Research Article

Rod-Shaped Magnetite Nano/Microparticles Synthesis at Ambient Temperature

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Here, we reported room temperature synthesis of Fe_3O_4 rod-shaped nano/microparticles by chemical reduction method from FeCl_3 precursor and NaBH_4 as the reducing agent in the presence of the pyrrole as a capping agent. The magnetic Fe_3O_4 particles were characterized by several methods, such as SEM, XRD, FTIR, and TGA. The average aspect ratio of Fe_3O_4 rod-shaped particles was ~ 2.8 . These particles were redispersed in deionised water to form a colloidal solution and showed magnetic properties. This economical synthesis route is scalable, and Fe_3O_4 particles can be exploited for various applications such as MRI contrast enhancement, biodiseparations, Ni-Fe batteries, and as a catalyst.

1. Introduction

Recently, magnetic nano- and microparticles have become one of the most exciting and rapidly growing areas in material chemistry, separation technology, biology, and biomedicine, leading to a number of potential applications [1]. Fe_3O_4 has received major attention, as one of the most important transition magnetic metal oxides due to its extensive applications. It has been considered as an ideal material for magnetic data storage [2], a candidate for biological application such as a tag for sensing and imaging [3], and a drug-delivery carrier for antitumor therapy [4]. Magnetite (Fe_3O_4) is widely exploited due to its strong magnetic properties as well as extensive applications in biotechnology and medicine [5]. Especially, the Fe_3O_4 nano- or microspheres have smooth and large-surface areas which can be used for maximal protein, enzymes, antibodies, and anticancer agents binding [6]. Ferrimagnetic iron oxide microparticles have been typically used for recording materials [7], but these particles are even used as tracers for investigating the behavior of air-borne matter in the human and animal respiratory tract [8] and the mechanical properties of living cells [9]. As they are chemically stable, nontoxic, and noncarcinogenic [10], they permit clearance studies in the human lungs over time periods up to 1 year. Ferromagnetic and Ferrimagnetic

particles can be detected in the human body by magnetopneumographic (MPG) methods [11]. Ferrimagnetic particles were also used for measurements of macrophage functions and cellular integrity (viscoelasticity) *in vivo* and *in vitro* [9]. Fe_3O_4 particles in the micrometer size range can be produced by either a crystallization process [12] or by nebulization of a colloidal solution [13]. Many techniques have been reported in the literature for chemical synthesis of these particles such as the sol-gel [14], microemulsion [15], sonochemical [16], ultrasonic spray pyrolysis [17], and microwave plasma [18]. Each preparation method has its advantages and disadvantages, which primarily relate to particles size distribution, production scale, and cost. Wet chemical processes are capable from the economical perspective but consist of many steps. The gas-phase synthesis process is one-step process with relatively high production rate, but production costs are high. Two important synthesis routes are the thermal decomposition [19] and the chemical reduction [20] methods. A characteristic and serious problem is in assembling and stabilizing magnetic particles as it has high affinity to agglomerate, which is an obstacle to its application for magnetic storage. This barrier can be resolved if the particles are dispersed using proper dispersing agent. Various dispersing agents were reported earlier such as SDS, Triton-X, and PAA; however, this more or less resulted in

TABLE 1: This shows length, width, and aspect ratio of Fe_3O_4 nano/microrods from Figure 1(F).

Length of Fe_3O_4 rods (nm)	Width of Fe_3O_4 rods (nm)	Aspect ratio
833.33	444.44	1.875
1555.55	444.44	3.500
1444.44	333.33	4.333
555.55	333.33	1.666

agglomeration of particles. Here, we attempted to solve this problem by synthesizing Fe_3O_4 nano/microparticles using chemical reduction method at ambient temperature using pyrrole as dispersing agent.

2. Experimental Section

2.1. Chemical and Reagents. Ferric chloride (FeCl_3 , AR grade), sodium borohydride (NaBH_4 , AR grade), and pyrrole ($\text{C}_4\text{H}_5\text{N}$, AR grade) were purchased from RANKEM Chemicals, Mumbai, India and used as received. Conductivity water is used throughout the experimental work. Soap solution and Aqua regia were used to wash the apparatus and MilliQ water to rinse the apparatus.

2.2. Synthesis of Fe_3O_4 Nano/Microparticles. 0.27 gm ferric chloride (FeCl_3) and 0.55 gm of pyrrole ($\text{C}_4\text{H}_5\text{N}$) were dissolved in 20 mL of deionised/conductivity water separately and mixed together (labeled as solution "A"). The colour of the solution changes from yellow to orange. Separately, 0.75 gm of NaBH_4 was dissolved in 10 mL of conductivity water (labeled as solution B) followed by addition of solution "B" into "A" under vigorous magnetic stirring. Gradually, with an addition of solution B, entire solution becomes dark and eventually turns into completely black.

