



Fatty acid as structure directing agent for controlled secondary growth of CoFe_2O_4 nanoparticles to achieve mesoscale assemblies: A facile approach for developing hierarchical structures



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ABSTRACT

Mesoscale hierarchical assemblies have emerged out as a new class of structures between fine dimension nanoparticles and bulk structures, having distinctly different physical properties from either side. Controlling the self-assembly process of primary nanoparticles and subsequent secondary growth mechanism is the key aspect for achieving such ordered structures. In this work, we introduce a new insight on achieving hierarchical assemblies of CoFe_2O_4 nanoparticles based on the temporal stability of the primary nanoparticles, where, the growth and stability of the primary particles are controlled by using oleic acid. It is found that the developed particles, at a critical concentration of oleic acid, prefer a secondary growth process, rather than promoting their individual growth. Domination of the attractive hydrophobic interaction over steric repulsion among the primary particles at this critical concentration of oleic acid is found to be the key factor for the initial aggregation of the primary particles, which eventually leads to the formation of spherical hierarchical assemblies via oriented attachment. It is also realized that the extremely well or poor stability conditions of the primary particles do not allow this secondary growth process. Estimated values of Co^{2+} distribution factor show that the cation distribution factor of CoFe_2O_4 system is not affected by the nature of dominant growth processes, when these are controlled. Interestingly, magnetic measurements reflect the stronger interparticle interaction in the hierarchical system and high magnetic moment values at low magnetic field.

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1. Introduction

Role of surfactants in controlling the growth and stability of materials in the nanometric regime is crucial for the development of high quality nanoparticles. Recently, surfactants have also been projected as the structure directing agents in the formation of assembled nanostructures with fascinating properties [1,2]. Hierarchical assembly, a class of such structures, can be achieved by self-assembling of nanometric subunits, where the growth of the subunits and the evolution of the assembled structures can occur simultaneously or at different time scales [3]. In this type of multistep growth processes, surfactants can control the growth of the subunits and their temporal stability for the formation of assembled structures. However, identifying and understanding the

critical conditions for achieving such structures are very important. The effect of a surfactant on controlling the growth and stability of nanoparticles basically depends on the binding strength of its hydrophilic head group, size of the hydrophobic tail group and the surfactant's molecular equivalent to precursor [4]. It is known that fatty acids possess both strong binding affinity towards metal ions like Fe, Co etc. through carboxylate (COO^-) head group and a long hydrophobic chain, for which they have been used for the controlled growth and stability of magnetic nanoparticles [5–7]. Therefore, utilization of fatty acids may have lots of scopes for controlling the growth and temporal stability of magnetic nanoparticles in such a way that the hierarchical assemblies of magnetic nanoparticles can be achieved at the end of the synthesis process. However, to the best of our knowledge, no works have been done in past, showing fatty acids as the structure directing agent for obtaining such secondary mesostructures.

Hierarchical assembly formation of magnetic nanoparticles has been emerged as a promising bottom up approach for achiev-

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ing the next generation of functional materials [8]. A few works on the hierarchical assembly formation of magnetic nanoparticles can be found in the literatures. Polyol method was used to develop spherical assemblies of magnetite nanoparticles, where poly(vinylpyrrolidone) was shown to be responsible for the formation of such structures; however the complete formation mechanism was not fully realized [9,10]. Role of π - π interaction among the primary magnetite nanoparticles in directing their uniform spherical assembly formation was studied, where magnetite nanoparticles were capped with 2-carboxyterthiophene (TTP-COOH) monolayer [11]. However, weak interaction among the particles in this assembly system was not adequate to make them stable in different conditions, prior to the applications. Binder effect of water molecules and the capping effect of alcohol groups over primary nanoparticles were shown to be responsible for the formation of Co_3O_4 iso-oriented spherical assemblies [12]. A ternary surfactant combination was found to act as the mortar for the formation of similar assemblies of magnetite nanoparticles in a solvothermal reduction reaction [13]. Functional polystyrene was also investigated as the mortar for magnetic nanoparticles assemblies. Iso-oriented assemblies of CoFe_2O_4 with both spherical and cubical structures were developed based on a boiling bursts technique on a high-boiling point solvent by periodic injection of hexane utilizing a mixed metal oleate precursor [14]. A normal micelles route using sodium dodecylsulfate (SDS) as surfactant was also used to form spherical secondary structure [15].

