

Zinc-Doped Ferrites As Novel Integrated Magnetofluorescent Imaging Probes

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Statement of Purpose: Magnetic-fluorescent nanomaterials are of great interests due to their promising applications in chemistry, biology and medicine [1]. Because of dual magnetic and fluorescent properties, these nanocomposites open up the unique opportunity of integrated molecular imaging of pathological markers with magnetic resonance imaging (MRI) and optical imaging methods. Multimodal molecular probes that exhibit superparamagnetism are typically equipped with additional complementary functionality such as luminescence. In order to attain this multifunctionality, dye molecules or optically active nanoprobe such as quantum dots are physically incorporated into the magnetic nanocomposite system [2]. This process not only requires complex synthesis and rational assembly but also increases the room for inhomogeneity along with being potentially toxic. In this research, we investigate nanosized zinc ferrite, $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ (Zn-SPIOs) as novel integrated multifunctional nanoprobe with high MRI sensitivity and fluorescent properties.

Methods: Zn-SPIOs nanoparticles were synthesized chemically using zerovalent diethyl zinc (Et_2Zn) as a Zn source with iron acetylacetonate ($\text{Fe}(\text{acac})_3$). Typically a mixture of $\text{Fe}(\text{acac})_3$ (0.83 mmol), along with 1,2-hexadecanediol (5 mmol), oleic acid (3 mmol) and hexadecylamine (3 mmol) was heated at 150 °C for 30 min under argon in a three-neck flask. Et_2Zn (0.17 mmol), was then injected into the reaction and temperature was raised to 325°C and held at that temperature for additional 30 min to 2 hrs. After the mixture was cooled to room temperature, ethanol was added and the Zn-SPIOs were isolated by centrifugation and then re-dispersed in hexane. Material characterization was performed using XRD, TEM, UV-Vis, FTIR, steady state and lifetime Fluorescence spectroscopy, SQUID and AGM.

Results: Addition of Zn to Fe_3O_4 results in formation of a mixed oxide $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ (with $x = 0, 0.14, 0.26, 0.34, 0.76$). The capability of Zn-SPIOs (5 nm) as a sensitive contrast agent had already been published by us in a recent paper [3]. Magnetic measurements on (8-10 nm) Zn-SPIOs indicate the increase in saturation magnetization (Ms) value from 19 emu/g for Fe_3O_4 to 48 emu/g for $x = 0.26$ Zn-SPIOs. The spinel structure of Fe_3O_4 has two cation binding sites: T_d sites and O_h sites. During Zn^{2+} substitution, when $x < 0.5$, replacement of Fe^{3+} (in Fe_3O_4 lattice) by Zn^{2+} at the T_d sites causes a redistribution of Fe^{3+} at the T_d and O_h site. This results in increased net magnetic moment due to the reduced antiferromagnetic interaction between the Fe^{3+} ions at T_d and O_h sites. The emission and excitation spectra on the as synthesized Zn-SPIOs in hexane were compared with Fe_3O_4 and ZnO excited both at 325 nm. Zn-SPIOs exhibits a broad peak centred at 390 nm while ZnO exhibits a broad peak centred at 425 nm. This result is rather surprising as there have been no reports in literature

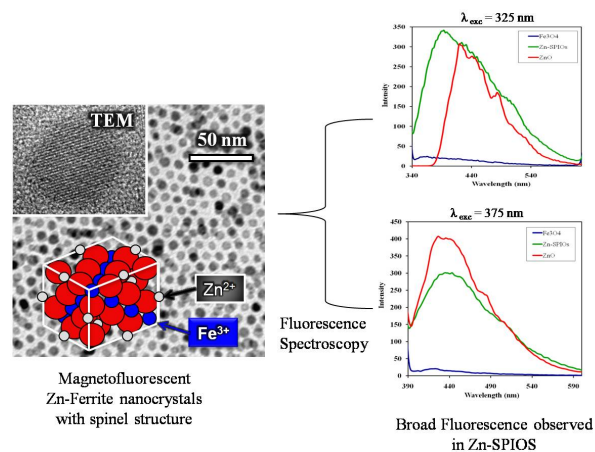


Figure 1: HRTEM and TEM image showing single crystalline behavior of Zn-ferrite (Zn-SPIOs). Fluorescence behavior of Zn-SPIOs at $\lambda_{\text{ex}} = 325$ and 375 nm respectively.

experimentally or theoretically of ferrites displaying any luminescent properties. Changing the excitation to 375 nm resulted in the shift of the broad peak to 440 nm indicating that the fluorescence behaviour is due to the presence of multiple defects on the nanoparticle surface. Lifetime measurements conducted using a N_2 dye laser (coumarin 440) with $\lambda_{\text{ex}} = 410\text{--}480 \text{ nm}$ and $\lambda_{\text{em}} = 480 \text{ nm}$ were fitted with a biexponential law leading to lifetimes of 3 and 9 ns.

Conclusions: The origin of fluorescence in Zn-SPIOs is attributed to the structural defects in the nanocrystal lattice. These defects could be due to the presence of interstitial zinc and/or oxygen vacancies within the crystal lattice [4]. Extensive material characterization indicates that the Zn-SPIOs are analogous to Fe_3O_4 while their optical properties follow the trends of ZnO (a wide band gap semiconductor). Further tuning of the emission spectrum will be accomplished by changing the electronic structure at the surface by introducing various capping ligands. Thus we report for the very first time the integration of both magnetic and optical properties in Zn-SPIOs leading to a dual functional magnetofluorescent material.

References:

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