Surface modification of SiO_2 micro spheres by $NiFe_2O_4$ nanoparticles

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ABSTRACT

The preparation of SiO_2 microspheres using base catalyst assisted sol-gel process and their surface modification by $NiFe_2O_4$ nanoparticles through sonochemical process. The phase and surface morphology of the prepared sample is studied using X - ray diffraction (XRD) and scanning electron microscope images (SEM). The thermal behavior of the sample is analyzed using thermogravimetric and differential thermal analysis (TG/DTA). The pure and surface modified SiO_2 spheres with $NiFe_2O_4$ are analyzed from the SEM – energy dispersive spectroscopy (EDS) spectral and elemental mapping results.

Keywords: $SiO_2/NiFe_2O_4$ nanocomposite, sol-gel and sonochemical processes, XRD, TG-DTA, SEM-EDS

1 INTRODUCTION

Nanocrystalline $NiFe_2O_4$ is a important magnetic material and it is useful in various applications like magnetic data storage, catalysis, ferrofluids, sensors, actuators as well as biomedical applications such as targeted drug delivery, hyperthermia, etc.[1-4]. Recently, $NiFe_2O_4$ is also used as an anode material in lithium ion battery [5-6]. The better performance of the anode material relies on its nanostructure and the structural stability at various physical and chemical environments. In order to improve the number of charge and discharge cycles, the capacity and the structural stability of the anode material, some modifications such as substitution, coating, etc., are implemented to the existing anode materials. Silica is found to be the best host matrix available in various forms to grow the crystals in and around the SiO_2. Synthesis process plays a vital role in the development of nanocrystalline and nanocomposite material, Sol-gel process is an efficient technique to prepare glass ceramic, monoliths, nanostructured powders with control over purity, composition and easy introduction of doping elements at lower temperature [7]. Hence, in this paper, we report the preparation of SiO_2 spherical particles using base catalyst assisted sol-gel process and the surface modification of SiO_2 spheres with $NiFe_2O_4$ nanoparticles by sonochemical process using ethylene glycol. The synthesized sample is characterized using XRD, FTIR, TG-DTA, SEM-EDS techniques to confirm the formation of $NiFe_2O_4$ nanocrystals over SiO_2 spherical particles.

2 EXPERIMENTAL SYNTHESIS

The surface modification of SiO_2 particles with $NiFe_2O_4$ nanoparticles involves the preparation of SiO_2 spheres using base catalyst assisted sol-gel process and the $NiFe_2O_4$ surface modification over SiO_2 using sonochemical process. Analytical reagent (AR) grade precursor chemicals tetraethylorthosilicate (TEOS), ethanol, ammonia solution, nickel nitrate tetrahydrate, ferric nitrate nanohydrate were used for the synthesis of surface modified SiO_2 spheres with $NiFe_2O_4$. The required amount of TEOS, for 5 gm end product, is mixed with ethanol and distilled water and slow addition of NH_4OH as a base catalyst under sonication for 5 minutes resulted the formation of SiO_2 particles. The TEOS and water molar ratio is maintained at 1:10. The TEOS and ethanol volume ratio is maintained at 1:14. Equal volume ratio of NH_4OH is added as base catalyst. The above solution is stirred for 3 hr for uniform growth of SiO_2 particles. The obtained SiO_2 particles are collected, washed with ethanol and finally dried at 333 K. The SiO_2 particles phase and morphology were analyzed using XRD and SEM-EDS techniques. The surface modified SiO_2 spheres with $NiFe_2O_4$ nanoparticles for the composition of 10% $NiFe_2O_4$ – 90% SiO_2 is prepared using sonochemical process. The dried SiO_2 particles are dispersed in ethanol medium and the required nickel nitrate tetrahydrate, ferric nitrate nanohydrate dissolved in 20 ml of ethylene glycol and it is added to the SiO_2 dispersed spherical particles under sonication for 30 minutes. The mixture is further stirred at 353 K for 5 hr to perform the uniform coating of $NiFe_2O_4$. The dried particles are calcined at different temperatures and characterized using XRD, TG-DTA, SEM-EDS techniques. The powder X- ray diffraction patterns were recorded using panalytical X'pertPRO diffractometer with Cu K_α radiation of wavelength λ=1.5418 A^o for the fine powdered surface modified SiO_2 spheres with $NiFe_2O_4$ is calcined at different temperatures. Approximately, 15 mg of polymeric intermediate of surface modified SiO_2 spheres with $NiFe_2O_4$ particles are placed in an alumina crucible and heated at a rate of 10 K per minute from 333 K to 1173 K under nitrogen atmosphere and the differential thermal analysis and thermal gravimetric curve was recorded using setaram Labsys TG-DTA instrument. The surface modified SiO_2 spheres with $NiFe_2O_4$ obtained at 673 K are sprayed over the carbon tape and coated with gold are used for taking SEM-EDS images and elemental mappings using Hitachi SN-3400 N SEM instrument.

