# † Electronic Supporting Information

## Quaternary ammonium bearing hyper-crosslinked polymer encapsulation on $Fe_3O_4$ nanoparticles

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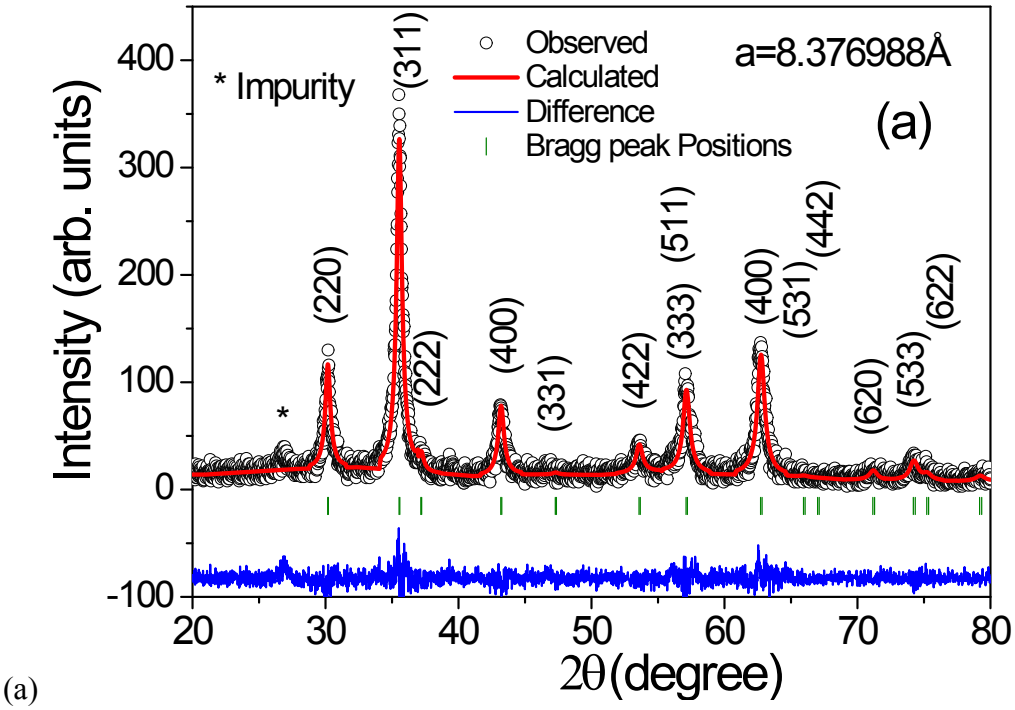
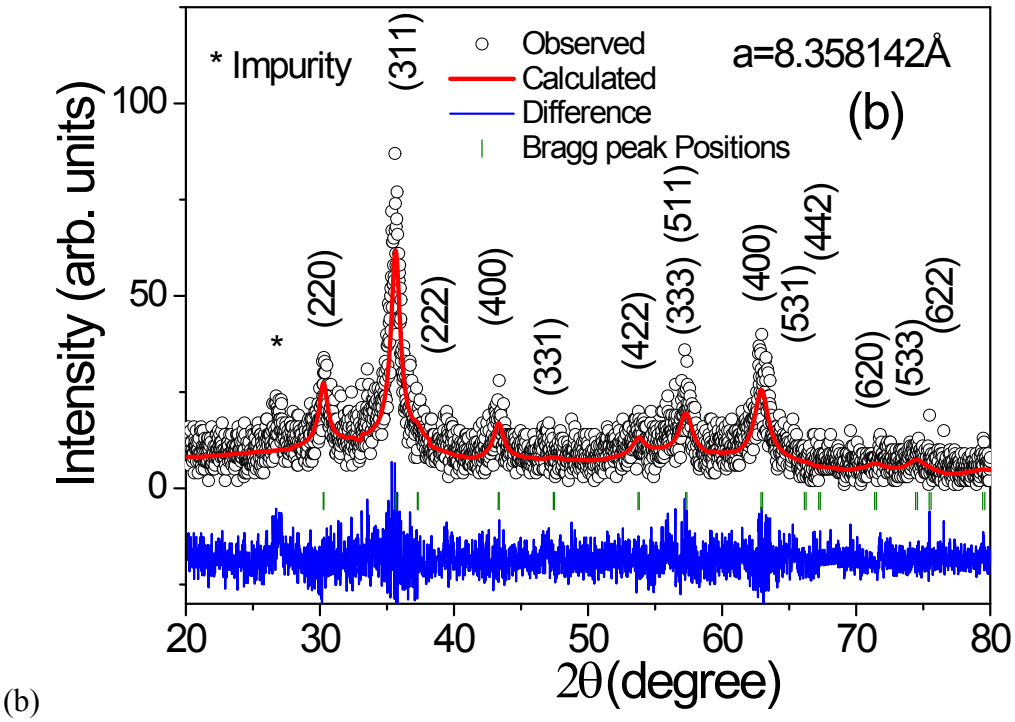
**Fig. S1** Rietveld refined X-ray diffraction patterns of $Fe_3O_4$ particles prepared by co-precipitation method using $Fe^{2+}$ salt (a) and 1:2 mol proportions of $Fe^{2+}$ and $Fe^{3+}$ salts (b).




