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RESEARCH ARTICLE

Synthesis of Polystyrenesulfonic Stabilized Magnetite Nanoparticles

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Abstract: Superparamagnetic magnetite (Fe_3O_4) nanoparticles have been synthesized via co-precipitation method in presence of organic sulfonic acid. The product were characterized by x-ray diffraction, UV-visible spectroscopy, fourier transform infrared spectroscopy, transmission electron microscopy and vibrating sampling magnetometer (VSM). X-ray diffraction data indicated that the successfully formation of Fe_3O_4 nanoparticles. As obtained Fe_3O_4 nanoparticles have spherical shape and size in the range of 5-6 nm without any aggregation of nanoparticles. VSM studies indicated that superparamagnetic properties of Fe_3O_4 nanoparticles.

Keywords: Magnetite nanoparticles, Co-precipitation, Superparamagnetism, Surfactant

Introduction

Superparamagnetic magnetite (Fe_3O_4) nanoparticles have attracted much attention to both fundamental research and technological applications such as targeted drug delivery systems, magnetic separation, magnetic storage media, contrast agents for magnetic resonance image (MRI), bio labelling and separation of biomoelucles[1-9]. All these applications requires the magnetite nanoparticles particles to be chemically stable, have particles size <20 nm with a narrow size distribution and to be well dispersed in aqueous medium[10]. However, Fe_3O_4 nanoparticles can easily agglomerate due to magnetic dipole-dipole interactions. Numerous approaches have been developed for synthesis of Fe_3O_4 nanoparticles using various capping agnets such as silica, gold, polymers and capping agents. Despite a few of papers concerning the preparation of Fe_3O_4 nanoparticles and their applications in biomedicines, their practical application is still limited. Usually an external magnetic field was used to suspend paramagnetic particles in biomaterial applications and the resulting materials were expected to do not agglomerate anymore after removal of the field. At present, the significant question is that magnetic particles can easily aggregate in the presence or even the absence of a magnetic field. Furthermore, the major difficulty lies in the interrelated effects in synthesis and assembly. Agglomeration of these particles originates from the strong interaction among the particles, which will diminish their magnetic properties. Therefore, it is of fundamental importance to develop a method to synthesize control size and shape Fe_3O_4 nanoparticles without any agglomeration.

In this paper, we present the synthesis of polystyrene sulfonic acid (PSS) stabilized Fe_3O_4 nanoparticles via co-precipitation method. The effect of PSS content on magnetic properties of Fe_3O_4 nanoparticles was investigated.

Experimental

Polystyrene sulfonic acid received from Aldrich and was used as received. Other reagents such as $FeCl_3·6H_2O$, $FeSO_4·7H_2O$, ammonia (NH_3H_2O), sodium hydroxide and methanol were purchased from Merck, India and used as received without any purification. Double distilled water was used throughout the synthetic processes. All other reagents were analytical grade and used without further purification.

Synthesis of PSS stabilized Fe_3O_4 nanoparticles

The PSS stabilized Fe_3O_4 nanoparticles were synthesized by a self-assembly method in presence of PSS via modified co-precipitation method. In a typical synthesis process, a 5 mL of PSS dissolved in 50 mL of distilled water under vigorous stirring at room temperature. The reaction mixture was constantly stirring for 2 hours to obtain a milky dispersion of PSS micelles. Then, 10 mL of 1 mol L^{-1} $FeCl_3·6H_2O$ and 10 mL of 0.5 mol L^{-1} $FeSO_4·7H_2O$ aqueous solutions were rapidly injected into the above reaction mixture and slowly heated up to 65 ^0C under stirring, followed by the addition of 5 mL of 25% NH_4OH. The colour of reaction mixture turns black indicating the formation of magnetite. The reaction was allowed to proceed for 5 h under vigorous stirring until a very viscous PSS stabilized magnetite nanoparticles were obtained. The resulting mixture was centrifugated and washed with distilled water and finally with methanol. The product was then dried under vacuum at room temperature for 12 h. The same procedure has been adopted for preparation of all PSS stabilized Fe_3O_4 nanoparticles, while varying the PSS content in the reaction mixture.

Characterization

The UV-Visible absorption spectra of the samples were recorded on a Perkin-Elmer double beam LS-50 spectrophotometer. The morphology, chemical composition and phase identification of Fe_3O_4/PANI nanocomposites were characterized by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), transmission electron microscopy (TEM) and x-ray diffraction (XRD). Powder x-ray diffraction (XRD) pattern were recorded on a Siemens D5005 x-ray diffractometer at 1 per min. Magnetic properties were investigated by vibrating sample magnetometer (VSM, Lake Shore, USA).