2.3. Characterization of Fe_3O_4 Nano/Microparticles. The characterization study was carried out using Bruker, D8-Advance X-ray Diffractometer between 2θ values 30° to 70° with low-angle scan. The thermal analysis of TGA and DTA was obtained at DTG-60H and DSC at DSC-60 instrument. The IR spectrum was obtained with a Shimadzu 8400 spectrophotometer.

3. Results and Discussion

The well-dispersed Fe_3O_4 particles in water (Figure 1(A)) were collected by external magnet as shown in Figure 1(B) from as-prepared solution (inset of Figure 1(B)). The reaction was accompanied by generation of numerous bubbles. The reaction was supposed to be complete once bubble formation ceased and completed after 24 hours under continuous magnetic stirring [21]. The pH of the solution was observed to be 9.9. To separate the Fe_3O_4 particles, a strong magnet was used as shown in Figures 1(B) and 1(D). The Fe_3O_4 particles were then washed, redispersed in conductivity water and dried overnight. To prevent agglomeration of Fe_3O_4

particles, dispersing agents were added during synthesis. Several commonly used dispersing agents were evaluated in this work including poly(vinylpyrrolidone), (PVP; average molecular weight 10000), poly(acrylic acid), and sodium dodecyl-benzenesulfonate (SDS, 80%). These surfactants were resulted in agglomeration. Nevertheless, we obtained Fe_3O_4 particles without agglomeration using pyrrole as a surfactant. Other surfactants used such as SDS, Triton-X, and PAA, however, resulted in agglomeration of particles and settled down immediately in the solution. This problem was solved by using pyrrole as a surfactant or dispersing agent. Pyrrole was well coated to the surface of the Fe_3O_4 particles [21]. Figures 1(E) and 1(F) show SEM images of Fe_3O_4 rod-like particles. The plausible mechanism of synthesis is as given on the next page [21].

Chen et al. [22] earlier reported that in this approach, the Fe_3O_4 spherical nanoparticles were treated with FeCl_3 solution. Because of common ion effect, Fe^{3+} ions were absorbed onto the surface of Fe_3O_4 nanoparticles, and Fe_3O_4 particles were then surrounded by positively charged (Fe^{3+}) shells to prevent their aggregation. This scheme does support our formation processes of pyrrole-coated rod-shaped Fe_3O_4 nano/microparticles as shown in Figure 2. Moreover, in this scheme [22], the formed Fe^{3+} ion shell was also served as the oxidant to polymerize pyrrole monomers which may lead to rod formation over the template of polymer. One more supportive model to prevent the aggregation of nanoparticles has also been proposed by Zhao and Nan [23]. As per their paper, the steric stabilization effect arises from the fact that polymers coating on the surface of particles occupy a certain amount of space. Thus, the space becomes compressed when nanoparticles are brought too close together. An associated repulsive force makes separate nanoparticles from each other and restrains the aggregation of nanoparticles.

The length and width of Fe_3O_4 particles were observed in the range between 555.55 nm and 1555.55 nm; 333.33 nm and 444.44 nm, respectively. The average aspect ratio that is, length divided by width, was found to be ~ 2.8 (Table 1).

Figure 3(a), spectrum 1 represents the spectra of the surfactant or dispersing agent, that is, pyrrole. Pyrrole contains secondary amine which shows characteristic peak at $3500\text{--}3300\text{ cm}^{-1}$ due to N-H stretching vibrations. Spectrum 2 represents the spectra of the as-prepared Fe_3O_4 particles. In this spectra, the wavelength is shifted, that is, 3432 to 3001 cm^{-1} ; it shows broad peak due to the coating of cationic surfactant, (pyrrole) which indicates the presence of surfactant that is, pyrrole coated on the surface of Fe_3O_4 particles. These wavelengths are shifted due to the attachment of secondary amine. The nitrogen group is attached to the carbon which is having lone pair of electrons. The peak at 1040 cm^{-1} shows that carbon is attached to nitrogen atom [24]. Spectrum 3 represents the spectra of the Fe_3O_4 particles after thermal analysis. Due to the decomposition of pyrrole and possible phase transition of iron, the wavelength was changed. On TGA analysis of a sample, removal of the water molecule and other impurities from Fe_3O_4 nano/microparticles takes place. The removal of impurities is exhibited by the weak bands at wavelengths 3186 to

FIGURE 1: In (A) and (C) are represented the colloidal solution and calcined powder of Fe_3O_4 particles, exhibiting their magnetic properties using external magnet (B) and (D), respectively. In (E) is represented lower magnification and in (F) higher magnification SEM image of Fe_3O_4 particles.

FIGURE 2: Schematic diagram of the formation processes of pyrrole-coated rod-shaped Fe_3O_4 nano/microparticles.

