Preparation and characterization of nanoflake composite multi core–shell $SrFe_{12}O_{19}/Fe_3O_4/PEG/PPy$

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Abstract. Nanoflake composite multi core–shell $SrFe_{12}O_{19}/Fe_3O_4/PEG/Polypyrrole$ was synthesized by in situ polymerization method. In this paper, the fabrication of $SrFe_{12}O_{19}$ nanoflake is as first core by sol-gel method. Then fabricated a shell layer from magnetic nanoparticles of Fe_3O_4, which synthesized by co-precipitation technique, onto the $SrFe_{12}O_{19}$ nanoflake. Polyethylene glycol (PEG) as a polymer layer and as second shell was coated onto the before core-shell. Than core–shell $SrFe_{12}O_{19}/Fe_3O_4/PEG$ was used as template for the preparation of $SrFe_{12}O_{19}/Fe_3O_4/PEG/Polypyrrole$ composite. Final composite has a conductive property among 4.23×10^{-2} Scm^{-1} and magnetic property about M_s=2.99 emu/g. Also final composite in soluble at organic solvent such as DMF and DMSO and has a flake structure. Conductivity and magnetic property respectively determine by four-probe instrument and vibrant sample magnetometer (VSM), morphology and article size determined by FE-SEM, TEM and XRD.

Keywords: nanoflake; conductive polymer; magnetic; PPy

1. Introduction

Recently, conducting polymer composites with both electrical and ferromagnetic properties have received tremendous attention, and study on this kind of composites has becoming one of the most active and promising research area. What make conducting polymer composites so attractive are their potential applications in batteries, electro-chemical display devices, molecular electronics, electrical-magnetic shields and microwave-absorbing materials, etc (Li *et al.* 2009, Hosseini *et al.* 2010). Conductive polymer plays an important role in technologies such as stealth, electro static charge dissipation and EMI shielding (Phang *et al.* 2008). Singh and cowprkers, synthesis of polyaromatic amine–ferromagnetic composite with nanosize TiO_2 (70-90 nm) and γ-Fe_2O_3 (10-15 nm) particles via in situ emulsion polymerization were reported. They were resulted polyaniline-TiO_2-γ-Fe_2O_3 nanocomposite has shown better shielding effectiveness due to absorption than the polyaniline-γ-Fe_2O_3 (Singh *et al.* 2010). Polymer–inorganic nanocomposite membranes where inorganic nanoparticles are dispersed inside polymer membrane matrix have been of great interest in recent years due to their intrinsic advantages over pure polymeric or inorganic membranes as well as their immense application potential in energy, environment, biomedical materials and devices

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(Pan *et al.* 2010). Conjugated polymers (CP) are a novel class of conductive materials which combine the optical and electrical properties of semiconductors with the processing advantages, good mechanical properties and low cost of polymers (Bereznev *et al.* 2005). The conducting polymers are promising candidates as counter electrode materials used in DSSC, because of their unique properties, such as inexpensive, high conductivity, remarkable stabilities, good specific capacitances and catalytic activity for I_2 reduction (Wu *et al.* 2008). Magnetic supports could overcome the limitation of separation from the liquid phase thus the photo catalyst could be effectively recycled by applying an external magnetic field (Zhang *et al.* 2009). The *M* type hexaferrites, $MFe_{12}O_{19}$ (*M* = Ba, Sr, Pb) have been studied for a long time because of their technical applications (Fu *et al.* 2007). During the past few years, considerable researches have been done on the synthesis of core–shell structure materials with desired compositions due to their wide potential applications in biotechnology, optical, electronic, magnetic, catalytic and sensing devices. However, the synthesized core–shell structures were usually of different components of core and shell. To the best of our knowledge, merely Fe_3O_4 homogeneous core–shell polyhedrons have been fabricated by a cetyltrimethyl ammonium bromide (CTAB) aided hydrothermal method (Ni *et al*. 2009). Conducting polymers are not molten in nature and generally insoluble in common solvents and the aggregation of magnetic particles is unavoidable due to the high surface energy and strong interaction between nanoparticles. Therefore it is difficult to prepare conducting polymer/magnetic particle composites by simple blending or mixing in solution or melt form. Yuvaraj *et al*. Polypyrrole/γ-Fe_2O_3 magnetic nanocomposites was synthesized in supercritical fluid, too (Yuvaraj *et al.* 2008).

