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Fabrication of Magnetite Nanocrystals in Alcohol/Water Mixed Solvents: Catalytic and Colloid Property Evaluation.

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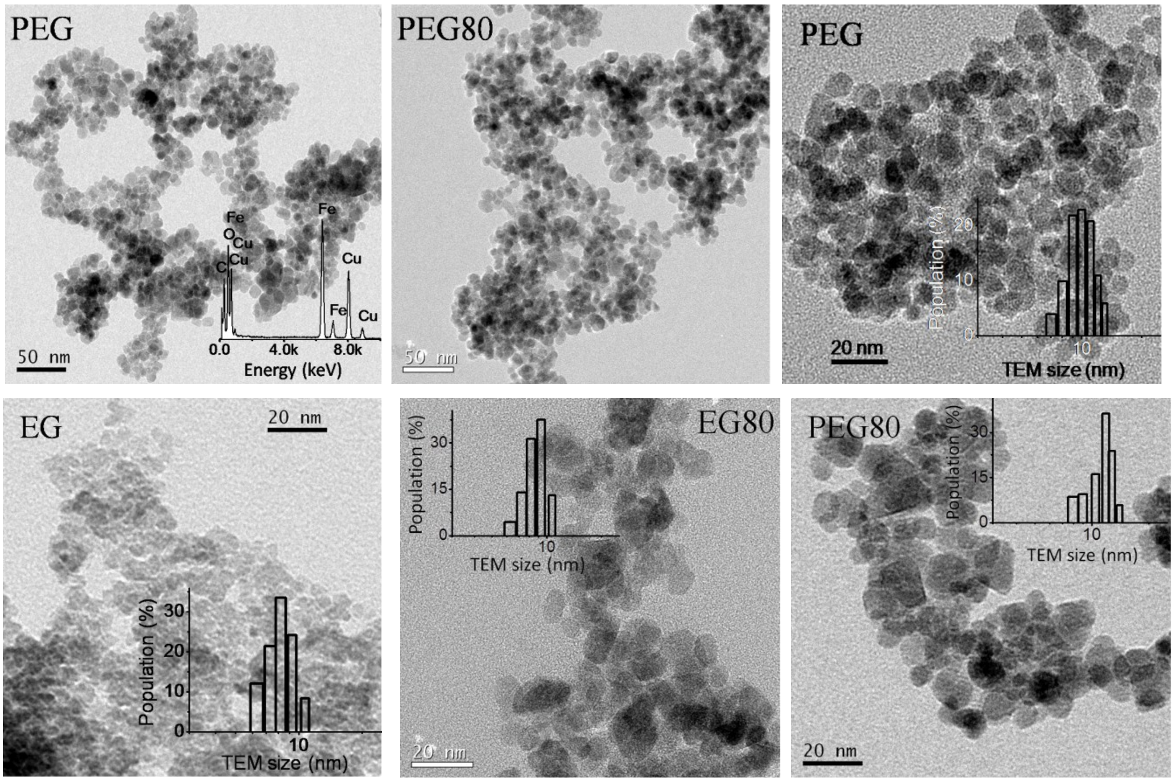

Fig. S1 TEM image of EG and PEG magnetite precipitated at 40 and 80 °C. Inset is the EDS pattern of PEG originates from the carbon-coated copper grid and size distribution of respective sample.

The mean size and its distribution of EG magnetite product have grown from 8.28±1.22 nm to 9.18 ±1.3 nm (EG80) as the precipitation temperature increased by two times. Similarly the average size for PEG and PEG80 were found to be 10.2±1.34 and 12.8±1.5 nm respectively. The atomic ratio of Fe to O from the EDS spectrum is 3:6.2 which is slightly oxygen rich due to the presence of hydrxyls compared to that in stoichiometric magnetite (3:4). It may be due to the surface OH group associated with under co-ordinated Fe atoms at the NPs surfaces and edges.