3 RESULT AND DISCUSSION

3.1 XRD

Fig. 1 and 2 show the X - ray diffraction patterns of pure SiO_2 dried at 333 K and surface modified SiO_2 samples with $NiFe_2O_4$ obtained at different temperatures. From fig. 1, it is observed that the peak free diffraction pattern with broad peak centered at 22^o corresponds to the amorphous phase of SiO_2.

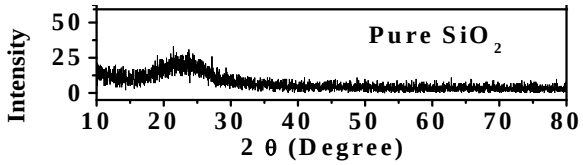

Fig. 1. X- ray diffraction pattern of pure SiO_2 spheres obtained at 333 K

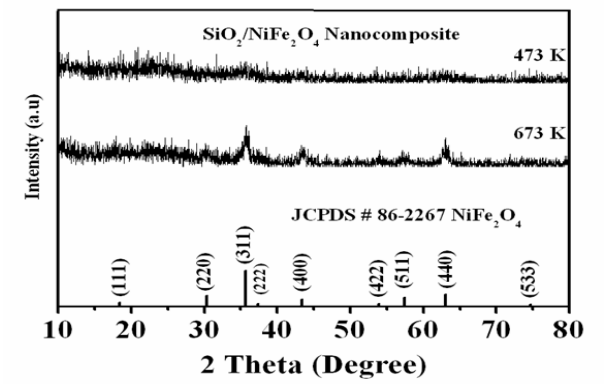

Fig. 2. X- ray diffraction patterns surface modified SiO_2 sample with $NiFe_2O_4$ calcined at different temperatures.

From fig. 2, the surface modified SiO_2 spheres with $NiFe_2O_4$ obtained at 473 K showed the diffraction patterns of $NiFe_2O_4$ and it confirms that the $NiFe_2O_4$ starts crystallizing over SiO_2 spherical particles around 673 K. Formation of crystalline $NiFe_2O_4$ phase is confirmed by comparing the observed diffraction XRD patterns with the standard JCPDS 86-2267 data. A broad reflection centered at 22^o confirms the amorphous phase of SiO_2 and it is not disturbed during the heat treatment. The crystallite size of $NiFe_2O_4$ was calculated using Scherrer's formula and it is found to be 10 nm for the sample calcined at 673 K. Hence, the XRD results confirm the formation of $NiFe_2O_4$ nanocrystals over the amorphous SiO_2.

3.2 FTIR

Fig. 3 shows the FTIR spectra of surface modified SiO_2 sample with $NiFe_2O_4$ obtained at 673 K. From figure 3, the IR bands are observed in the region 3420, 1630, 1100, 950, 800, 600, 472 and 418 cm^{-1}. The band at 3440 cm^{-1} corresponds to the stretching vibration of O-H molecules and it is associated with the presence of water in the sample. The IR band at 1630 cm^{-1} is due to the Si-OH vibrations.

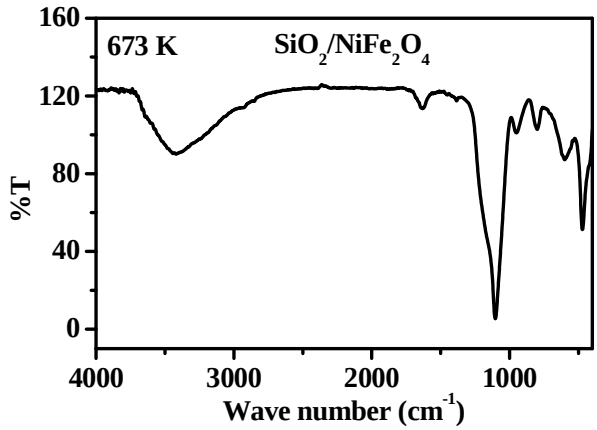

Fig. 3. FTIR spectrum of surface modified SiO_2 samples with $NiFe_2O_4$ calcined at 673 K

The absorption band at 1100 cm^{-1} is assigned for ≡Si-O-Si≡ of the SiO_4 tetrahedron and a shoulder band at 1180 cm^{-1} corresponds to the asymmetric stretching bonds of Si-O-Si. The IR band observed at 950 cm^{-1} corresponds to Si-O-Fe and Si-O-H stretching. The absorption band at 472 cm^{-1} corresponds to Si-O-Si and O-Si-O bending mode [7- 9]. The bands at 1110, 800 and 472 reflect and confirm the formation of silica network. The observed two peaks at 599 cm^{-1} and 410 cm^{-1} were attributed to the vibrational modes of metals in tetrahedral and octahedral sites of ferrites [10-11]. Hence, the FTIR results confirm the formation of $NiFe_2O_4/SiO_2$ nanocomposites.

