with iron/iron carbide nanoparticles and their applications in magnetorheological fluids

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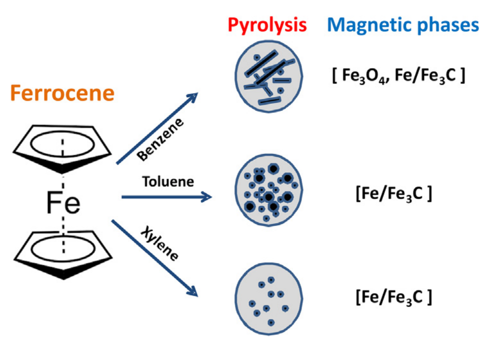
HIGHLIGHTS

- Benzene, toluene and xylene were used as carbon sources for synthesis of carbon globules via pyrolysis.
- The core–shell magnetic particles are distributed inside the matrix of the carbon globules.
- Benzene leads to rod shaped magnetic particles while xylene and toluene produces spherical magnetic particles.
- Magnetization of samples synthesized using toluene was higher than those by benzene and xylene.
- Carbon coated magnetic particles render chemical and dispersion stability to magnetorheological fluids.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon globules embedded with magnetic iron/iron carbide nanoparticles were synthesized by pyrolysis route using different organic solvents (benzene/toluene/xylene) along with ferrocene as iron catalyst precursor. All other synthesis parameters were kept constant (e.g. reaction temperature ≈ 950 °C, heating rate of 3 °C/min). We observed a variation of magnetic phase composition with the type of solvent (carbon source) used for synthesis, although the morphology of all the samples was similar. Improved sample crystallinity, distribution of particles and saturation magnetization were obtained, when toluene was used as solvent. Interestingly, rod shaped magnetic particles were observed in case of benzene, whereas for toluene and xylene, all iron-based magnetic particles were spherical. Due to higher saturation magnetization, we have used the particles prepared using toluene as a solvent to demonstrate the magnetorheological behaviour of these carbon-coated magnetic nanoparticles. We observed good magneto-response for the samples suggesting that these particles are potential candidate for magnetorheological applications.

1. Introduction

Chemical vapour deposition (CVD), arc discharge, laser ablation and pyrolysis etc. are important synthesis routes for the preparation of exotic carbon-based nanostructures [1,2]. Benzene, toluene and xylene are among the most commonly used organic solvents in

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the growth of carbon based materials by CVD method. Ferrocene is a common source of catalyst particles for the controlled growth of carbon nanostructures [3]. It is well known that ferrocene has very high solubility in benzene [4]. A well dissolved precursor solution can be expected to lead to a more uniform end product with fairly good size-control via CVD. Hence, use of an appropriate solvent is preferred over solid precursor mixtures. However, as benzene is carcinogenic, alternative solvents like toluene and xylene were therefore used, although ferrocene has slightly less solubility in these solvents. Apart from the uniformity of the products, use of various solvents with varying carbon content in its molecular structure can effectively change the overall carbon content in the end products, and thus, can modify the properties of the products.

Among the synthesis methods, pyrolysis holds advantage over most of these techniques in utilizing a variety of precursors in various forms (solid/liquid/vapour). In this method, biomass and waste materials like hair, exoskeleton or fibrous plant tissue (e.g., groundnut shells, coconut coir, vegetable peels) etc. have also been demonstrated as economical sources to obtain carbonaceous nanoparticles [5,6]. However, a systematic study on the effect of the carbon content of the solvent molecules on the structure and properties of the end products synthesized via pyrolysis is lacking in the literature. In this work we compared the morphology and properties of carbon nanostructures synthesized via one-step pyrolysis technique using three different carbon sources, viz. benzene, toluene and xylene.

Furthermore, the morphology and properties of the carbon nanomaterials can be tuned by varying the synthesis parameters, viz. concentration of precursors, reaction time, reaction temperature, pressure etc. In line with this, synthesis parameters governing the structure and morphology of the carbon-nanostructures grown by one-step pyrolysis technique were reported earlier [7,8]. As stated earlier, the synthesis parameters can be varied to control the morphology of the carbon nanostructures. For example, during pyrolysis a high heating rate ($\sim$20 °C/min) favours formation of carbon-nanotubes, whereas a low heating rate ($\sim$3 °C/min) favours the formation of globules [9]. At higher reaction temperatures, higher graphitization and formation of lower amount of Fe_3C phase in the carbon nanostructures were observed. Low concentration ($\leq \sim$5 mg of ferrocene per ml) or high concentration ($\geq \sim$50 mg of ferrocene per mL) of benzene leads to formations of amorphous carbon globules, whereas a medium concentration (i.e., $\sim$10 mg of ferrocene per ml of benzene) helps in forming carbon nanotubes [10]. According to earlier observations, a low ferrocene concentration facilitates formation of smoother spherical globules than that using high concentration [11].