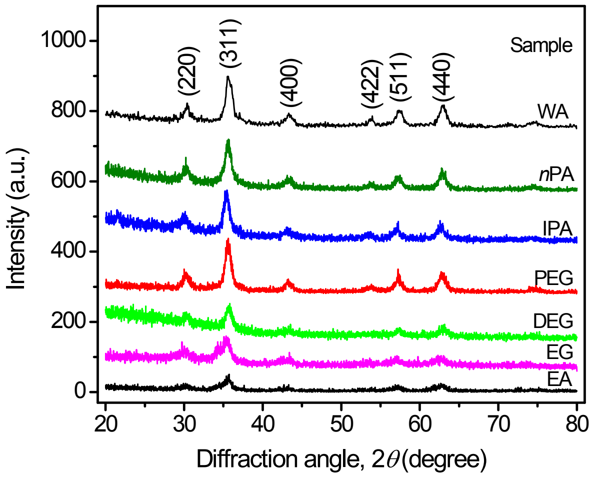

Fig. S2 Magnetite nanocrystals co-precipitated at 80 °C in water and alcohol/water medium.

The crystallinity index of the synthetic magnetite was calculated using the following formula (eqn 1):

$$CI(\%) = \frac{(I_{311} - I_{am})}{I_{311}} \qquad (1)$$

where I_{311} is the maximum peak intensity of the (311) plane at a 2θ angle between 35.3° and 35.4° and I_{am} is the peak intensity of the amorphous magnetite, which is taken at a 2θ angle between 32° and 33° where the intensity is minimal.

Table S1 Crystallinity indices (%) of synthetic magnetite

Solvent	Crystallinity Indices (CI) at precipitation temperature	
	40 °C	80 °C
WA	91.30435	95.45455
EA	82.13559	88.57143
*n*PA	84.89209	83.87097
IPA	88.92734	88.88889
EG	78.88889	77.64706
DEG	82.64463	89.88764
PEG	81.63265	87.57764

FTIR

FTIR spectra on dried magnetite specimens were taken at room temperature on a Shimadzu, IR Prestige-21 model FTIR spectrophotometer in the 550–4000 cm^{-1} range to ensure the structural aspects, attachment and interaction of the alcohol/glycol molecules with magnetite. All spectra were collected with 400 scans in transmission mode, resolution of 2 cm^{-1}. The background was corrected by a reference of KBr pellets. The interaction of dried magnetite NPs obtained with poly-ol (PEG & DEG)/ molo-ol were confirmed by FTIR spectra Fig. S3. The intense characteristic absorption bands of MNPs at 638 and 581 cm^{-1} in all samples are attributed to Fe^{3+}/ Fe^{2+}–O_2 of tetrahedral and octahedral sites respectively in the spinel structure of Fe_3O_4.[1] Sharp absorption bands are also observed at 3135, 1405, 638 and 581 cm^{-1} when compared to pure magnetite.

