Electronic Supplementary Information

Fe$_3$O$_4$-Mn$_3$O$_4$ nanocomposites with moderate magnetism for *in-vitro* cytotoxicity studies on macrophages

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ESI 1. Absorption spectra of Fe$_3$O$_4$ NPs and Fe$_3$O$_4$−Mn$_3$O$_4$ NCs

The absorption spectral features of Fe$_3$O$_4$ NPs and Fe$_3$O$_4$-Mn$_3$O$_4$NCs in the solid state and determination of their band gap are described in Fig. SI 1. Panel A shows the solid state absorption spectra of Fe$_3$O$_4$ NPs and Fe$_3$O$_4$−Mn$_3$O$_4$NCs. The electronic absorption spectrum of Fe$_3$O$_4$ NPs shows three well-defined regions: the first portion below 400 nm, the second from 400 to 550 nm and the third one finishing at 800 nm. The first portion is assigned to the allowed O^{2-} → Fe^{2+} and O^{2-} → Fe^{3+} charge transfer transitions, and the last two can be reasonably related to d-d crystal-field transitions, ^{3}E$_g$(G) ← ^{3}T$_{1g}$, ^{3}A$_{2g}$(F) ← ^{3}T$_{1g}$, ^{3}A$_{2g}$(G) ← ^{3}T$_{1g}$, ^{3}T$_{2g}$(H) ← ^{3}T$_{1g}$, ^{3}T$_{1g}$ (H) ← ^{3}T$_{1g}$, and ^{3}E$_g$(H) ← ^{3}T$_{1g}$, on octahedral Fe^{3+} species (J. Tang, M. Myers, K. A. Bosnick and L. E. Brus, *J. Phys. Chem. B*, 2003, **107**, 7501−7506). Upon addition of manganese precursor and subsequent hydrolysis, the absorption spectrum corresponding to
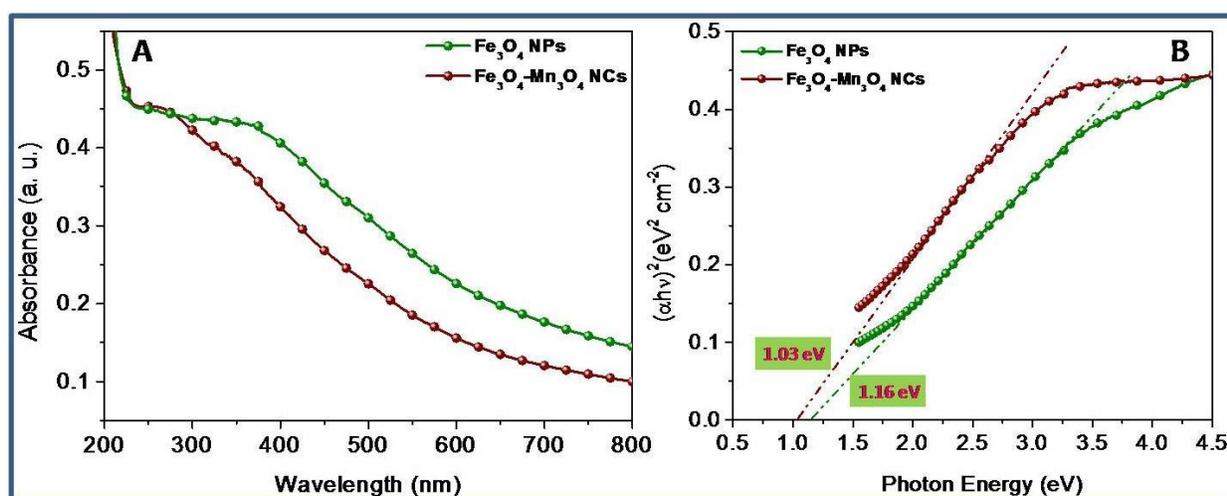
Fig. SI 1. (a) Absorption spectra in the solid state and (b) plot of (αhv)^2 as a function of hv of Fe$_3$O$_4$ NPs and Fe$_3$O$_4$−Mn$_3$O$_4$ NCs.