(a)




(b)

**Fig. S2** VSM magnetization curves for the Fe3O4 particles (MNP) coated with TEOS, TEOS+APTES, and APTES.

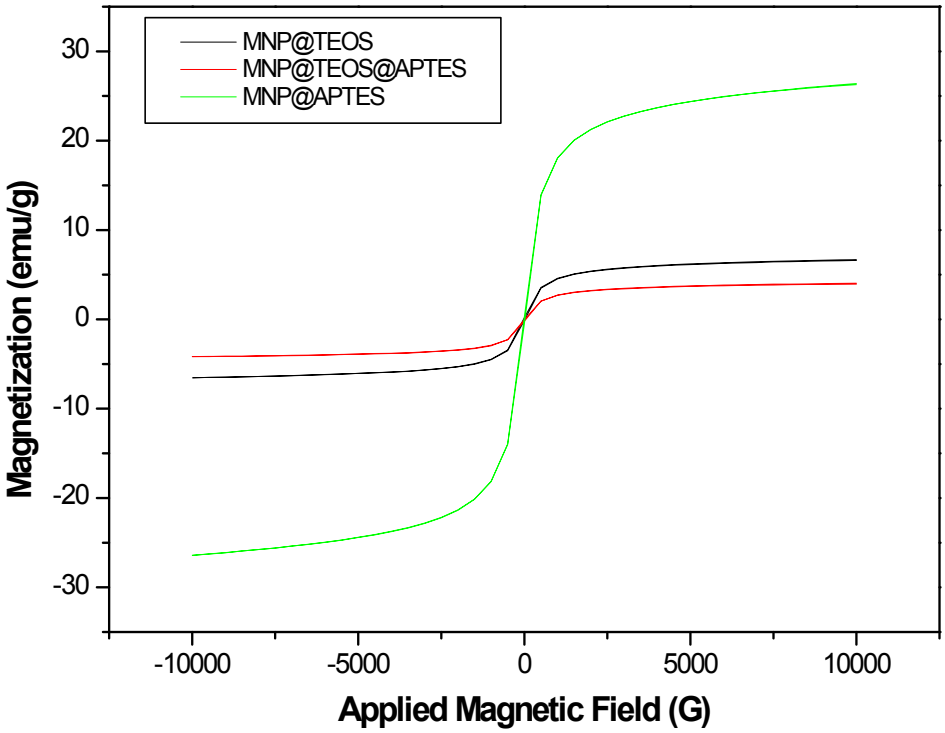
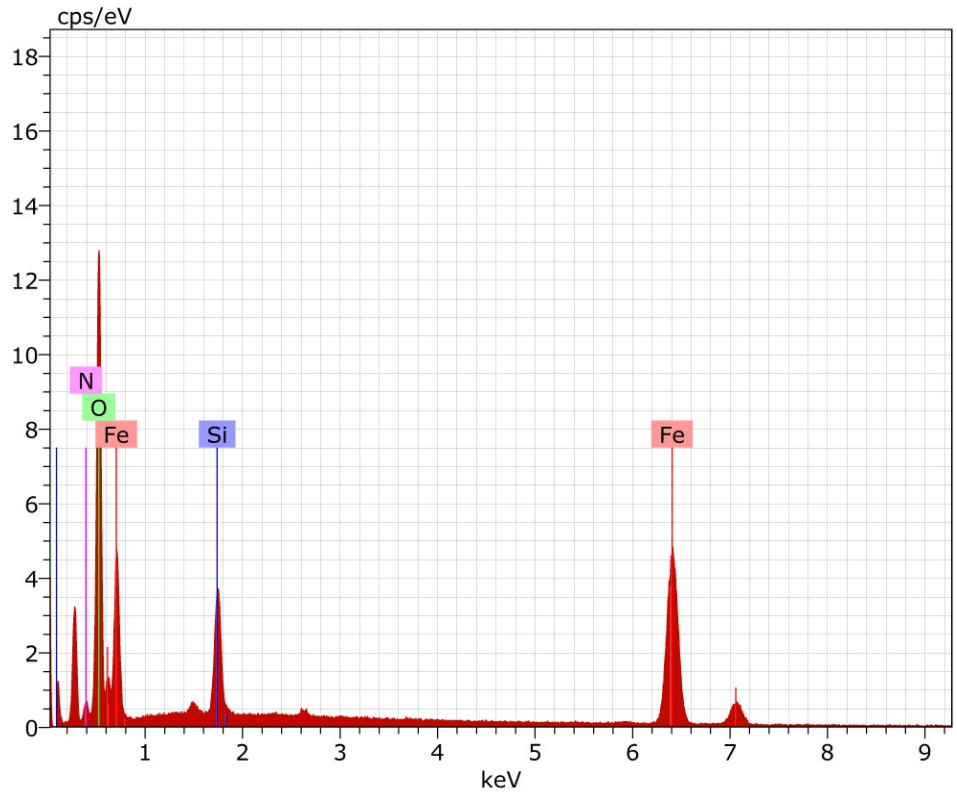