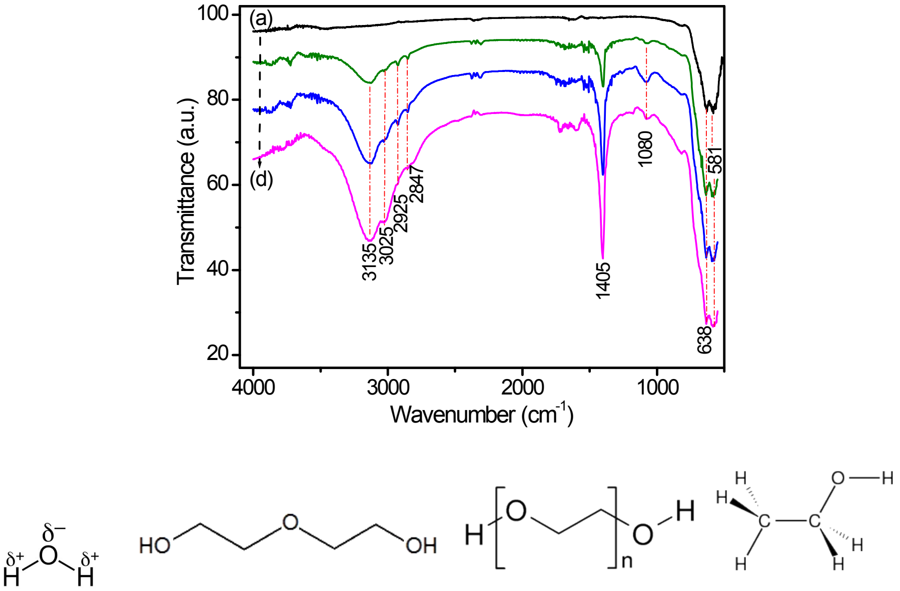

Fig. S3 FTIR spectra of magnetite powder precipitated in (a) water, (b) DEG/water, (c) PEG/water and (d) ethanol/water medium.

The bands due to C–O stretching mode were merged in the very broad envelope centered on 1080 cm^{-1} arising from C–O, C–O–C stretches and C–O–H bends vibrations of NPs in Poly-ols. Also, the aliphatic C–H stretching, in 1405 cm^{-1} were due to C–H bending vibrations. There were more broad vibration bands at 2847, 2925 and 3025 cm^{-1} due to symmetric and asymmetric CH$_2$ stretching. Furthermore, the strong and broad OH stretching mode centered at 3135 cm^{-1} in the case of DEG, PEG and EA labeled NPs confirms the presence of corresponding alcohol/glycol on the surface, which provided a hydrophilic component to NPs, increasing their water solubility.[2] Therefore, the FT-IR spectra showed the existence of van der Waals interactions between the chain of glycol/ethanol and MNPs and this is the reason for high aqueous dispersibility.[3] The exposed hydroxyl groups also present the possibility for further functionalisation or binding with bioligands for biomedical applications.

Colloidal properties

The colloidal stability of PEG fractal aggregates in water with different dilution was monitored in static mode as a function of time by fixing the DLS machine variables such as attenuator index and measurement position. The particle sizes of magnetite nanocrystals determined by XRD, BET, TEM and DLS techniques are summarized graphically in Fig. [illegible]

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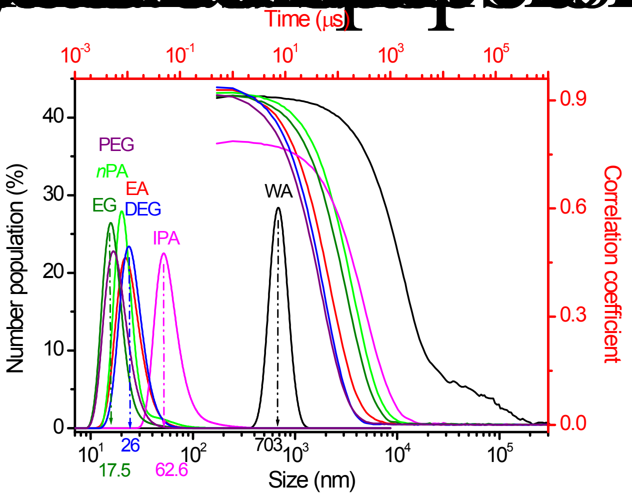

Fig. S4 The number size distribution profiles and its normalized self-correlation coefficient (correlograms) of the magnetite NPs synthesized at 40 °C recorded by Malvern Zetasizer from the corresponding intensity size distribution.

Particle sizes estimated from different techniques provide different meaningful information. The size obtained from the X-ray profile fitting (D_{XRD}) indicates the average crystallite size of particles.

