

Electronic Supplementary information

Greener Saponin Induced Morphologically Controlled Various Polymorphs of Nanostructured Iron oxide Materials for Biosensor Applications

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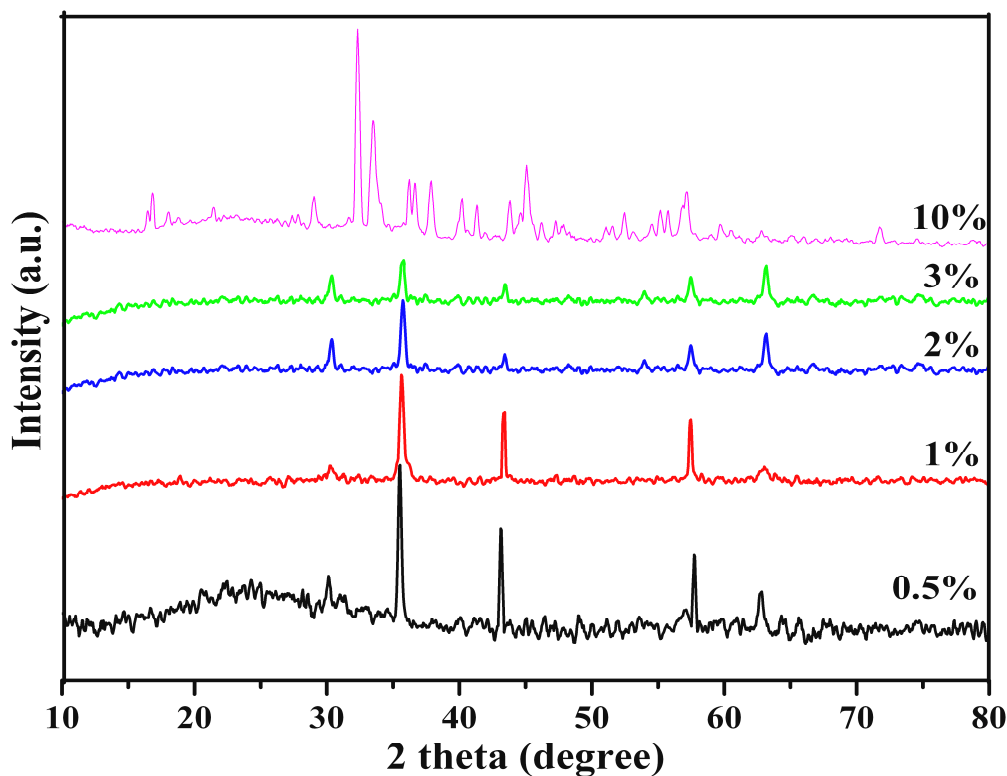


Fig. S1 XRD patterns iron oxide nanostructures synthesized at various concentration of bio-surfactant at 30 °C in 2 hrs.

All the reflections peaks can be indexed to a cubic spinel phase of JCPDS No. γ -Fe₂O₃ Maghemite, JCPDS No. 89-5892 and pure rhombohedral phase of α -Fe₂O₃ Hematite, JCPDS No. 33-0664. The γ -Fe₂O₃ nanoribbon grows through oriented attachment particularly along the $\langle 311 \rangle$ direction, which gives rise to relatively intense diffraction peak of the (311) plane up to 3% bio-surfactant (Fig. S1†). However, the iron oxide samples synthesized from increased bio-surfactant concentration of 10%, the samples show pure α -Fe₂O₃ phase of spherical nanoparticles. The intensity of the diffraction peaks is a size dependent behavior, the aspect ratio of the nanoribbon increases with increasing concentration of bio-surfactant and the diffraction pattern shrinks.¹