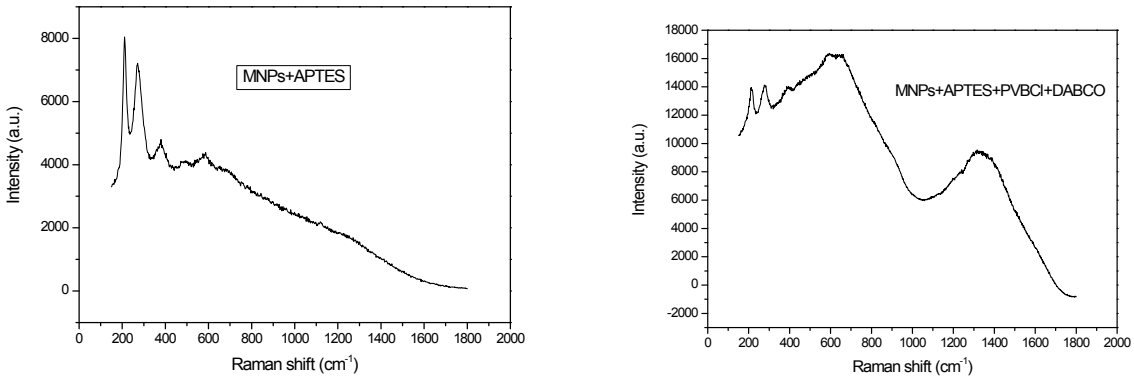
**Fig. S3** EDS spectrum of $Fe_3O_4$@PVB-DABCO-DBO showing the presence of expected elements.




Spectrum: A 282

| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error (1 Sigma) [wt.%] |
|---|---|---|---|---|---|---|
| Fe | 26 | K-series | 51.36 | 48.42 | 20.25 | 1.55 |
| O | 8 | K-series | 32.19 | 30.35 | 44.29 | 3.81 |
| C | 6 | K-series | 14.75 | 13.91 | 27.04 | 2.06 |
| Si | 14 | K-series | 4.80 | 4.52 | 3.76 | 0.23 |
| N | 7 | K-series | 2.97 | 2.80 | 4.67 | 0.59 |
| | | Total: | 106.07 | 100.00 | 100.00 | |

