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## Synthesis and Characterization of Composite Nanoparticles for Imaging†

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Dual functions of magnetic and fluorescent properties were created in composite particles that incorporated magnetite ( $Fe_3O_4$ ) nanoparticles (MNPs) as particle cores and fluorescent pyrene in particle shells of poly lactate-co-glycolide (PLGA). The  $Fe_3O_4$  nanoparticles were prepared by co-precipitation method and surface modified with oleic acid. MNPs were prepared by co-precipitating iron(II) and iron(III) in alkaline solution and then treating under hydrothermal conditions. Surface modification of magnetic nanoparticles by organic surfactants is known to provide them with solubility in organic solvents. The structural, magnetic and adsorption properties of iron oxide nanoparticles are derived in the presence of oleic acid as the capping agents. The surfactants provide them with excellent stability and solubility in organic solvents like toluene or chloroform. The presence of capping agents or high reaction temperatures favours the formation of smaller nanoparticles. The adsorption of the surfactants (chemisorption) was identified with FT-IR spectroscopy. Then, the magnetite particles were coated with the pyrene/PLGA by emulsion-diffusion method. The composite particles prepared had both magnetic and fluorescent properties. The present work proposes a method for synthesizing the dually functional particles, which have a core-shell structure. The particles in this work consist of an inner core of  $Fe_3O_4$  nanoparticles and a hybrid shell of polymer and organic dye. A basic technique of this work is polymer coating on  $Fe_3O_4$  nanoparticles. The prepared nanoparticles were characterized by scanning electron microscopy, particle size analyzer, X-ray diffraction, Gauss meter, Fourier transform infrared spectroscopy and fluorescence spectroscopy. The nanoparticles have great potential in diagnostic magnetic resonance imaging.

Key Words: Magnetic nanoparticles, Magnetic and fluorescent property, Core-shell structure.

#### **INTRODUCTION**

Nanoparticles are mesostructures with some unique properties compared to bulk materials on one hand and atomic or molecular structures on the other. Compared to the bulk materials with constant physical and chemical properties regardless of their sizes, the nanoparticles have size-dependent properties for example, super paramagnetism in magnetic nanoparticles.

Composite microspheres with dual functions of magnetic and fluorescent properties have recently received much attention in various fields such as cell labeling, biosensing and in the drug delivery system<sup>1-6</sup>.

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is a common ferrite that has a cubic inverse spinel structure and exhibits unique electric and magnetic properties based on the transfer of electrons between Fe<sup>2+</sup> and Fe<sup>3+</sup> in the octahedral sites. When the diameter of Fe<sub>3</sub>O<sub>4</sub> particles is in nano scale, Fe<sub>3</sub>O<sub>4</sub> regarded as single magnetic domain has the superparamagnetic property<sup>7,8</sup>.

### **EXPERIMENTAL**

All materials were purchased from Merck except PLGA which was purchased from Lakeshore. Pluronics F-127 was purchased from Sigma Aldrich. All the materials were used without further purification.

**Synthesis of superparamagnetic iron oxide nanoparticles (SPION):** Chemical reaction of Fe<sub>3</sub>O<sub>4</sub> precipitation is given by

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \longrightarrow Fe_{3}O_{4} + 4H_{2}O$$

According to the results of thermodynamic modeling of this system, a complete precipitation of  $Fe_3O_4$  is expected in pH value of 7.5-14 while maintaining a molar ratio of  $Fe^{2+}/Fe^{3+}=1:2$  under a non-oxidizing environment.

**Coating SPIONS with oleic acid:** After the precipitation of SPIONS, oleic acid (40 %, w/w of formed magnetite) was added dropwise during 10 min and the flask was heated for 0.5 h. After drying, a black powder was obtained.

Formation of SPIONs encapsulated with poly lactate-co-glycolide: The synthesized SPIONS were encapsulated by emulsification-diffusion method. The SPION was dispersed in 5 mL CHCl<sub>3</sub> by sonication for 15 min with a bath type sonicator. In a separate vessel PLGA (150 mg) was sonicated in 10 mL of DCM for 15 min to make solution. Aqueous ammonia (1:1) was added to PLGA solution to bring the pH to 10 and the mixture was further sonicated for 5 min. To the resulting PLGA solution, previously made SPION dispersion was added drop-wise and then sonicated for 2 h. The mixture was stirred mechanically at 70 °C for 20 h.

Embedding pyrene on poly lactate-co-glycolide coat: To the PLGA coated SPION mixture, ca. 5 mg of pyrene was added and homogenized for 5 min while chloroform was added. It was then ultrasonicated for 15 min and kept for 8 h magnetic stirring at 70 °C. Finally, pyrene gets embedded on the PLGA coat of the SPIONS.

**Detection method:** The size of the particles was determined using particle size analyzer, Microtrac Inc. Model Bluewave S4521.

The morphology of the synthesized SPIONS was determined using SEM (scanning electron microscope) JEOL JSM 6701 f field emission scanning electron microscope. (FESEM) The crystallinity of SPIONs was diffraction (XRD) model Bruker D8 Focus.