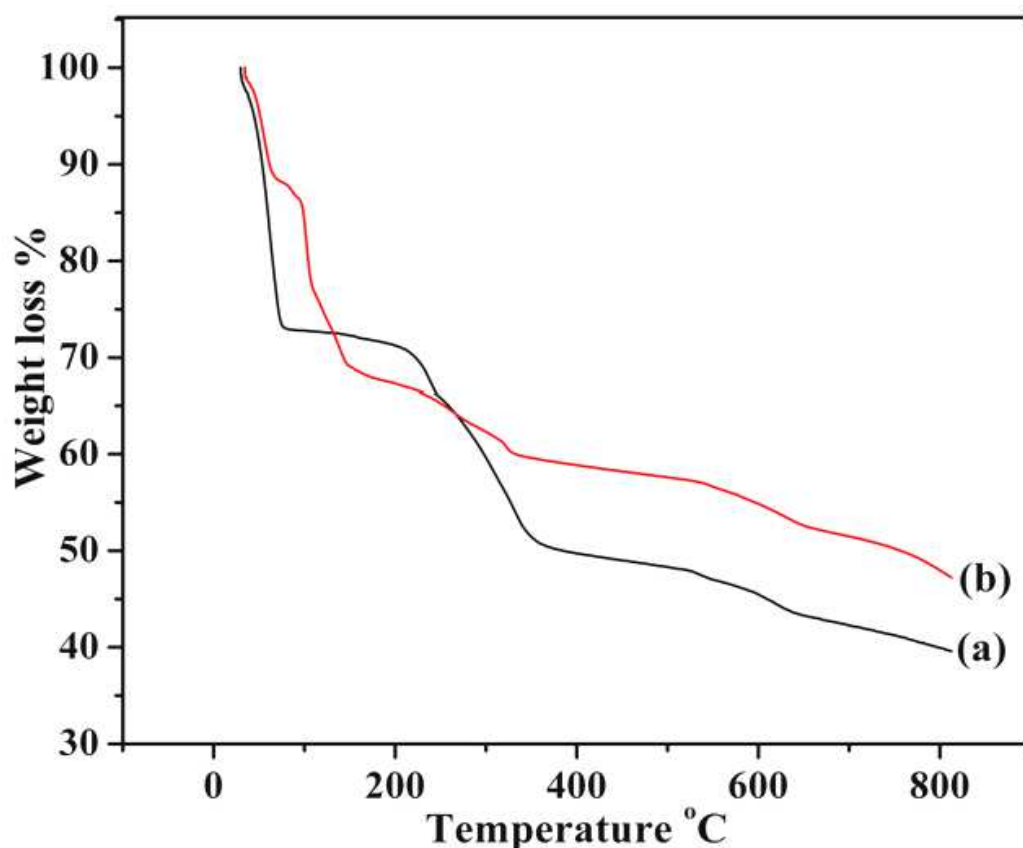


Fig. S2 TGA curves iron oxide nanostructures synthesized at 2% concentration of bio-surfactant (a) Fe₃O₄ nanospheres at 30 mins (b) γ-Fe₂O₃ nanoribbon at 2hrs.

The TGA curves show that the iron oxide nanostructures have weight loss steps from room temperature to 800 °C under air atmosphere. The first stage of weight loss between 30-150 °C corresponded to the removal of water weakly adsorbed to the surface of the iron oxide nanostructures (Fig. S2†). The Fe₃O₄ nanospheres synthesized at 30 minutes show 27.4% weight loss below 110° C resulting from the removal of adsorbed water which is only 11.3% for the 120 minutes grown γ-Fe₂O₃ nanoribbon. This peculiar interesting behavior may be due to the surface availability (finite size effect) to anchoring the water molecule. A notable weight gain has been observed for Fe₃O₄ nanospherical particles at 200 °C, which is due to the oxidation behavior of Fe₃O₄ to γ-Fe₂O₃, which is overlapped with the decomposition of the bio-surfactant.² Above 330 °C, the weight of the precursors or no longer changes, which indicates that the stable residue could reasonably be ascribed to the pure γ-Fe₂O₃ phase.