Results and Discussion

The synthesis of Fe_3O_4 nanoparticles is based on modified co-precipitation chemical in the presence of excess of PSS as soft-template. The template, PSS is believed to serve as the nanoreactor. Because of its hydrophilic group (-SO_3H) and hydrophobic group (-$C_{12}H_{25}$), PSS easily forms micelles in an aqueous solution. Micelle-assisted synthesis had previously been used widely to prepare nano particles in which the particle sizes were controlled by the micelle “reactor” sizes[11]. The presence of excess PSS can prevent the formation of larger particles via steric hindrance and thereby producing nanometer sized nanoparticles. Fe_3O_4 nanoparticles were also formed inside PSS micelles “reactor” during the sedimentation process. PSS having –SO_3^- group can stabilize Fe_3O_4 nanoparticles, while long alkyl hydrophobic chains act as a barrier to protect the particles from agglomeration[12].

Molecular structure and phase identification was characterized by x-ray diffraction pattern (XRD) and UV-Visible spectroscopy. Figure 1 show the XRD patterns from PSS stabilized Fe_3O_4 nanoparticles. The diffraction peaks at $2\theta = 30.47^o$, 35.63^o, 43.35^o, $57.\ 22^o$, $63.06^{o,}$ can be indexed as (220), (311), (400), (511) and (440) planes of magnetite, respectively.

Figure 2 depicts the UV-Visible spectra of PSS stabilized Fe_3O_4 nanoparticles which is in complete agreement with literature reports[13]. The UV-Visible absorption spectrum showed a characteristic absorbance band at 304 nm. Besides this peak, there is a sharp peak at 290 nm due to the $\pi \rightarrow \pi^*$ transition in the benzenoid rings of PSS, which confirms the capping of PSS to the surface of Fe_3O_4 nanoparticles.

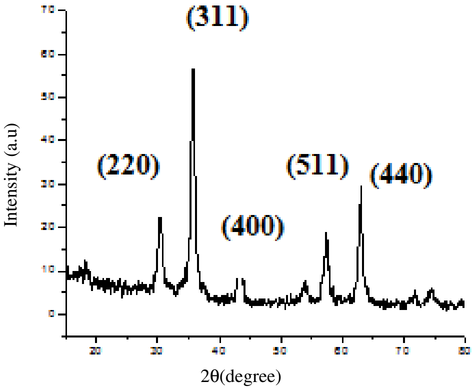

Figure 1. The XRD patterns from PSS stabilized Fe_3O_4 nanoparticles

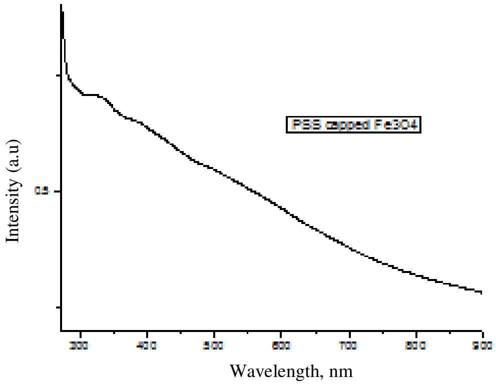

Figure 2. The UV-Visible spectra of PSS stabilized Fe_3O_4 nanoparticles

According to the reflections peaks shown in Figure 1 & 2, the main phases can be indexed as magnetite, which are in good agreement with the standard magnetite card (card No. PDF#01-1111). The XRD patterns of PSS stabilized Fe_3O_4 nanoparticle is indicated that the crystalline in nature and completely agree with previous literature.

The morphology of PSS stabilized Fe_3O_4 nanoparticles have been investigated by scanning electron microscopy. Figure 3 shows the scanning electron microscope (SEM) image of Fe_3O_4 nanoparticles prepared via co-precipitation method in presence of PSS. It can be clearly seen from SEM image that Fe_3O_4 nanoparticles were of sphere like morphology.

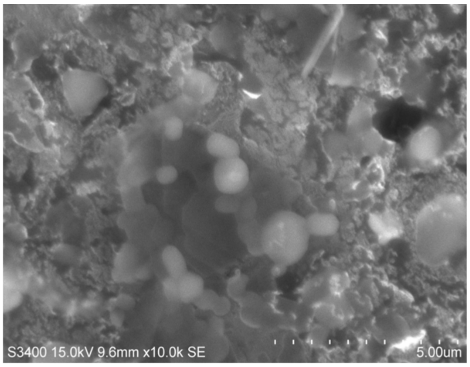

Figure 3. SEM image of PSS stabilized Fe_3O_4 nanoparticles

Transmission electron microscopy (TEM) image of as prepared PSS stabilized Fe_3O_4 nanoparticles displayed in Figure 4, shows Fe_3O_4 nanoparticles are nearly spherical with an average diameter ranges from 5-6 nm. It can be seen that the vast majority of particles exhibit a diameter close to 5-6 nm without particles aggregation, because as synthesized Fe_3O_4 nanoparticles were coated with PSS.