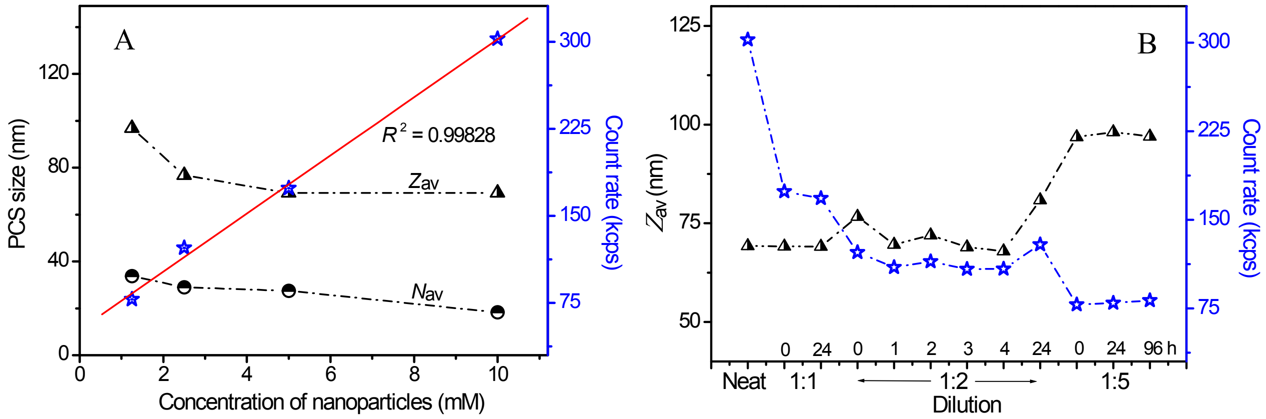

Fig. S5 The hydrodynamic size examined at various concentrations with mean count rate **(A)** immediately after dilutions and (B) the colloidal stability as a function of time for MNPs PEG suspension.

Particle size from BET surface area (D_{BET}) is calculated from the nitrogen adsorption–desorption isotherms with the assumption that the particles are spherical. However, the D_{TEM} is the physical size obtained by direct viewing of particles under transmission electron microscope. In many cases $D_{\mathrm{XRD}} < D_{\mathrm{TEM}}$, as D_{XRD} calculated employing Scherrer equation ignores broadening of the diffraction peaks due to the microstrain in the lattice and X-ray does not often involve the amorphous layer on the magnetite NP surface.[2]

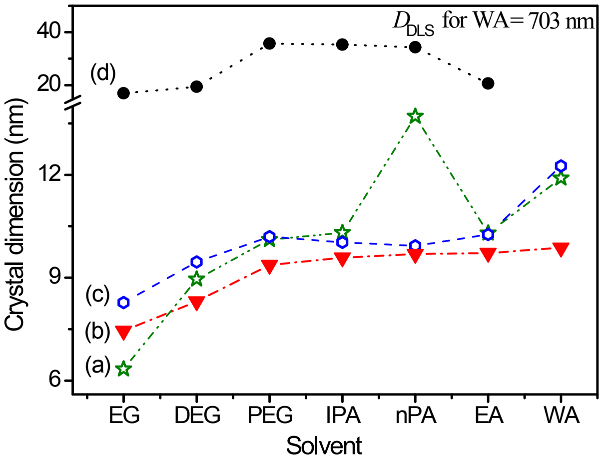

Fig. S6 Particle sizes obtained from (a) BET, (b) XRD, (c) TEM and (d) DLS techniques on magnetite synthesized at 40 °C.

Surface charge (zetapotential)

The variations in the zeta potential of magnetite as a function of the pH and their phase plots are shown in Fig. S7. The main objective of this analysis is to understand the behavior of the NPs in the presence of a pH boundary. Since the inter-particle repulsions are mainly generated by coulomb forces, changing the pH value would alter the surface charge and largely affect the colloidal stability in aqueous nanosuspensions. It has been mentioned that the surface properties of magnetite are extremely sensitive to pH fluctuations.

