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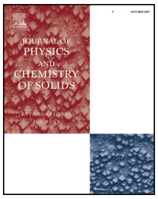

Effect of reaction time on structural and magnetic properties of green-synthesized magnetic nanoparticles

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ABSTRACT

Fe_3O_4 magnetic nanoparticles (MNPs) were prepared using the modified green synthesis method and the effects of reaction time on the structural and magnetic properties of MNPs were evaluated. For the synthesis of MNPs, green tea extract and ethylene glycol were used as a reducing agent and solvent, respectively. The MNPs were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), thermogravimetric analysis and vibrating sample magnetometer. It was observed that the reaction time strongly influenced the magnetic and structural properties. With increasing reaction time, the crystallite size was found to be increased from 7.5 to 12 nm along with improvement in saturation magnetization (M_S). The magnetic measurement study revealed that MNPs were superparamagnetic at room temperature, while at 60 K they have ferromagnetic as well as superparamagnetic contributions. The effect of an increase in particle size with reaction time was also reflected with an increase in blocking temperature, which is consistent with the Stoner–Wohlfarth theory.

1. Introduction

Magnetic nanoparticles (MNPs) offer interesting physicochemical properties such as superparamagnetism, large surface area, high surface-to-volume ratio and low toxicity based on their size and shape [1]. Owing to these properties, MNPs have widespread applications in the field of magnetic resonance imaging (MRI) [2], magnetic separation [3], catalysis [4], environmental remediation [5], targeted drug delivery [6], etc. A number of physical synthesis methods of MNPs such as gas-phase deposition, mechanical techniques and chemical synthesis methods which include sol-gel, coprecipitation, hydrothermal, solvothermal and thermal decomposition have been developed [7]. These physical and chemical methods have several disadvantages as they require high reaction temperature, high pressure and use of toxic chemicals, which create biocompatibility issues if MNPs have to be used for bioapplications. Hence, the development of simplistic, cost-effective and reliable green chemistry methods for the synthesis of MNPs is gaining importance. Considering these facts, several green synthesis methods such as leaf extracts, peels extracts and seed extract mediated reduction routes with the combination of solution hydrogen reduction were developed to reduce the environmental hazards [8]. These green synthesis methods are a good alternative to other methods as they are environment-friendly and have high yield, good reproducibility and good scalability at low cost [9]. There are several reports on the green synthesis of iron oxide nanoparticles (NPs) using plant extracts of *Camellia sinensis*, *Azadirachta indica*, *Tridax procumbens*, green tea, *Punica granatum*, ridge gourd peels and *Aloe vera*, etc. [10]. Green tea extract is one of the most important reducing agents used for the production of diverse metal and metal oxide NPs. Green tea is highly rich in nutrients and contains important antioxidants known as polyphenols. It contains catechin polyphenols, specifically (−)epigallocatechin-3-gallate (EGCG) [11]. These polyphenolic compounds from green tea extracts are mainly water-soluble, biodegradable and nontoxic. Polyphenols form metal chelating complexes with dissociated metal ions from the precursor and reduce them into zero-valent metallic states. In addition, different alcoholic functional groups present in tea extract also

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participate in the reduction as well as stabilization of NPs [12]. Different green tea and higher plants extracts have been used to obtain iron and iron oxide NPs. Ahmmad et al. described the preparation of mesoporous and crystalline α-Fe_2O_3 iron oxide NPs using a combination of green synthesis and hydrothermal methods [13]. Kumar et al. prepared Fe_3O_4 MNPs using Andean blackberry leaf extract and used them as an efficient photocatalyst for the degradation of dyes [14]. Phumying et al. synthesized Fe_3O_4 NPs with particle sizes of ~6–30 nm by hydrothermal method using ferric acetylacetonate and *Aloe vera* plant extract solution [15]. Makarov et al. prepared iron/iron oxide NPs using aqueous tea extracts of *Hordeum vulgare* and *Rumex acetosa*, which contain several organic acids such as oxalic and citric acids, which are responsible for stabilization and reduction of iron/iron oxide NPs [16]. Prasad et al. prepared spherical magnetite MNPs using ridge gourd peels (RG) extract as reducing and capping agents, with a size of 20–35 nm [17]. Xiao et al. prepared magnetite MNPs coated with green tea extracts, namely epigallocatechin gallate and epicatechin and showed that green tea catechins can act as efficient reducing agents [18]. All these reports use water as a solvent to prepare iron and iron oxide NPs. These iron and iron oxide NPs have low saturation magnetization (M_S) and wide particle size distribution. Therefore, solvents other than water need to be explored. The viscosities of polyols increase with the growing hydrocarbon chain length [19]. Ethylene glycol (EG), which belongs to the polyol family, is highly viscous compared to ethanol- and water-based solvent systems and is a commonly used solvent in the solvothermal process. Due to its high viscosity, EG strongly affects the particle growth rate in solvothermal synthesis processes and offers better control over particle size distribution compared with other solvents. Because of this, EG can be considered one of the best solvents in the solvothermal synthesis process.