Fe$_3$O$_4$ NPs become perturbed indicating the electronic interaction amongst the individual components in the formation of nanocomposites (H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. Sun, *Nano Lett.*, 2005, **5**, 379–382). The original color of Fe$_3$O$_4$ particles is brown as seen in the present experiment and that of Mn$_3$O$_4$ particles is yellowish brown, while the resulting Fe$_3$O$_4$-Mn$_3$O$_4$ nanocomposites is reddish brown. This suggests that the finally formed Fe$_3$O$_4$-Mn$_3$O$_4$ nanocomposites have inherited the colorimetric character of Fe$_3$O$_4$ nanoparticles. The direct band gap energy (E$_g$) of the Fe$_3$O$_4$ NPs and Fe$_3$O$_4$–Mn$_3$O$_4$ NCs could be determined by fitting the absorption data to the direct band gap transition equation as (S. Tsunekawa, T. Fukuda and A. Kasuya, *J. Appl. Phys.,* 2000, **87**, 1318–1321),

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{1}$$

where, α is the absorption co-efficient, $h\nu$ the photon energy and A a constant. The absorption coefficient (α) is defined as: $\alpha = 2.303\ A/L\ c$, where, A is the absorbance of the sample, c the loading of sample (g L^{-1}), L the path length (= 1 cm). From the profiles showing the plot of $(\alpha h\nu)^2$ as a function of $h\nu$ (panel B), the estimated direct band gap of the Fe$_3$O$_4$ NPs and Fe$_3$O$_4$–Mn$_3$O$_4$ NCs was found to be 1.16 eV and 1.03 eV respectively; these values are considerably different from the reported value (~0.1 eV) of bulk Fe$_3$O$_4$ (B. Gilbert, J. E. Katz, J. D. Denlinger, Y. Yin, R. Falcone and G. A. Waychunas, *J. Phys. Chem. C*, 2010, **114**, 21994–22001).

ESI 2. Raman spectrum of Fe$_3$O$_4$-Mn$_3$O$_4$ NCs

The room temperature Raman spectrum of Fe$_3$O$_4$–Mn$_3$O$_4$ nanocomposites on silicon substrate with excitation at 488 nm (2.55 eV) of 5 mW air cooled Ar$^+$ laser is shown in Fig. SI 2. It is well established in the literature that the Raman spectrum of Mn$_3$O$_4$ (C. M. Julien and M. Massot, *J. Phys.: Condens. Matter*, 2003, **15**, 3151–3162) exhibits five phonon peaks: a (triply degenerate) T$_{2g}$ symmetry mode at 290 cm^{-1}, a (doubly degenerate) E$_g$symmetry mode at 320 cm^{-1}, T$_{2g}$ symmetry modes at 375 cm^{-1} and 479 cm^{-1}, and a (singly degenerate) A$_{1g}$ symmetry "breathing" mode at 660 cm^{-1} while the Raman spectrum of Fe$_3$O$_4$ (M. Kim, X. M. Chen, Y. I. Joe, E. Fradkin, P. Abbamonte, and S. L. Cooper, *Phys. Rev. Lett.*, 2010, 104, 136402 1–3) exhibits a prominent band centered near 670 cm^{-1} associated with the A$_{1g}$ phonon mode of Fe$_3$O$_4$ with inverse spinel structure. In the present experiment, weaker signals located at 311, 368 and 511
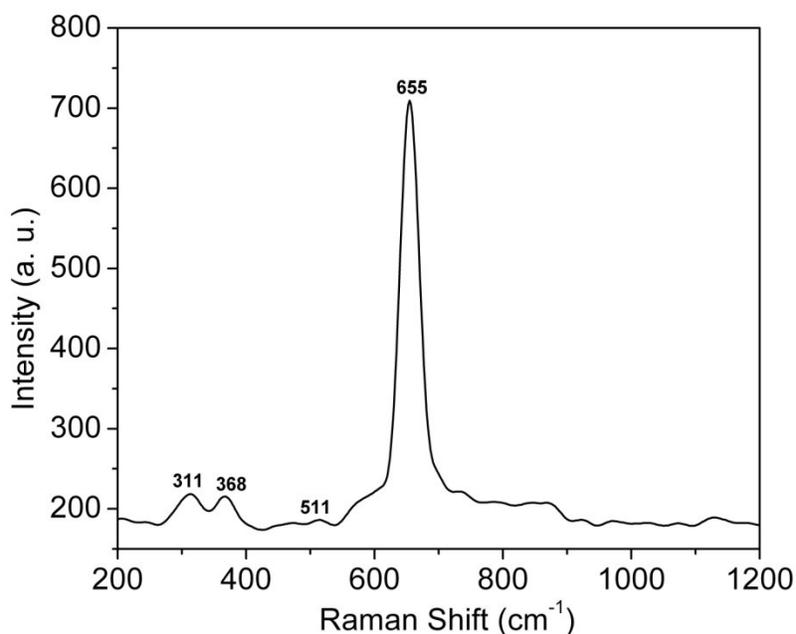
Fig. SI 2. Raman spectrum of Fe_3O_4-Mn_3O_4 nanocomposites