3.3 TG/DTA

Fig. 4 shows the TG-DTA thermograms of surface modified SiO_2 sample with $NiFe_2O_4$. In fig. 4, the TG-DTA curves showed one endothermic peak and two exothermic peaks. The first endotherm between 309 and 411 K corresponds to the evaporation water molecules and ethanol from the sample with a weight loss of 6%. The exotherm between 411 and 486 K corresponds to decomposition of nitrates from the precursor sample with a weight loss of 16.2 %. The decomposition of ethylene glycol is observed in the form of exotherm along with the crystallization of $NiFe_2O_4$ between 550 and 674 K with a weight loss of 9.7

%. The sample obtained at 673 K is free from organic impurities, which are also confirmed from FTIR results.

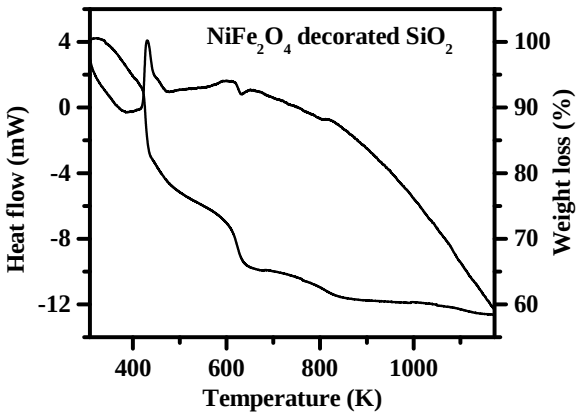

Fig. 4. TG-DTA thermogravimetric curve for the $NiFe_2O_4$ polymeric resin coated SiO_2 particles.

3.4 SEM-EDS

Fig. 5 shows the SEM images of pure SiO_2 particles, which are found to be spherical in shape and the size is varied from 200 to 300 nm. Fig. 6 and 7 show the SEM-EDS spectrum and elemental mappings of pure SiO_2 particles and the SEM-EDS result confirm the formation of pure SiO_2 particles. Fig. 8 shows the SEM images of surface modified SiO_2 spheres with $NiFe_2O_4$ obtained at 673 K. From fig. 8, it is observed that the size of the $NiFe_2O_4$ nanoparticles is found to be ~ 40 nm, which are coated over the SiO_2 spheres of size 200 to 300 nm. Fig. 9 and 10 show the SEM-EDS spectrum and elemental mappings of surface modified SiO_2 spheres with $NiFe_2O_4$ obtained at 673 K showed the presence and uniform distribution of Ni, Fe, Si and O elements in the surface modified SiO_2 spheres with $NiFe_2O_4$. Hence, SEM images and SEM-EDS results of pure and surface modified SiO_2 spheres with $NiFe_2O_4$ confirm the formation of $NiFe_2O_4$ nanoparticles over SiO_2 spheres.

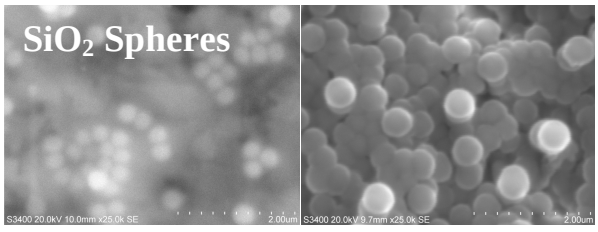

Fig. 5. SEM images of pure SiO_2 spheres

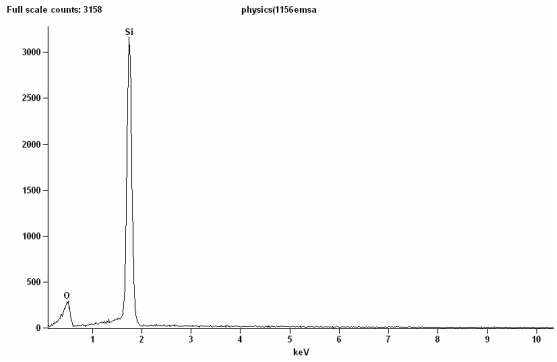

Fig. 6. SEM-EDS elemental spectrum of SiO_2 spheres.