In this work, nanoflake $SrFe_{12}O_{19}/Fe_3O_4$/PEG/Polypyrrole composites were prepared in an emulsion polymerization system. The samples were characterized by various experimental techniques and magnetic properties and the conductivity of nanoflake $SrFe_{12}O_{19}$/Fe_3O_4/PEG/Polypyrrole composites were investigated.

2. Experimental

2.1 Materials

Chemicals including metal salts, and polyethylene glycol (PEG), citric acid are analytical grade (Merck) and were used without further purification. Water was deionized, doubly distilled and deoxygenated prior to use. Ethanol, Oleic acid and chloroform (analytical grade, Merck) was distilled to remove the inhibitor. Pyrrole monomer (analytical grade, Merck) was distilled twice under reduced pressure. DBSA and micro cellulous were of industrial grade.

2.2 Preparation of nanoflake SrFe$_{12}$O$_{19}$

$SrFe_{12}O_{19}$ nano-particles were prepared using the absorbent micro cellulous as template by sol–gel method. The detailed process could be described as follows. Sr (NO_3)$_2$ and Fe (NO_3)$_3$·$9H_2O$ (with 11.5 Fe^{3+}/Sr^{2+} mole ratio) were dissolved in 200 ml de-ionized water. Then citric acid (with 1:1 citric acid/metal ion mole ratio) was added to the above mixture. The *pH* value was adjusted to 8 by NH_4·OH after the solution was agitated homogeneously. Subsequently, the solution was heated and agitated until to form sol. The sol was dripped onto the prepared dry absorbent micro cellulous.

Further, the dipped absorbent micro cellulous was dried for 24 h at room temperature and then dried in a drying cabinet at 70°C. The dried gels were calcined under 850°C for 2 h to obtain nanoflake SrFe$_{12}$O$_{19}$.

2.3 Preparation of Fe$_3$O$_4$ nanoparticle

FeCl$_3$.6H$_2$O (24.3 g) and FeSO$_4$.7H$_2$O (16.7 g) were dissolved in 100 ml de-ionized water under nitrogen gas with vigorous stirring at 80°C. Then 50 ml of ammonium hydroxide were added rapidly into the solution. The color of the solution turned to black immediately. Oleic acid (3.76 g) was added after 30 min. Then the suspension was kept at 80°C for 1.5 h. The magnetite nanoparticles were washed with de-ionized water until the *pH* value of the system reached neutral. The as-synthesized sample was dried in vacuum at room temperature.

2.4 Preparation of SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$ core–shell

0.1 g nano-sized particles of prepared SrFe$_{12}$O$_{19}$ or Fe$_3$O$_4$ were dispersed in 200 ml water solution with *pH*=6 under ultra sonification for 2 min. At this *pH*, the surface charge of SrFe$_{12}$O$_{19}$ in the solution is expected to be positive, and that of Fe$_3$O$_4$ be negative. The two solutions were mixed at 1/19 volumetric ratio (1/19 weight ratio of SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$) and subjected to sonification for 2 min so that SrFe$_{12}$O$_{19}$ particle was coated with Fe$_3$O$_4$ particles. The solution was then filtered using ultra filtration membrane and dried at room temperature.

2.5 Preparation of SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG

0.1gr of SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$ core–shell dispersed in 200 ml water solution with *pH* = 8 under ultra sonification for 2 min. Than PEG added in solution (mass ratio of PEG/nanocomposite were 12:1), and sonification is for 5 minutes. The solution was than filtered and dried at room temperature.

2.6 Preparation of SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy nanocompositse

Nanoflake composite SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy was prepared in the in situ polymerization system in the presence of DBSA as the surfactant and dopant and FeCl$_3$ as the oxidant. The DBSA was dissolved in distilled water with vigorous stirring for about 20 min. In the other hand, 1.5×10^{-3} mmol of new distilled pyrrole was solved in 30 mL acetone/DMF (10:1) and it was added to the DBSA solution under stirring and sonification for approximately 1 h. Then 0.2 gr nanoflake composite SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG added in solution and mixture sonification for 10 minutes. Finally FeCl$_3$ was added into the above mixture and mixture stirring at 0°C for 2 h. The mixture filtered and black precipitates were washed with ethyl alcohol, form any times respectively. The product was dried at the room temperature and SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy nanoflake composite was obtained.