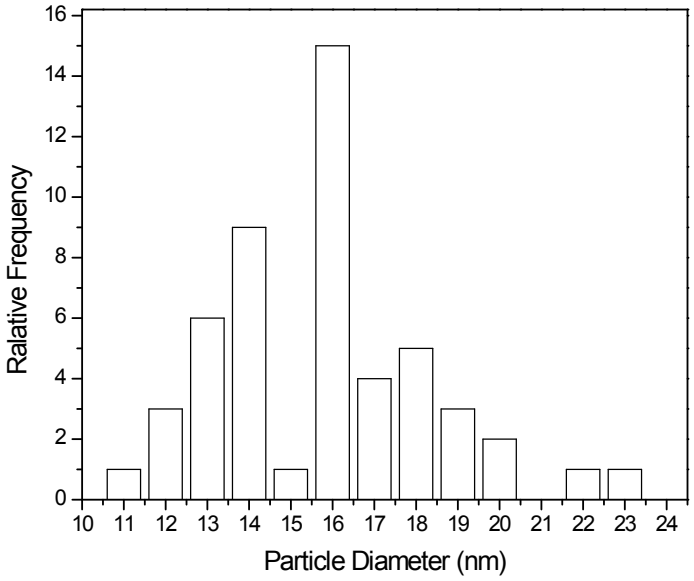
**Fig. S4** Raman spectra of APTS coated $Fe_3O_4$ (a) and $Fe_3O_4$@PVB-DABCO-DBO (b) particles.



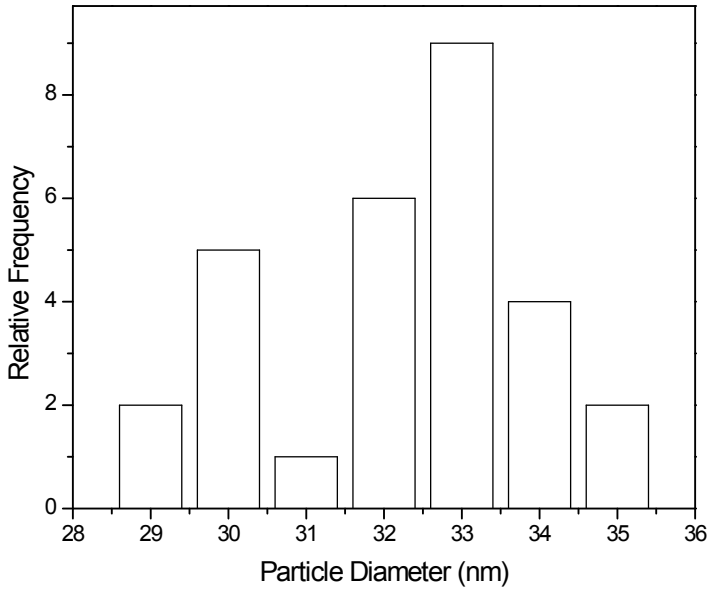

(a) (b)

Silane:- 500-520 $cm^{-1}$
MNPS:- Peak between 200-500 $cm^{-1}$
Rest peaks are alphatic chain and aromatic chain ring vibrations.

**Fig. S5** Histograms of size distributions of pristine $Fe_3O_4$ particles (a) and $Fe_3O_4$@PVB-DABCO-DBO (b) obtained from the FE-SEM images.




(a)




(b)

(c) **DATA ANALYSES SECTION**

**XRD Analysis**

The average crystallite size ($D_{XRD}$) of the nano phase particles were determined by using the Debye-Scherer formula

$$D_{XRD} = \frac{K\lambda}{\beta \cos\theta}$$

Where $K$ is the Scherrer's constant (shape factor $K$ =0.9, assumes spherical crystallites), λ is the wavelength of the Cu $K_\alpha$ radiation (λ= 1.541874 Å) and $\beta$ is the full width at half maximum (FWHM) in radians calculated using Gaussian fitting and $\theta$ denotes the Bragg angle. The average crystallite sizes for both the samples are given in Table 1. It is observed that the lattice constant decreases with decreasing crystallite size.[1] The crystallite size calculated by using three most intense peaks (220, 311 and 400).

**Table S1.** Crystallite size and Lattice constants of $Fe_3O_4$ particles prepared by co-precipitation method.

| **Sample** | **Average Crystallite size $D_{XRD}$ (nm)** | **Lattice constant ($a_r$) (Å)** |
|---|---|---|
| Using single ferrous salt | 25 | 8.376988 |
| Using ferrous + ferric salts | 13 | 8.358142 |

