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Highly stable- silica encapsulating magnetite nanoparticles (Fe_3O_4/SiO_2) synthesized using single surfactantless- polyol process

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Abstract

We developed a new one-pot synthesis method for silica coated magnetite nanoparticles by way of a cheap- modified polyol process. In this reaction, polyethylene glycol was used as a solvent media and it has been found to play a key role to act as a reducing agent, stabilizer as well as a linker for silica coating, simultaneously. The Fe_3O_4/SiO_2 sample prepared by this new method was compared with other seed Fe_3O_4 and Fe_3O_4/SiO_2 samples synthesized through the modified Stober method and characterized using different analysis techniques such as transmission electron microscopy, X-ray diffraction, energy dispersive spectroscopy, thermogravimetric analysis and Fourier transform infrared spectroscopy. The magnetic properties of the seed Fe_3O_4 and silica coated magnetite nanoparticles were studied by vibrating sample magnetometer at room temperature. The produced composite sample showed excellent stability against oxidation when annealed at 600 °C in presence of hydrogen gas. Thus, the facile new polyol process adopted in our study appears to be a promising route for synthesis of highly stable, hydrophilic silica coated magnetite nanoparticles.

Keywords: C. Magnetic properties; Fe_3O_4/SiO_2; Core/shell; Polyol method; Stober method

1. Introduction

In recent years, the magnetic nanoparticles (NPs) have raised much interest in many kinds of technological applications such as data storage, spintronics [1,2], and biomedical applications like targeted drug delivery, hyperthermia and magnetic resonance imaging enhancement [3]. Magnetic nanoparticles are also very useful for environmental protection applications, such as the treatment of wastewater by removing either organic compounds like methylene blue or inorganic heavy metals like (Cd^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}) [4,5]. In particular, Fe_3O_4 or magnetite nanoparticle is considered as the most promising kind of magnetic oxide material due to its excellent magnetic properties. Especially in biomedical applications, for which the materials require high standard of stability and nontoxicity in addition to hydrophilic properties, the magnetite nanoparticles tend to produce some of the good stability and less toxicity properties compared with their metal magnetic counterparts like iron and cobalt. Further, a non-magnetic surface coating to the Fe_3O_4 nanoparticles is reported to help in offering an inert shell layer with increased biocompatibility thus enabling the core magnetite nanoparticles not only to survive in vivo but also to work well in specific targeting [6].

Among different kinds of coating materials like metal oxide, noble metals and polymer material, silica is considered very promising as an oxide coating material. The use of silica as a coating layer to the magnetite nanoparticles not only helps in enhancing the advantages of their high biocomptability,

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hydrophilicity, dielectric property and stability against degradation but also facilitates easy surface modification due to the availability of abundant silanol groups (–SiOH) on the surface. This includes strong surface functionalization with amine, thiol and carboxyl groups, and consequently the resultant functionalized nanoparticles become a good choice for biolabelling, drug delivery and targeting applications [7,8]. Furthermore, silica-coated magnetic nanoparticles also showed useful catalytic activity, especially in the conversion of syngas ($CO–H_2$ mixtures) into a wide range of long chain hydrocarbons and oxygenates via the Fischer–Tropsch [9].

Recently, the microemulsion and the alkaline hydrolysis of tetraethyl orthosilicate (known as the Stober method) approaches have been emerged as the major methods for core-shell nanoparticles [10,11]. Following these famous approaches, several groups have made attempts with little modifications to coat silica on magnetic nanoparticles with considerable success [6,8,12]. However, though these methods are capable of producing nanoparticles surfaces with complete silica coating, they need long reaction times (of about 20 h or more) and require multi-step procedures, where the first step is for preparation of magnetic nanoparticles and the second step is for coating, for the synthesis of such core-shell nanoparticles, and thus these procedures involve high costs in their execution. Furthermore, some of these methods may require to undergo phase transitions from hydrophobic to hydrophilic or vice versa to be suitable for surface coating with silica.

