Electronic Supplementary

Solvent mediated control synthesis of α- Fe₂O₃ with high energy facets oriented mesocrystal for energy storage

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Table 1. Synthesis of various shape of hematite particles and their properties studied using EG as solvent

Synthesis Methods	Morphology	Property	Ref
Electro deposition in Fe ²⁺ precursor solution + EG + annealed at 450 °C.	Nano-rods length 20 nm diameter 120 nm	Optical and structural properties	[1]
FeCl ₃ .6H ₂ O+ Urea + tetra butyl ammonium bromide +EG+ Refluxed at 195 °C.	3D flowerlike nano	Adsorption properties As (V) and Cr (VI)	[2]
FeCl ₃ .6H ₂ O + NaOH + EG + deionized water, hydrothermal treatment at 200°C, 10 h.	Cubes to hexagonal sheets with quasi sphere	The magnetic properties	[3]
Sol–gel route	Worm-like particles of size less than 100 nm	Charge-discharge capacity of 193 Fg ⁻¹ . Retention in capacitance is about 92 % up to 1000 cycle	[4]
Iron foil + EG + NH ₄ F Anodization with a platinum foil	Nanotube	Photo electrochemical properties	[5]
Ferric potassium oxalate + distilled water, hydrotherma treatment at 150°C, 48 h.	Honey comb Il mesoporous structure	Gas sensor and electro- chemical activity in lithium ion battery.	[6]
FeCl ₂ +EG, hydrothermal treatment at 250°C, 8 h	Neck-structured morphology with 50-60 nm	Feasible in cancer therapy	[7]

FeCl ₃ .6H ₂ O + sodium dodecyl benzene sulfonate + EG + NaOH, hydrothermal treatment at 200° C, 30 min.	Hollow spheres & Nano sheet	Photo catalytic property and removal capacity for methyl orange	[8]
$FeCl_{3.}6H_{2}O + urea + EG$ refluxed, 196.5°C, 30 min	Flower	Ferromagnetic property at room temperature with coercive force of 127Oe.	[9]
$Fe(NO_3)_3 \cdot 9H_2O + water + NH_3 \cdot H_2O + EG, 208^{\circ}C 10 h.$	Rice-Shaped	Magnetic properties were studied	[10]
Fe(NO ₃) ₃ ·9H ₂ O + water+ NH ₃ ·H ₂ O + EG heated to 280°C, 10 h.	Cube- Shaped		[10]
Ethylene diamine + Fe $(NO_3)_3 \cdot 9H_2O + NH_4F +$ EG autoclaved, 200 °C, 24h	2D hollow micro platelets	Photodegradation of RhB under visible light irradiation	[11]
$Fe(NO_3)_3 \cdot 9H_2O + EG$ autoclaved, 200 °C, 30h	Nano-plates to nano-spindles	Photo catalytic and electrochemical properties	[12]

Physico-chemical analysis. The % iron analysis of the samples obtained at different time intervals under various temperatures with Fe:EG ratio 1:1 were shown in Figure S₁. The % iron analysis of iron oxide samples with varying Fe:EG ratios coded as $FeEG_{0.25}$, $FeEG_{0.5}$, $FeEG_1$, $FeEG_2$, $FeEG_3$, and $FeEG_4$ were shown in Figure S₁. It was observed that as the temperature and time of the precipitation reaction increased, the iron content of the samples increased. This is due to loss of water from the precipitate during crystallization process as embryo iron hydroxide polymers undergo condensation and dehydration. While during the variation of concentration of the precursor solution, % iron increased up to Fe:EG ratio 1:1 and then decreased till a ratio of 1:3. With further increase of EG concentration (Fe: EG ratio to 1:4), the % iron increased. This has been attributed to solvation, ligation and adsorption of EG during nucleation process and formation of different phases due to multi effect of EG.



Figure S₁: % Iron for (a) samples obtained at different time intervals under different temperatures with Fe:EG ratio 1:1; (b) samples obtained by varying Fe: EG ratio from 3:1 to 1:4 namely FeEG_{0.25}, FeEG_{0.5}, FeEG₁, FeEG₂, FeEG₃, and FeEG₄ respectively.