Fluorescence of the composite nanoparticles was determined using fluorescence spectrometer Model LS 45 Perkin Elmer. The magnetic property of the synthesized SPIONs was checked using bar magnet. Elemental analysis to confirm the presence of iron is done using EDAX (energy dispersive analysis of X-ray). The magnetic field strength of the SPIONs was found by GAUSS meter.

The absorbance was determined by UV-visible spectrometer from Perkin-Elmer. The presence of coating on SPIONs was determined by FTIR (Fourier transform infrared spectroscopy) from Perkin Elmer.

# RESULTS AND DISCUSSION

**Particle size analysis report:** The particle analysis report shows that, the mean hydrodynamic radii of the SPIONS to be  $8 \mu$  with narrow size distribution (Fig. 1).

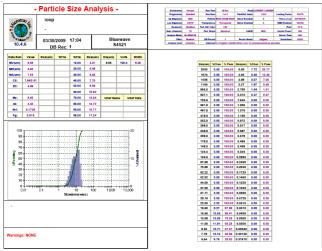


Fig. 1. Particle size analysis of the size distribution of iron oxide

**GAUSS meter:** At a thickness of 30 mm, the magnetic property was cut off and a gauss value of 8 was measured for uncoated SPIONs. This shows that at a very low Gauss value is sufficient to sensitize the uncoated SPIONS.

SEM images is shown in Fig. 2.

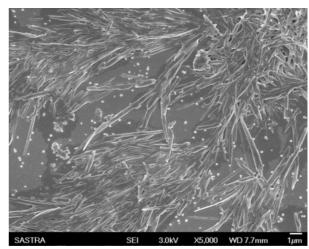


Fig. 2. SEM image showing spherical SPIONS among the salt crystals

**Diffraction analysis:** The XRD shows two peaks in the  $2\theta$  range of  $30\text{-}35^\circ$  which shows that the SPIONS are crystalline in nature. These two peaks are the characteristic peaks for pure  $Fe_3O_4$  (Fig. 3, Table-1).

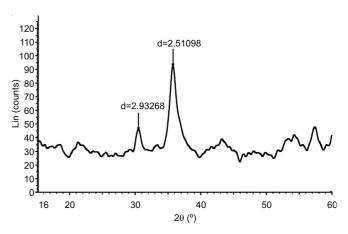


Fig. 3. Diffraction analysis report for uncoated SPIONS

TABLE-1			
Peak No.	2θ	d value (Å)	Intensity (%)
1	30.456	2.93268, 45	49.4
2	35.730	2.51098	92.8

**Fluorescent spectrometry:** The excitation wavelength was kept at 390 nm and the fluorescent emission spectrum was obtained which showed a high intensity peak around 360 nm which is emitted from the pyrene embedded on PLGA (Fig. 4).

**FTIR spectrum of uncoated SPIONS:** The presence of peak at 1589 is attributed to the carboxylate unit vibration modes, shows that oleic acid is bound through the carboxylate anions (Fig. 5).

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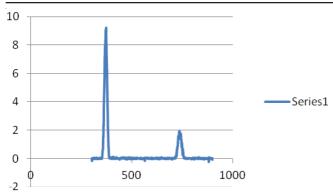


Fig. 4. Fluorescent spectra for pyrene embedded SPIONS

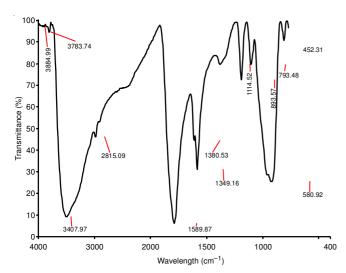
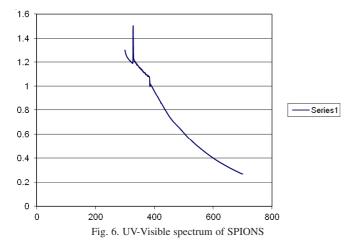


Fig.5 FTIR of oleic acid coated SPIONS

**UV-Visible absorbance analysis:** UV-VIS absorbance of SPIONS using Na (Fig. 6).



Superparamagnetic iron oxide nanoparticles were prepared by the co-precipitation method from ferrous and ferric ion solutions with a molecular ratio of 1:2. The uncoated SPION prepared by the controlled chemical co precipitation process can be expected as magnetite. Based on the results from XRD, it can be clearly seen that the particles do not show sharp diffraction peaks corresponding to extended crystalline structure. Instead, a broad band appears in each spectrum.

#### Conclusion

In summary, innovations in nanoparticle technology over the last several years have provided many benefits to imaging. Composite particles with a magnetic core and fluorescent polymer shell was prepared by emulsion-diffusion polymerization in the presence of pyrene. The fluorescent spectra showed there is no interference between the magnetic component in the core and the fluorescent particle in the shell. The amount of pyrene added to the system was 10 mg. Thus, these magnetic nanoparticles can be very interesting for magnetic resonance imaging to control the drug delivery localization after a local administration in tumors yielding a better treatment efficacy and lesser treatment induced side effects.

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