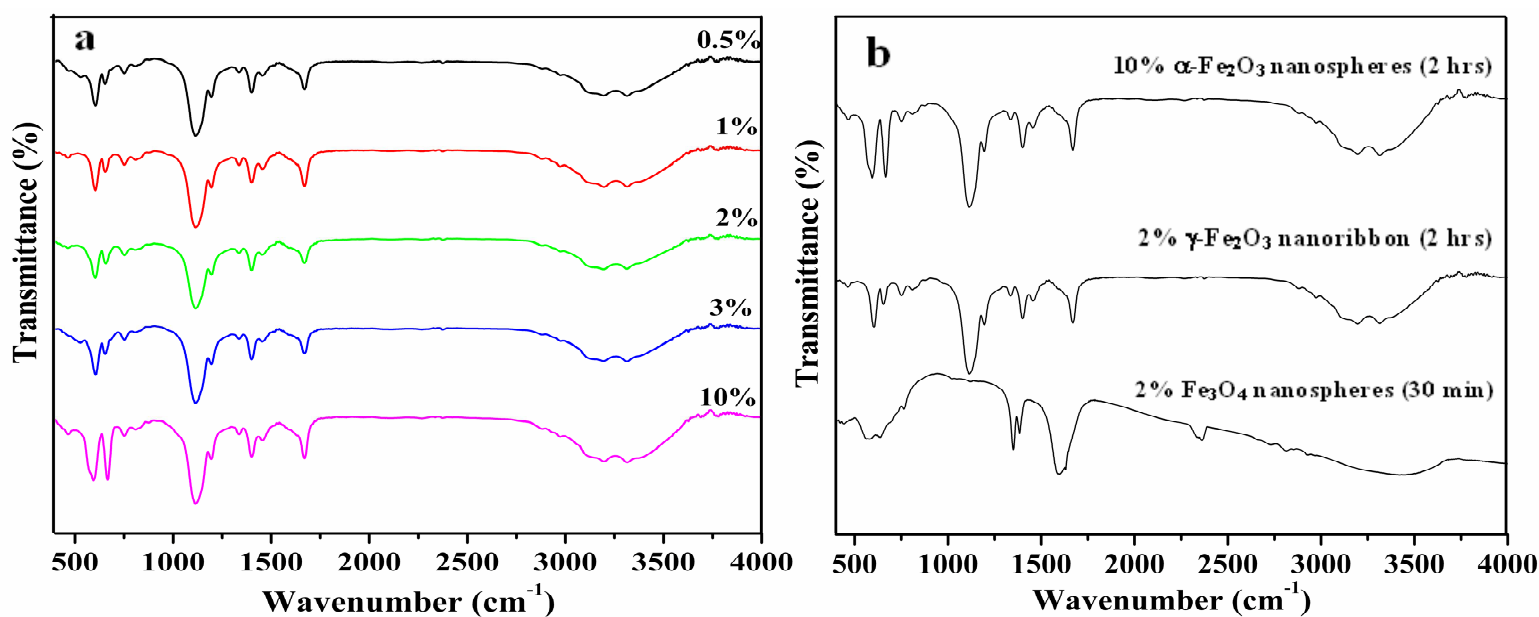


Fig. S3 (a) FT-IR spectra of iron oxide nanostructures synthesized at various concentration of bio-surfactant at 2 hrs (b) FT-IR spectra of different polymorphs of iron oxide nanostructures.

The FT-IR spectra of Fe_3O_4 nanospheres, $\gamma\text{-Fe}_2\text{O}_3$ nanoribbons and $\alpha\text{-Fe}_2\text{O}_3$ nanospheres synthesized at different % (0.5%, 1%, 2% 3% and 10%) of bio-surfactant and various time intervals have been given in the Fig. S3†. The intense and broad band appeared in the region $3200 - 3600\text{cm}^{-1}$, it can be noted that the iron oxide surfaces are readily bound with hydroxyl groups in an aqueous environment. The absorption band below 700 cm^{-1} is attributed to Fe-O stretching vibration. The absorption peaks in $\alpha\text{-Fe}_2\text{O}_3$ are consistent with the main peaks of $\alpha\text{-Fe}_2\text{O}_3$, in which two peaks at 582 cm^{-1} and 476cm^{-1} indicate the formation of $\alpha\text{-Fe}_2\text{O}_3$. This blue shift can be attributed to the lattice strain developed as a result of the particle size reduction.³ The Fe_3O_4 nanospheres and $\alpha\text{-Fe}_2\text{O}_3$ nanospheres lead to a blue shift because of the increased lattice strain generated by the surface tension. The blue shift of the samples indicates that the particles have an average diameter of 10 and 12 nm. Because of our nanoribbons have relative larger diameter; the shift seems too large. Considering that there may be small nanoparticles trapped in the samples, a certain amount of the blue shift is possibly contributed by the nanoparticles.