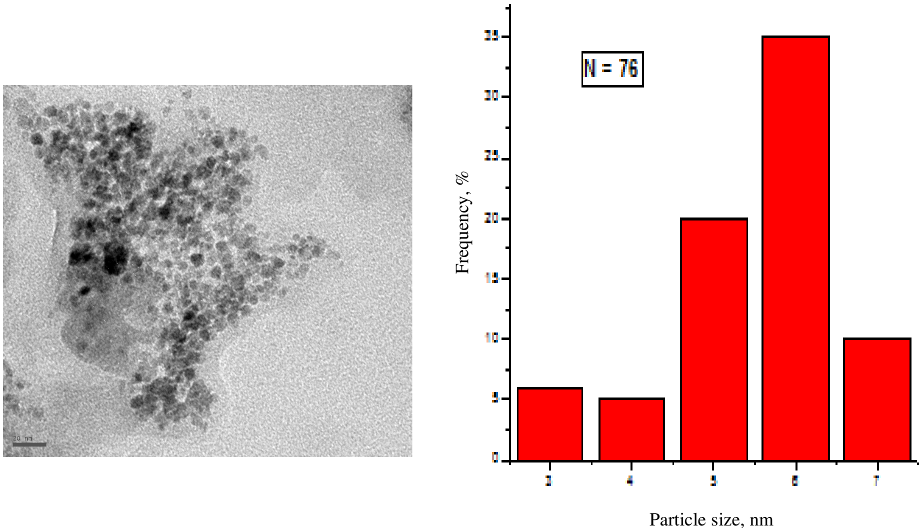

Figure 4. Representative TEM image and particle size of Fe_3O_4 nanoparticles prepared by modified co-precipitation method.

To investigate the influence of the PSS on magnetic properties of Fe_3O_4 nanoparticles and hysteresis loops of samples prepared at different content of PSS were analyzed by vibrating sampling magnetometer (VSM), as shown in Figure 5. The magnetization curve shows no remanence or coercivity at room temperature, suggesting superparamagnetic behaviour with saturation magnetization values: 11, 9, 2.3, 2.5 and 2 emu/g for the samples prepared at different content of PSS. These Ms values were much more lower than bulk Fe_3O_4 value[14].

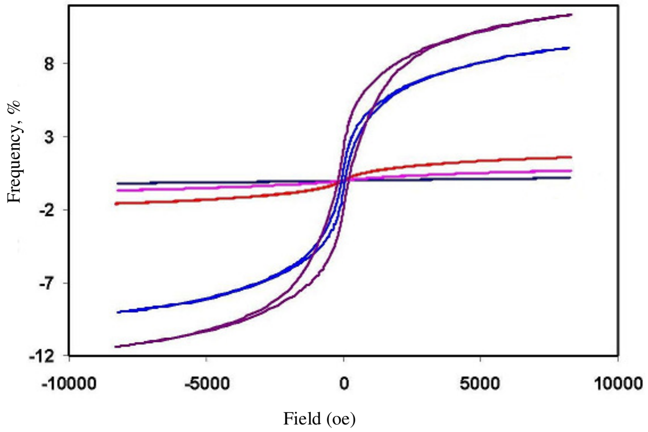

Figure 5. Room temperature magnetization curves of Fe_3O_4 nanoparticles prepared at different content of PSS

It can be observed that the magnetic saturation (M_s) values of Fe_3O_4 nanoparticles were decreased by increasing content of non magnetic PSS coating on Fe_3O_4 nanoparticles. The changes in the magnetic properties of the samples can be attributed to the modification of the crystallinity and crystallite sizes dependent on the content of PSS. The energy of a magnetic particle in the external field is proportional to its particle sizes via the number of molecules in a single magnetic domain. Therefore, the decrease of the M_s values with the decrease of particle sizes can be attributed to surface effects that are the result of finite-size scaling of nanocrystallites[15-16].

Conclusion

In summary, we have demonstrated a simple, reproducible and facile method of preparation of Fe_3O_4 nanoparticles via co-precipitation method in presence of PSS. The spectroscopic and XRD results indicated that the successfully formation of agglomerate free Fe_3O_4 nanoparticles. Fe_3O_4 nanoparticles have superparamagnetic nature with much lower saturation magnetization than bulk magnetite.

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