2.7 Measurement and characterization

The structure of the samples was determined by X-ray diffractometer (Cu Kα radiation, λ = 0.154056 nm) studies. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a
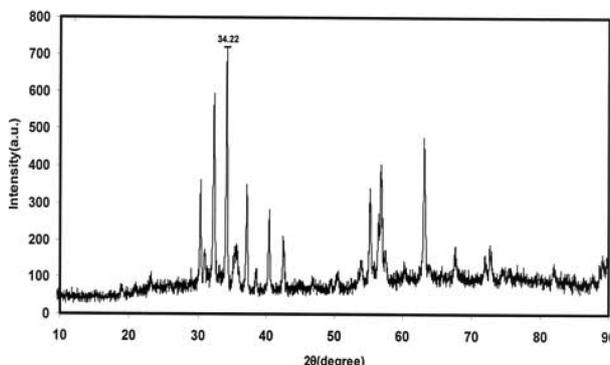
Fig. 1 X-ray diffraction pattern of nanoflake SrFe$_{12}$O$_{19}$ calcined at 850°C for 2 h

PerkinElmer spectrum FTIR using KBr pellets. The morphology of as-prepared SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy nanoflake composite and SrFe$_{12}$O$_{19}$ nanoflake was investigated by field emission scanning electron microscope (FE-SEM). The morphologies of as prepared samples were examined with transmission electron microscopy (TEM) by ZWISS-EM900. Samples of TEM were prepared by dispersing the final nanoparticles in ethanol; the suspension was then dropped on copper grids. The magnetic measurements were carried out at room temperature using IRI-Kashan vibrating sample magnetometer (VSM) with a maximum magnetic field of 10 kOe. The conductivity was measured on a four-probe instrument at room temperature.

3. Result and discussion

Fig. 1 shows the X-ray diffraction pattern of nanoflake SrFe$_{12}$O$_{19}$ that are calcined at 850°C for 2 h. It could be observed that the products are composed of γ-Fe$_2$O$_3$ phase. Size of nanoparticle can be determined as follows (Ni *et al.* 2009)

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where $k = 0.89$, is the Scherrer constant, λ is X-ray wavelength, β is the line broadening measured at half-height and θ is the Brag angle of the particles. The calculated size of the nanoparticle is about 31.66 nm.

The FT–IR spectra of nanoflake SrFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy composite were showed at Fig. 2. It was observed from Fig. 2a; that there was the peak at the 599.02 cm^{-1} (correspond to vibrations of the tetrahedral and octahedral sites for SrFe$_{12}$O$_{19}$) in each curve (Zhang *et al.* 2009). The peak of 574.55 cm^{-1} was related to *F-O* vibrations of Fe$_3$O$_4$. In Fig. 2b; the peaks at 1031 cm^{-1} and 1299 cm^{-1} attributed to the characteristic *S=O* symmetric and asymmetric stretching of the DBSA, the peak at 1158 cm^{-1} correspond to *C-O* bending of PEG, the peaks at 1450 cm^{-1} and 1537 cm^{-1} stretching of the quinoid and benzenoid rings, the peak at 3434 cm^{-1} correspond to *N-H* stretching mode of PPy.