FIGURE 3: In (a) are represented FTIR spectra of cationic surfactant pyrrole (spectrum 1), as-prepared Fe_3O_4 particles (spectrum 2), and Fe_3O_4 particles after thermal analysis (spectrum 3); (b) XRD of Fe_3O_4 micro/nanoparticles after calcinations; (c) thermogravimetric analysis (1) differential thermogram analysis (2) patterns of Fe_3O_4 particles.

3498 cm^{-1} as a result of the shift in a wavelength [25]. At wavelengths 1341 , 1365 and 1467 cm^{-1} , C-H stretching was observed due to methyl group. The peaks at 1547 and 1464 cm^{-1} can be assigned to C=C and C-N stretching vibrations, respectively. The peaks at 1182 and 901 cm^{-1} indicate the C-H in-plane bending and ring deformation, respectively. The peaks observed at 457 to 430 cm^{-1} are the characteristic peaks of Fe-O stretching vibrations [26]. Similar patterns were also observed in pyrrole-Fe [OH] microcomposites. The obvious spectral differences between pure pyrrole and the composites indicate that pyrrole exhibits a different chain structure, and there are physical interactions between particles and pyrrole. The presence of Fe_3O_4 particles was strongly supported by a new peak at 588 cm^{-1} [26]. Figure 3(b) shows the X-ray diffraction pattern (XRD) of Fe_3O_4 particles after calcinations under nitrogen atmosphere. The 2θ values of the standard Fe_3O_4 particles were 30.18° , 35.68° , and 37.28° which correspond to the Bragg reflections

TABLE 2: Observed and standard 2θ values of Fe_3O_4 particles with respective (hkl) planes.

Observed 2θ values	Standard 2θ Values	Respective (hkl) planes
30.0°	30.087°	(220)
35.4°	35.439°	(311)
37.4°	37.071°	(222)

(220), (311), and (222), respectively, (PDF no. 79-0418 of Fe_3O_4 , wavelength = 1.54060), whereas the 2θ values of calcinated Fe_3O_4 nano/microparticles were 30.0° , 35.4° , and 37.4° , which corresponds to the Bragg reflections (220), (311), and (222), respectively (Table 2). By comparing the X-ray diffraction patterns prepared of Fe_3O_4 nano/microparticles with standard data, we concluded that the particles were mainly composed of Fe_3O_4 nano/microparticles [27, 28].

To determine the degree of oxidation of the Fe_3O_4 particles, TGA analysis was performed, and the result is shown in Figure 3(c), curve 1. When the Fe_3O_4 particles were heated in air up to 750°C at $10^\circ\text{C min}^{-1}$, a significant weight loss was observed, which can be attributed to the oxidation of the Fe_3O_4 core [19]. The thermal stability of Fe_3O_4 particles was investigated by TGA measurements. The black particles were observed to turn red upon test completion, a characteristic of Fe_3O_4 rather than black carbon, indicating the complete loss of pyrrole. The weight loss at temperatures lower than 592.56°C is due to loss of moisture, while the major loss at temperatures higher than 700.39°C is due to the decomposition of pyrrole. The difference in the residue reflects the different amount of Fe_3O_4 particles present. The thermal stability increases slightly with increasing particles loading, which is believed to be due to both the lower mobility of the polymer chains when the polymer chains are bound to the particles and stronger chemical interaction [19]. Figure 3(c) curve 2—represents differential thermogram analysis (DTA) of Fe_3O_4 particles from this figure, it is clear that endothermic reaction takes place. The first broad peak was observed at 77.77°C and; a second at 647.40°C due to the decomposition of pyrrole and the possible phase transition of Fe_3O_4 , respectively. As compared with no obvious phase transition in the pure Fe_3O_4 particles, the observed phase transition is likely due to an intermediate product of pyrrole. This cheap method of Fe_3O_4 synthesis is scalable and can be exploited for various applications such as MRI contrast enhancement, catalyst for carbon nanotubes growth and, is currently being pursued.

4. Conclusion

We synthesized Fe_3O_4 rod-shaped nano/microparticles by chemical reduction of Fe^{3+} ions using NaBH_4 reducing agent and pyrrole as a surfactant. The X-ray diffraction pattern concluded that the particles are mainly composed of Fe_3O_4 crystals. The SEM images confirm rod shape of Fe_3O_4 particles. The average aspect ratio of the stated particles was ~ 2.8 . TGA analysis revealed that the surfaces of particles were oxidized containing about 5% weight loss of iron oxide. The FTIR spectra of Fe_3O_4 rod-shaped particles clearly indicated that the particles were coated by dispersing agent pyrrole. The colloidal solution of Fe_3O_4 particles exhibited magnetic properties. This synthesis route is economical and convenient method to fabricate Fe_3O_4 particles, which could be suitable for various applications such as MRI contrast enhancement, biodispersions, Ni-Fe batteries, and as a catalyst.

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