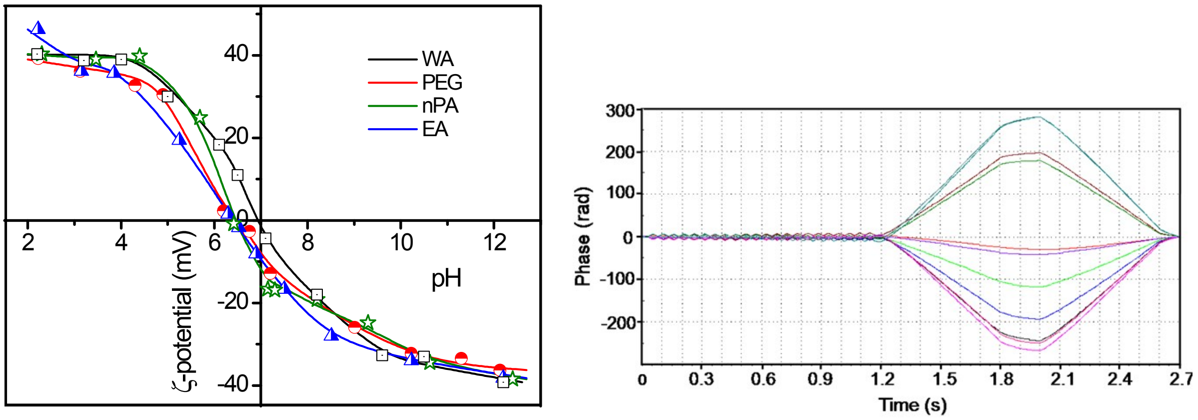

Fig. S7 Variations in the zeta potentials of synthetic magnetite dispersion in Millipore water are shown as a function of the pH of the surrounding medium and the associated phase changes (left side).

For a period of almost 6 months, the ferrofluid was kept at room temperature in a tightly closed transparent glass vials. The results demonstrate that there was no precipitation appearing in the dispersion after standing for reasonable time period as mentioned in Table S2 and the hydrodynamic size almost did not change. With increase of precipitation temperature from 40 to 80 °C, the transparency of dispersion drops gradually due to poorer dispersibility.

Table S2 Colloidal properties such as intensity weighted mean hydrodynamic diameters (Z_{av}), the number weighted mean size (N_{av}), polydispersity index, stability and the surface charge for all the samples

Solvent	Zeta (mV)	pH	D_{PCS} (nm)		PDI	Stability (Weeks)
			Z_{av}	N_{av}		
WA	15	6.18	1215	703	0.518	0.03
EA	40.9	3.85	51.4	24.9	0.258	6½
*n*PA	34.1	5.69	135.7	23.4	0.253	5
IPA	33.1	5.95	227.2	62.6	0.351	¾
EG	43	5.53	100.5	17.5	0.271	7
DEG	40.8	5.8	38.7	16.1	0.264	18
PEG	38.9	4.3	34.1	18.8	0.209	>24
WA80	4.9	6.68	4820	956.9	0.664	0.006
EA80	36.3	5.98	90.3	20.6	0.233	2
*n*PA80	32.9	6.93	140.3	33.6	0.271	1½
IPA80	20.3	6.83	354	89.3	0.776	½
EG80	33.4	6.15	160.7	19.7	0.286	3¾
DEG80	31	6.29	146.3	27.5	0.243	4
PEG80	37.7	5.87	124.6	25.3	0.21	5½

References

1. A. L. Andrade, D. M. Souza, M. C. Pereira, J. D. Fabris and R. Z. Domingues, *Ceramica,* 2009, **55**, 420.
2. A. Ebrahiminezhad, Y. Ghasemi, S. Rasoul-Amini, J. Barar and S. Davaran, *Bull. Korean Chem. Soc*., 2012, **33**, 3957.
3. K. Gupta, P. C. Jana and A. K. Meikap, *Synth. Met*., 2010, **160**, 1566-1573.