Morphology analysis done by TEM and SEM. Figs. 3(a) and (b) show TEM images from SrFe$_{12}$O$_{19}$, which upholds nanoflake shape of strontium ferrite. These figures presented the
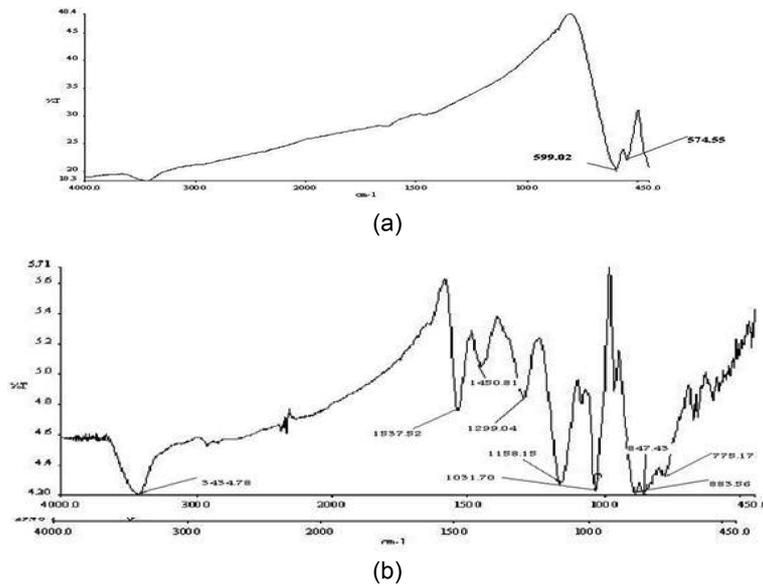
(a)

(b)

Fig. 2 The FT–IR spectra of (a) nanoflake SrFe$_{12}$O$_{19}$ and (b) PPy/SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$ /PEG composite

(a)   (b)
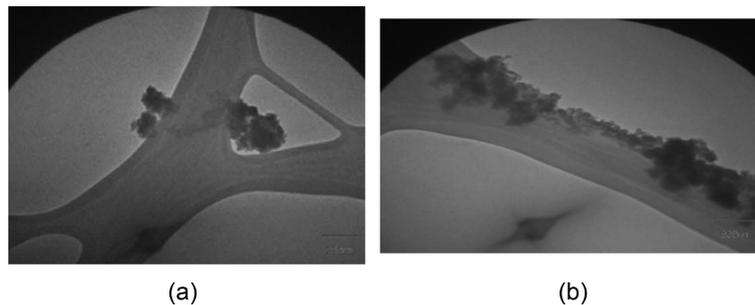
Fig. 3 TEM of nanoflake SrFe$_{12}$O$_{19}$ calcined at 850°C for 2 h

morphology of the sample that calcined at 850°C for 2 h. As was show in Figs. 4 (a-c) shows the nanoflake SrFe$_{12}$O$_{19}$ synthesized. Diameter of the flake SrFe$_{12}$O$_{19}$ before ultrasonication was about 180 nm (Fig. 4a) and after 12 h sonication was abuts 35 nm (Fig. 4b). Fig. 4c show that morphology nanocomposite multi core-shell SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy which synthesized by in situ polymerization method. That diameter obtained nanocomposite is about 47 nm. It was related to diameter of composites coating.

The magnetic properties of the nanoflake SrFe$_{12}$O$_{19}$ and nanoflake SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy composites were inspected by VSM. The magnetization under applied magnetic field for the nanoflake SrFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy composites exhibited a clear hysteretic behavior. The magnetic properties of nanomaterials summarized at Figs. 5(a-d) and Table 1. The magnetic properties of the nanoflake SrFe$_{12}$O$_{19}$ show that hard magnetization because its coercivity (H_c) is 4506 Oe. But after magnetic and polymeric multi core-shell structure, H_c was decreased. As show in Fig. 5, M_S and M_r nanocomposites were decreased, too. Because the PPy and PEG are nonmagnetic material, ferrite was magnetic material. The magnetic properties of

(a)
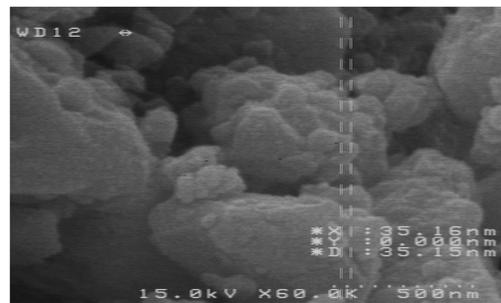
(b)

(c)