cm^{-1} and strong signal at 655 cm^{-1} are seen. It is, therefore, apparent that the peak positions are, substantially, shifted to that of the original positions which indicates the formation of Fe_3O_4—Mn_3O_4 nanocomposites.

ESI 3.Thermogravimetric analysis of Fe_3O_4 -Mn_3O_4 nanocomposites

Thermogravimetric analysis (Fig. SI 3) of the as-dried powder sample shows two weight loss steps in the curve: 1.9 wt% loss corresponding to the water desorption (up to 200 °C), and a weight loss of 8.7 wt % over 200—800 ℃ as a result of the decomposition of the polymer, verifying that the polyethylene glycol molecules employed for the stabilisation of Fe_3O_4 nanoparticles are, even, incorporated into the nanocomposites (H. —P. Cong and S. —H. Yu, *Adv. Funct. Mater.*, 2007, **17**, 1814–1820).
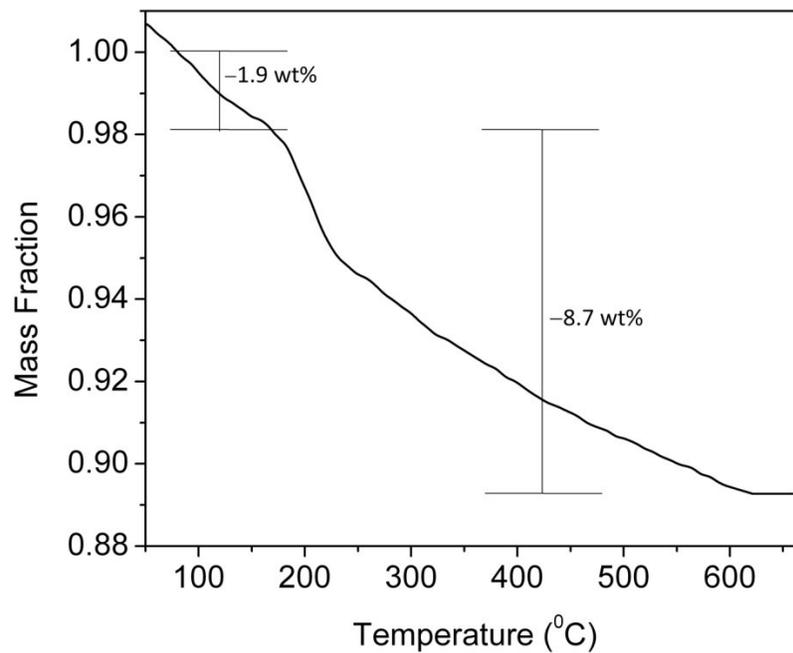
Fig. SI 3. Thermogravimetric analysis of Fe_3O_4–Mn_3O_4 nanocomposites as-dried in air