Here, oleic acid, an unsaturated fatty acid has been used for achieving hierarchical assemblies of cobalt ferrite nanoparticles. The used synthesis method is a modified co-precipitation route, where, the addition of an extremely polar solvent, Dimethyl sulfoxide (DMSO) with water made the oleic acid miscible in the reaction. The concentration of oleic acid is varied systemically so as to understand how oleic acid can control the growth of the primary particles and their subsequent aggregation behaviour to form hierarchical assemblies. Moreover, the importance of DMSO in obtaining spherical assemblies has been explained. Structural information obtained from the SAXS (Small-angle X-ray scattering) have been used along with direct evidences obtained from TEM (Transmission Electron Microscopy) to probe different length scales and to reveal the nature of interparticle correlations in all the developed systems. Observed morphological characteristics of the hierarchical assembly system are also corroborated to its collective magnetic properties.

2. Experimental section

2.1. Materials

Ferrous sulphate heptahydrate ($\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$, 99%), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 97%), Dimethyl sulfoxide (DMSO, 99%), Oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, 98%), Tetramethylammonium hydroxide (TMAOH, 25% concentration in aqueous solution) were purchased from Merck. All chemicals were used directly without further purification. Milli-Q water was used throughout all the reactions.

2.2. Synthesis of CoFe_2O_4 assemblies and nanoparticles

CoFe_2O_4 nanoparticles and assemblies were developed using a modified co-precipitation method. For this, 6 mmol $\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ and 3 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were taken to 45 ml mixed solution of water and DMSO (1:3.5 of water and DMSO). A measured amount of oleic acid was added and subsequently TMAOH was added drop wise to the above salt solution with slow stirring. The resultant solution was refluxed at 145 °C for 30 min with slow stirring. It

was observed that after the addition of 7 ml TMAOH drop wise the colour of the solution gradually transformed from greenish to blackish, which confirmed the nucleation and growth of cobalt ferrite nanoparticles. Three samples, CF1, CF2 and CF3 were prepared with three concentrations of oleic acid, 0.07 M, 0.14 M and 0.21 M respectively, while keeping unchanged the other reaction parameters. The concentrations of oleic acid were calculated in reference to the total volume of water and DMSO mixture solution. At the end of the refluxing process, the black precipitates were separated by addition of ethanol and subsequent centrifugation. The precipitate was washed multiple times with excess amount of high grade ethanol and dried in vacuum overnight.

2.3. Characterizations

The phase and crystallinity of the prepared nanosystems have been characterized using X-ray diffraction technique. The XRD patterns of the samples were recorded in the powder form at room temperature in the 2θ range 10–80° using a diffractometer (Rigaku) with intense $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). A pattern decomposition procedure using a pseudo-Voigt profile shape function and subsequent single-line analysis based on the equivalent Voigt representation was used for the determination of average crystallite size and lattice strain (Eqs. (1) and (2) respectively) [16].

$$\langle D_{\text{XRD}} \rangle = \frac{\lambda}{\beta_c^f} \cos\theta \quad (1)$$

$$e = \frac{\beta_g^f}{4\tan\theta} \quad (2)$$

where λ is the wavelength of the X-ray, β_c^f and β_g^f are the integral breadths of the Cauchy and Gaussian fit of the structurally broadened profile and θ is the Bragg angle. High resolution transmission electron microscopy (HRTEM) were taken using a JEOL 2100 electron microscope operating at an accelerating voltage of 200 kV. For HRTEM, the powder samples were dispersed in *n*-hexane followed by ultra-sonication for 10 min. After that a few drops of that dispersion were taken on a carbon coated copper grid and dried at gentle temperature. The size distributions of the nanoparticles were estimated based on the statistics of 200 particles chosen from multiple images at bright field mode. Small angle X-ray scattering (SAXS) of the powder samples were performed using a laboratory based point collimation small-angle scattering instrument. The scattered intensities $I(q)$ were recorded as a function of scattering vector transfer $q (=4\pi \sin\theta/\lambda)$, 2θ being the scattering angle and λ the X-ray wavelength (1.54 Å). The intensities were corrected for sample absorption [17]. The nature of the surface capping over the nanoparticles was characterized with Nicolet Fourier transforms infrared (FTIR) spectrometer. Thermogravimetric analysis was carried out using a thermogravimetric analyzer (TGA-50, Shimadzu), where, the samples were heated in N_2 atmosphere with flow rate of 20 ml/min. The heating rate was 30 °C/min and the temperature range of measurement was 50–650 °C. The Raman spectra of the samples were recorded using a Laser Micro Raman System (LabRam HR) with Ar^+ laser excitation source of wavelength 514.5 nm. Magnetic measurements such as isothermal magnetization and temperature dependent magnetization measurements were carried out using a re-liquefier based 9T Quantum Design Physical Property Measurements system (PPMS) equipped with a vibrating sample magnetometer (VSM). Temperature dependent magnetizations were measured using ZFC (zero field cooling) and FC (field cooling) protocols. For ZFC, the sample was cooled from room temperature to 5 K in absence of magnetic field and subsequently magnetization was measured with the application of probe field (500 Oe) while warming the sample from 5 K to 350 K. The similar procedure was applied for the FC also, except here the cool-

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