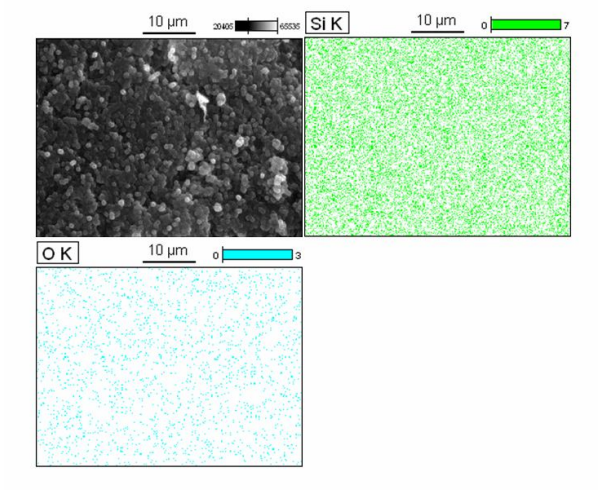

Fig. 7. SEM image and SEM-EDS elemental mappings of pure SiO_2 spheres obtained at 333 K

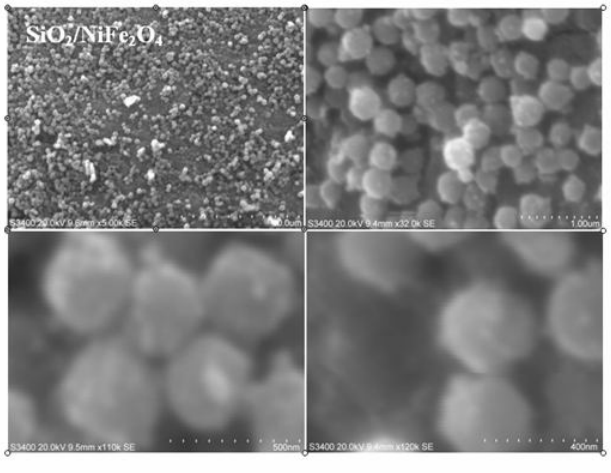

Fig. 8. SEM images of surface modified SiO_2 spheres with $NiFe_2O_4$ obtained at 673 K.

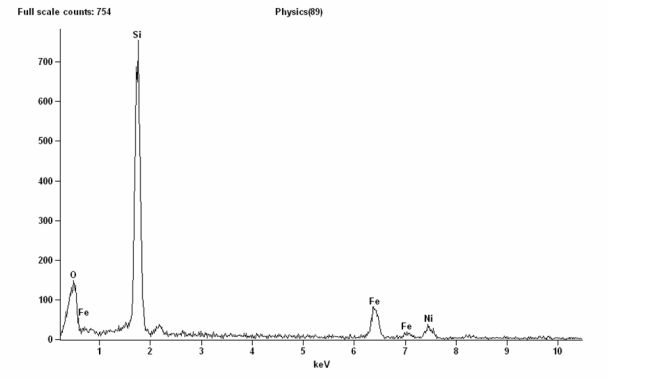

Fig. 9. SEM-EDS elemental spectrum of surface modified SiO_2 spheres with NiFe2O4 obtained at 673 K.

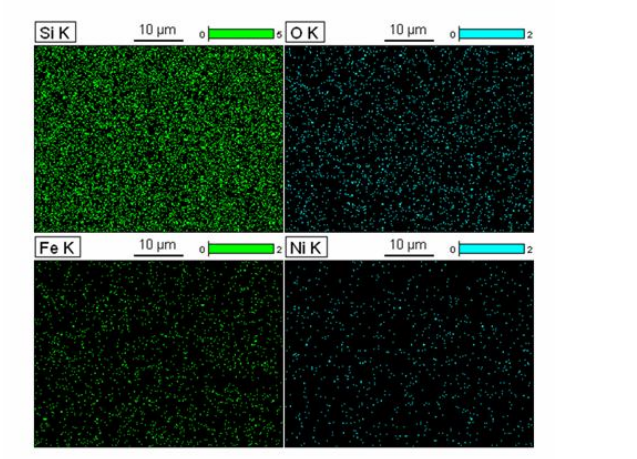

Fig. 10. SEM image and SEM-EDS elemental mappings of surface modified SiO_2 spheres with NiFe2O4 obtained at 673 K.

4 CONCLUSIONS

The uniform spherical SiO_2 particles were prepared successfully by base catalyst assisted sol-gel process. The surface modified SiO_2 spheres with $NiFe_2O_4$ were obtained using sonochemical process. The phase and micro structures of pure SiO_2 and surface modified SiO_2 spheres with $NiFe_2O_4$ were confirmed respectively from XRD and SEM images. The SEM images showed the size of SiO_2 spheres are in the range of 200 to 300 nm and the $NiFe_2O_4$ nanoparticles are ~ 40 nm. TG-DTA results confirm the crystallization of $NiFe_2O_4$ and the complete removal of impurities from the sample. The SEM-EDS spectral and elemental mapping results confirmed the coating of $NiFe_2O_4$ nanoparticles over SiO_2 spheres and also the distribution of Si, Ni, Fe and O elements in the surface modified SiO_2 spheres with $NiFe_2O_4$.

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