Fig. 4 The FE–SEM of (a) nanoflake $SrFe_{12}O_{19}$ before sonication, (b) nanoflake $SrFe_{12}O_{19}$ after 12 h sonication and (c) nanoflake composite $SrFe_{12}O_{19}/Fe_3O_4/PEG/PPy$

composites depended on not only the volume fraction of magnetic particles but also the demagnetization effect as the adding of the nonmagnetic material. On one hand, according to the formula $M_S = \varphi m_S$. (M_S represents the saturation magnetization of the composites; φ represents the volume fraction of magnetic particles, m_S represent the saturation magnetization of single particle). As the decrease of the volume fraction of magnetic particles, the saturation magnetization of the composites decreased. On the other hand, as the insulation effect became more evident. The demagnetization field became stronger. The two effects result to the decrease of M_S and M_r. In this paper H_c also decreased, because have nanoparticles paramagnetic
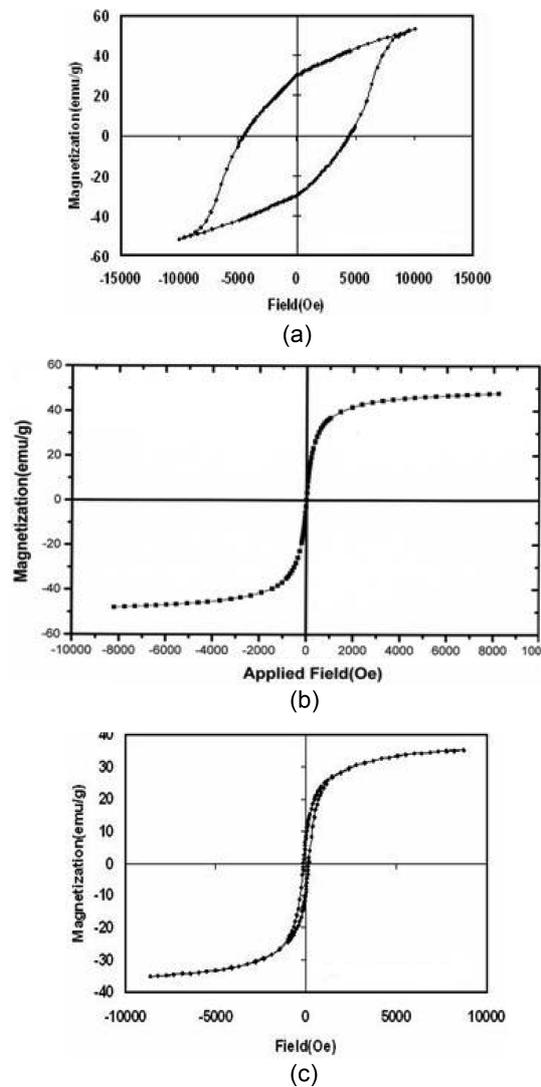
Fig. 5 Magnetic properties of samples (a) nanoflake SrFe$_{12}$O$_{19}$, (b) Fe$_3$O$_4$ nanoparticle, (c) core–shell SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$ and (d) nanocomposite SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy

properties, until this nanoparticles coated on the nanoflake SrFe$_{12}$O$_{19}$, H_c core–shell SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$ decreased. The change of the saturation magnetization and the coercivity can be attributed to the existence of Fe$_3$O$_4$ on the surface of SrFe$_{12}$O$_{19}$ nanoparticles which can result in the inter-particles interaction at the interface of two phases.

The electrical conductivity of SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG/PPy with 1:15 mass ratio SrFe$_{12}$O$_{19}$/Fe$_3$O$_4$/PEG to PPy was measured 0.58 Scm^{-1}. Conductivity lies on two aspects: microscopic conductivity and macroscopic conductivity. Microscopic conductivity depends upon the doping level, conjugation length and chain length. However, the macroscopic conductivity depended on some external factors such as compactness of the samples and molecular orientation.

4. Conclusions

Polypyrrole/nanoflake-$SrFe_{12}O_{19}$/Fe_3O_4/PEG composite was prepared by in situ polymerization method. Morphology of nanocomposite is also flaky. This nanocomposite has conductivity and magnetic properties. In addition, it was found that the magnetization under applied magnetic field for the as prepared composites exhibited a clear hysteretic behavior. It was found that M_S, M_r and H_c for the composites exhibited a decrease with addition shell on the previous core in any stage. Also this nanocomposite is soluble in some of organic solvent such as DMF and DMSO.

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