Furthermore, carbon coated magnetic (Fe-containing) nanoparticles can also be synthesized by the single-step, pyrolysis technique [9–11] which is cost-effective. Such magnetic nanoparticles are the thrust materials for development of magnetorheological fluids (MRFs). The MRFs are smart fluids whose viscosity can be tuned via an external magnetic field. The ability of MRFs to mitigate mechanical shock and dampen mechanical vibrations render them suitable for such applications [12–14]. The most relevant magnetorheological parameter of an MRF is the yield strength developed in the MRF under an applied field. Conventionally, high yield strength is expected from MRFs containing metallic magnetic particles with high saturation magnetization, e.g. carbonyl iron [15–19]. However, MRFs containing these magnetic particles suffer from many disadvantages in terms of poor sedimentation stability and extremely difficult redispersibility of the sedimented particles in carrier fluid as well as the chemical instability in ambience/work environment. Although there are methods to circumvent the sedimentation instability and redispersibility through the use of additives in MRFs [20–23] or coating a non-magnetic layer on the particles [24–27], the magnetic properties of particles are deteriorated and the response of the MRF becomes slow. Moreover, cumbersome synthesis [17,18,28–30] and stringent conditions for preservation of such magnetic particles add to the cost of such MRFs.

To overcome the above limitations, alternate light-weight magnetic nanoparticles with high saturation magnetization are useful for this purpose. High dispersion stability of the particles in various fluid media (oil/water/organic fluids) requires a thin and light-weight non-magnetic coating on the highly magnetic particles. In this regard, carbon encapsulation on the magnetic nanoparticles can provide an easy and efficient means to increase dispersibility, additionally protecting them against oxidation and from harsh chemical environments [31]. Recently, carbon nanotubes [32,33], graphene oxide [34] and polymers [18,24,35] have been used as non-magnetic coating on the magnetic nanoparticles, to improve their rheological properties. Different strategies like solvothermal, ultrasonication and polymerization, have been employed to coat the magnetic nanoparticles with carbon moieties.

As pyrolysis can be handy in addressing the above problems via synthesis of carbon coated magnetic particles, we have synthesized carbon globules embedded with magnetic particles [9–11]. Heating rate [9], temperature [10] and precursor concentration [11] were identified as the major contributors in determining the distribution of magnetic nanoparticles in amorphous carbon matrix. In the present work, we investigate the effect of organic solvents viz. benzene, toluene and xylene on the structure, phase composition and magnetic properties of the carbon coated Fe/Fe_3C nanostructures, using ferrocene as the organometallic precursor. Based on the magnetic properties, silicone oil based magnetorheological fluid was prepared using the carbon-coated magnetic globules. The steady state shear response demonstrated this MRF as a potentially useful candidate for magnetorheology application. This current work is a step towards optimization of the one-step pyrolysis synthesis procedure to obtain highly magnetic carbon coated magnetic particles.

2. Experimental details

To demonstrate the effect of solvents on the morphology, magnetic properties and phase composition of carbon nanostructures we have used pyrolysis method in a closed chemical vapour deposition (CVD) system. The details of the synthesis procedure is discussed earlier [9,10]. In a typical synthesis, 250 mg of ferrocene (Spectrochem Chemicals) and 1 ml of organic solvent (benzene/toluene/xylene) were taken in a quartz tube of 50 cm length and 1 cm diameter. The ferrocene amount was intentionally kept higher than our earlier reports [10,11] to obtain more magnetic particles. The tube was closed at one end and was attached to a rubber bladder at the open end. The tube along with the precursors at the closed end was carefully inserted in a tube furnace having a constant temperature central hot zone of 10 cm length. The furnace was heated to 950 °C at a rate of 3 °C min^{-1}, with the closed end of the tube kept at 40 cm within the furnace as shown in Fig. 1. The reaction was carried out for 12 h. Once the furnace was cooled down to room temperature, the products were selectively scraped out from the A-zone (20–30 cm from the closed end as indicated in Fig. 1) and studied in detail. This zone contains more magnetic particles and the product has higher saturation magnetization as demonstrated in our earlier work [11]. The samples synthesized using benzene; toluene and xylene were labelled as B1, T1 and X1, respectively. These samples were characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Mössbauer Spectroscopy and Vibrating Sample Magnetometry (VSM). The T1 sample was selected for magnetorheology studies, due to its highest saturation magnetization (M_s) (as discussed later).