In the present study, zero-valent iron NPs were prepared using green tea extract as a reducing agent, and thermal treatment was given for different time to enhance the M_S of Fe_3O_4 MNPs.

2. Experimental section

2.1. Materials

All chemicals used in the experiments are of analytical reagent grade and used without further purification. Ethylene glycol ($CH_2(OH)\cdot CH_2OH$) and ferric nitrate ($Fe(NO_3)_3\cdot 9H_2O$) were purchased from SD Fine-Chem, India. Tetley green tea bags were used to prepare the extract.

2.2. Synthesis of magnetic nanoparticles

A single standard green tea bag (weight 1.5 g) was used to prepare green tea extract. The tea bag was dipped in 100 ml double-distilled water (DDW) and the solution was kept boiling for 30 min to obtain the green tea extract. The solution was then filtered twice through Whatman No. 1 filter paper and stored at 4 °C for further use.

For MNP synthesis, 0.1 M ferric nitrate solution was prepared in EG. Then green tea extract was continuously mixed with ferric nitrate solution in a 1:2 ratio at room temperature and stirred for 30 min. The greenish-black colored solution was obtained after complete addition of reactants, which indicated the formation of zero-valent iron NPs. In our previous work, we have confirmed the formation of zero-valent iron NPs by UV–visible spectroscopy by measuring the absorbance of ferric nitrate, green tea and zero-valent iron nanoparticle solutions [20]. The solution was then moved to Teflon liner, which was sealed and kept in the furnace at 200 °C for 2–10 h under ambient atmosphere. After completion of the reaction, the furnace was allowed to cool down to room temperature and the product was separated magnetically and washed several times with ethanol and DDW. The MNPs were then washed after thermal treatment to remove unreacted EG and the loosely bound organic content on the surface. Next, the MNPs were dried under vacuum at room temperature. In this modified green synthesis process, the reactions were carried out for 2, 4, 6, 8 and 10 h and samples were named G1, G2, G3, G4 and G5, respectively.

2.3. Characterizations

X-ray diffraction (XRD) measurements were performed using a Bruker AXS D2 phaser diffractometer using Cu-Kα radiation (K = 1.5406 Å). A field emission scanning electron microscope (FESEM) (Zeiss model Ultra 55) was used for the surface morphology and particle size investigations. Thermogravimetric analysis (TGA) was done using a TA Instrument-SDT Q600 V20.9 Build 20, in a nitrogen atmosphere with a heating rate of 10 °C/min. The magnetization measurements were carried out using the Quantum Design's VersaLab 3 T, Cryogen-free Physical Property Measurement System. Magnetization versus field (MH) loops for all samples were measured at 300 K and 60 K in magnetic fields up to 30 kOe. Zero field-cooled (ZFC) and field-cooled (FC) magnetization measurements were performed in the temperature range 50–300 K in an applied magnetic field of 500 Oe.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of all samples. All diffraction peaks for samples G1 to G5 can be assigned with the lattice planes (220), (311), (400), (511) and (440) of Fe_3O_4 with inverse spinel structure (JCPDS 01-088-0315). Intensities of the peaks in all XRD patterns were increased with increasing reaction time, indicating increasing crystallinity. The thermal treatment affects the iron seeds formed at the initial

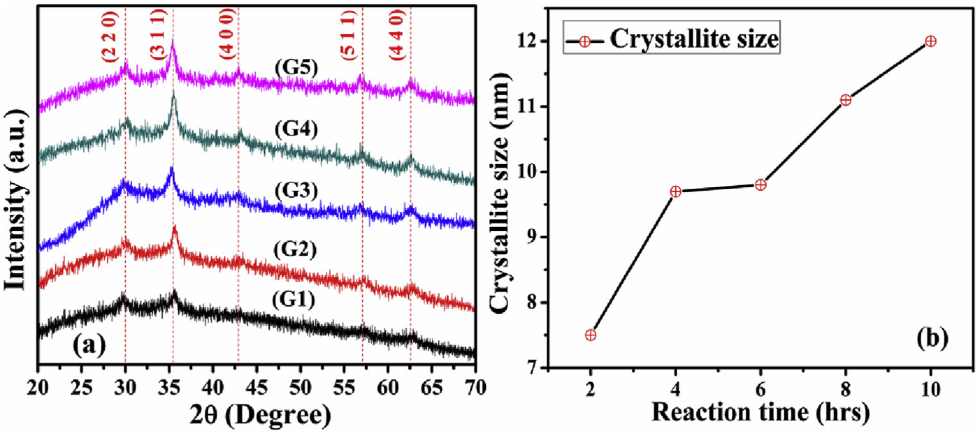

Fig. 1. (a) X-ray diffraction patterns of Fe_3O_4 MNPs. (b) Change in crystallite size as a function of reaction time.