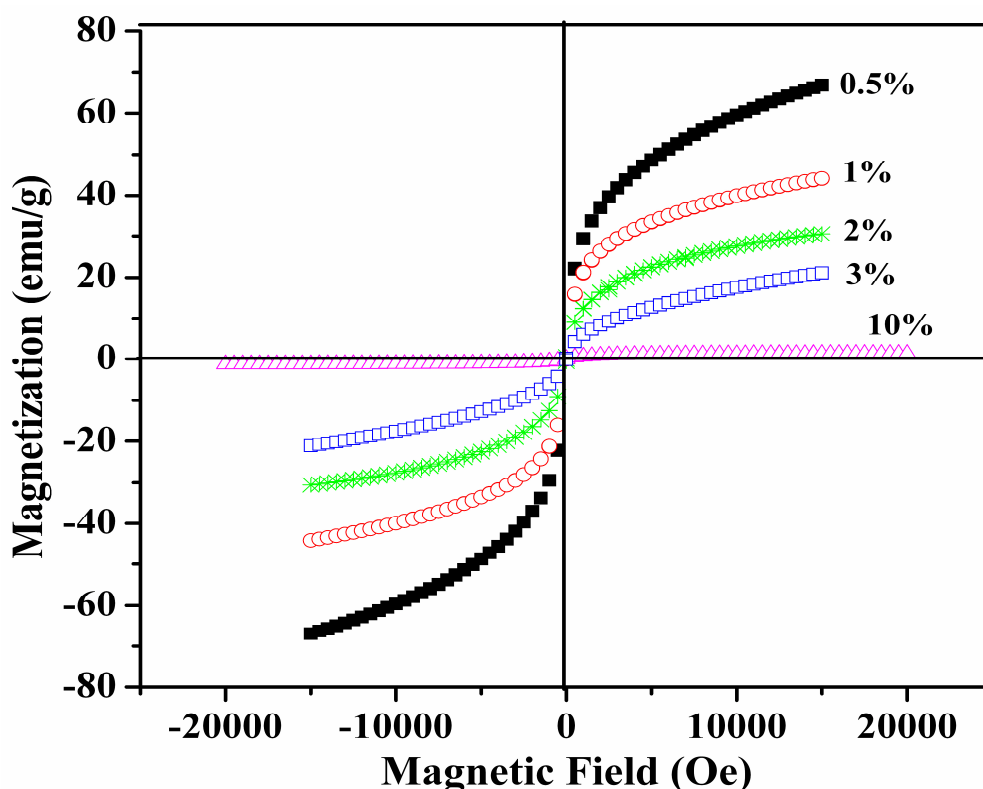


Fig. S4 Magnetization curves of iron oxide nanostructures synthesized at various concentration of bio-surfactant at 30 °C.

The M_s value of iron oxide nanostructures decreases with increasing concentration of bio-surfactant. It is known that in nanosized iron oxide with lower magnetization is associated with surface atoms which may not be coherently spin-coupled with the inner atoms (due to easy axis anisotropy and/or surface disorder) or which are bound to surfactant molecules.⁴ Our results can be explained well by this concept. The surface to-volume ratio (S/V) is higher in a sphere than in the ribbon, and it decreases further as the ribbons grow longer. It follows that the measured M_s values scale down with increasing the particle S/V , as they indeed reflect the proportional increase in the surface phase, which is characterized by a reduced magnetization (Fig. S5†).

References

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