**Mössbauer Studies**

**Table S2.** The Hyperfine magnetic field ($H_{hf}$), isomer shift ($\delta$), quadrupole splitting ($\Delta$), linewidth ($\Gamma$) and relative intensity (RI) in percentage of tetrahedral and octahedral sites of $Fe^{3+}$ /$Fe^{2+}$ions for $Fe_3O_4$ ferrite MNPs derived from Mössbauer spectra recorded at room temperature. Isomer shift values are relative to Fe metal foil ($\delta$ = 0.0 mm/s). Sextet A: Tetrahedral site ($Fe^{3+}$), Sextet B: Octahedral site ($Fe^{3+}$and $Fe^{2+}$), C: ($Fe^{3+}$), Doublet: ($Fe^{3+}$) .

| **$Fe_3O_4$** | **Iron sites** | **Relative area ($R_A$) %** | **Inner line width, ($\Gamma$) mm/s** | **Isomer shift, ($\delta$) mm/s** | **Quadrupole splitting, ($\Delta$) mm/s** | **Hyperfine field ($H_{hf}$) Tesla** | **Fitting quality ($\chi^2$)** |
|---|---|---|---|---|---|---|---|
| Sample-1 | Doublet | 3.82 | 0.435 | 0.358 | 0.680 | -- | 1.9094 |
| | Sextet A | 15.57 | 0.384 | 0.295 | -0.023 | 48.91 | |
| | Sextet B | 24.69 | 0.728 | 0.463 | -0.029 | 45.30 | |
| | Sextet C | 55.92 | 1.91 | 0.375 | 0.036 | 39.08 | |
| Sample-2 | Doublet | 33.92 | 0.497 | 0.372 | 0.666 | -- | 1.1645 |
| | Sextet A | 13.21 | 0.500 | 0.192 | -0.045 | 46.97 | |
| | Sextet B | 17.01 | 1.208 | 0.618 | 0.179 | 46.04 | |
| | Sextet C | 35.84 | 1.135 | 0.482 | 0.003 | 40.18 | |

The value of $\delta_A < \delta_B$,[2-7]and $H_{hf}$ are higher for tetrahedral site than that of the octahedral site in $Fe_3O_4$ ferrite.[8-9] The value of the quadrupole splitting was almost zero for sextets for sample-1 indicating the cubic crystal structure.[10] The detailed analyses of Mössbauer spectra are given in the supporting information. Mössbauer spectra of both samples show a paramagnetic doublet with $\delta$, $\Delta$, $\Gamma$ and $R_A$ values as $\delta$ = 0.358 and 0.372 mm/s, $\Delta$ =0.680 and 0.666 mm/s, $\Gamma$ = 0.435 and 0.497 mm/s, $R_A$ = 3.82 and 33.92 %, respectively. These values are indicating the presence of $Fe^{3+}$ ions in high spin state and situated in distorted local lattice environments. The value of quadrupole splitting of the doublet is larger than that of the sextets. It is because the particle sizes represented by the doublet are small and their magnetic structure is not complete. These signify

more crystal defects and lattice distortions, which result in reducing the symmetry around the Fe ions. The relative percentage of sextet to doublet patterns for the samples a and b are found to be 96.18:3.82 and 76. 08: 33.92, respectively, indicating that the superparamagnetic fraction is small in sample a.

According to the theory of superparamagnetic blocking temperature ($T_B$) for nanometer size particles, the $T_B$ is directly proportional to particle volume ($V$) and can be represented as $T_B = KV/25k_B$, where $K$ is the anisotropy energy density constant and $k_B$ is the Boltzmann's constant. The nanosized magnetic particles are single domain particles and they become superparamagnetic below a critical size ($dc$) and above the blocking temperature ($T_B$). i.e. magnetization direction fluctuates spontaneously (superparamagnetic relaxation) with a relaxation time ($\tau$). When $\tau$ is less than or equal to $10^{-9}$ s, it results in the disappearance of the magnetic splitting to show the superparamagnetic doublet,[10-11] as observed in the Mössbauer spectra for both the samples (Figure 2). The relative areas of the nanosized particles of the samples a and bare 3.8 and 33.9 %, respectively when their $T_B$ is below the room temperature. The value of line width of sextet A and B is higher for sample (b) due to the comparatively lower particle size. It is also further confirmed from the hyperfine magnetic field of tetrahedral A site (sextet A). The value of $H_{hf}$ is found to be reduced for tetrahedral A of sample (b). The value of $H_{hf}$ is observed to decrease with decrease in particle size as observed in the Mössbauer spectrum.[11] When the particle size decreases the value of will be reducing in It is also confirmed from the room temperature XRD data that the sample-b is having smaller particle size compared to sample-a.

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