Thus the objective of our work was to develop a new method for the synthesis of silica coated magnetite nanoparticles along with the preparation of the same materials by an existing approach, and comparison of the results obtained by both these methods as well as with the results of magnetite nanoparticles without silica. For this purpose, the first approach employed was a modified process of the well-known Stober method using a two step procedure, firstly by synthesizing 10 nm magnetite (Fe_3O_4) nanoparticles as seeds based on our previous method [13], and the second step in this approach was that of coating with silica directly by hydrolysis and condensation of tetraethyl orthosilicate (TEOS). And, the second approach employed was a new one-pot polyol process in which the synthesis step of magnetite nanoparticles and the coating process with silica was done in single polyol reaction, where the polyethylene glycol plays a key role as high-boiling solvent, reducing agent, stabilizer, and linker for silica coating, simultaneously. The crystalline structure and shapes of the produced silica coated magnetite nanoparticles (Fe_3O_4/SiO_2) by the two different routes along with the seed Fe_3O_4 nanoparticles were examined by different analyzing techniques, and the magnetic properties were measured by the vibrating sample magnetometer (VSM) at room temperature.

2. Experimental

2.1. Materials

Iron chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), polyethylene glycol (PEG), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH) and ethyl alcohol were purchased from Sigma-Aldrich and used in synthetic reaction without any further treatment.

2.2. Synthesis of Fe_3O_4/SiO_2 nanoparticles by the modified Stober method

Firstly, we synthesized hydrophilic magnetite nanoparticles (of about 10 nm in size) exactly in the same manner as described in our previous work [13]. These synthesized seed nanoparticles are separated into two batches; one batch (herein after referred to as S1) was kept as it is for comparison studies with the subsequently synthesized core-shell nanoparticles by two different methods. And the second batch of seed nanoparticles were used for silica coating on them by the modified Stober method. This coating was performed by the hydrolysis of TEOS in the presence of magnetite NPs [6]. Typically 90 mg of the synthesized magnetite NPs were dispersed in 32 mL of distilled water by using an Ultrasound water bath for 20 min. Then, the dispersed solution was mixed with 160 mL of ethyl alcohol while slowly adding 4 mL of ammonia solution. After that, 1.6 mL of tetraethyl orthosilicate (TEOS) was added dropwise with violent stirring at room temperature. The solution stirring was continued for 20 h. Then, the product precipitates were separated by an external permanent magnet and washed several times using ethanol and water. It was subsequently dried in a vacuum oven to obtain ultrafine Fe_3O_4/SiO_2 NPs (herein after referred to as S2).

2.3. Synthesis of Fe_3O_4/SiO_2 nanoparticles in a new one-pot polyol process

We dissolved 12 mM of $FeCl_2 \cdot 4H_2O$ in 80 ml of PEG using magnetic stirrer in a 250 ml three–neck round bottomed flask equipped with condenser, magnetic stirrer, thermometer and heating system. The pH of the solutions was adjusted in between 10 and 11 by adding NaOH. The temperature of the solution was now increased to 200 °C for 30 min. 2 mL of tetraethyl orthosilicate (TEOS) was injected at this stage to the solution and then the PEG-metal salts solution was gradually heated up to 300 °C while stirring continuously using a magnetic stirrer, and refluxed at this temperature for 2 h. On completion of the above period of soaking, the heating system was switched off and the solution was allowed to cool naturally down to room temperature. Then the precipitate was collected using a magnet and washed several times using ethanol and water. It was subsequently dried in a vacuum oven to obtain ultrafine Fe_3O_4/SiO_2 NPs (herein after referred to as S3). The stability of the sample was investigated by annealing at 600 °C in presence of hydrogen gas for 2 h

2.4. Characterization

The crystal structures of the synthesized nanoparticles were analyzed by X-ray powder diffraction technique (XRD, Rigaku D/max-2500 at a voltage of 40 kV, a current of 300 mA and a scanning rate of 2 deg/min with step size 0.01°). The size and morphology of the nanoparticles were characterized using