FTIR study. FTIR spectra of various samples were shown in Figure S₂. The kinetic samples obtained at different temperatures at Fe:EG ratio 1:1 showed peaks at 793 and 890 cm⁻¹ (encircled in Figure) which could be assigned to δOH in plane bending and γ OH out-of-plane bending of α -FeOOH respectively.^{1,2} These bands became weaker as the time and temperature are increased. Finally at 100°C and at 5 h, the peak was diminished, confirming that the sample was free of α -FeOOH phase. This observation supports the XRD results confirming the complete formation of hematite at higher temperature and longer time. The broad band around 3400-3300 cm⁻¹ was assigned to stretching mode of hydroxyl group. The strong and broad absorptions in the range of 400-800 cm⁻¹ are from the inherent lattice vibrations of α -Fe₂O₃.Very sharp band at 559 cm⁻¹ corresponds to Fe–O stretching mode of hematite whereas the band at 460 cm⁻¹ can be assigned for lattice mode of FeO₆.^{3,4} The Fe–O frequencies of the samples prepared at higher temperature are sharper and stronger which show the better crystallinity of the nanostructures at higher temperature.^{5,6} Group theoretical analysis predicts that there are six infrared active modes for α -Fe₂O₃ lattice vibrations, two polarized along the c-axis (|| modes) and the four perpendicular to the c-axis (\perp modes). The infrared spectra changed due to the polarization change induced by external electromagnetic field at crystal surface. The absorptions at 440 and 522 cm⁻¹ are in (\perp modes) mode while that at 650 cm⁻¹ is in || mode. In present sample the latter

is absent. Presence of very weak band at 1608 cm⁻¹ supports the presence of asymmetric band of OH bond due to the absorption of water molecules by nanoparticles during sample preparation. The other bands at 883 and 1380 cm⁻¹ were attributed to the characteristic vibrations of the FeO-(OH) and the Fe-O stretching vibration, respectively, which established the pure phase development of hematite.⁷ There are three types of surface hydroxyls based on their different coordination modes: singly, doubly, and triply coordinated hydroxyl group. The surface hydroxyl configuration on the various crystal faces of hematite was quite different. Ethylene glycol is a common bidentate ligand, which can also coordinate with metal ions to form the metal-glycolate complex.^{8,9} The peaks at 2971, 1049, and 880 cm⁻¹ could be assigned to the vibrational bands of CH₂-, the stretching band of C-OH, and the stretching band of C-C, respectively. The surface complex between the ethylene glycol and Fe atoms at the sites of the contiguous singly coordinated hydroxyls on (100), (110) and (012) facets, was possible but the adsorption capacities and affinities for ethylene glycol were much lower for the (001) facet, where the surface hydroxyls are all inert doubly coordinated.¹⁰ FTIR spectra also confirm that there was a small amount of capping agent (organic ligand) on the surface of prepared products along with the stability of Fe₂O₃ nanoparticle. Peak position shifts upward for the stretching mode and downward for the deformation mode which is a typical signature of weakening of strengths of hydrogen bonding.



Figure S₂. FTIR spectra of synthesized samples obtained at different temperature with Fe:EG, 1:1 and at different ratio of Fe:EG at 100°C for 5 h.

Raman study. The Raman spectra of the samples shown in Figure S₃ describe two modes of A_{1g} (211, 491 cm⁻¹) and five E_g modes (272, 388, 598, 645 and 708 cm⁻¹) for hematite phase. From the above study, it was confirmed that the samples obtained was pure phase of hematite.^{11,12,13,14-17} The absence of any extra peaks confirmed that α -Fe₂O₃ free from other iron oxides and iron oxyhydroxide. The positions of the peaks are in good agreement with the typical frequencies observed from α -Fe₂O₃. The decrease in the particle dimensions to the nanometer scale could cause a wavenumber shift and broadening of Raman peaks as a result of phonon confinement.



Figure S₃. Raman spectra of synthesized samples obtained at different temperature with Fe:EG, 1:1 and at different ratio of Fe:EG at 100°C for 5 h.

The relative intensity of the A_{1g} mode at 211 cm⁻¹ decreased sharply as compared with other Raman-active E_g modes, when more EG was added into the reaction. It is quite possible that the Raman absorption is attributed to the shape modifications. With a shape change from pseudo cubic to flowery shape particle, the A_{1g} mode was highly reduced. It has been reported earlier that both E_g and A_{1g} modes are greatly orientation-dependent.^{14,15} A_{1g} modes are allowed in a single crystalline *zz* configuration, while in the crossed *xz* and *yz* polarization, only the Eg modes were allowed and only a small residue of the intense A_{1g} mode could be observed.¹⁵ In the present Raman spectrum of flowery fashion nano plates, the intensity of A_{1g} mode is remarkably weak, indicating the very small crystal thickness confined to the A_{1g} vibration mode along the [0001] direction as observed earlier.¹⁸ Besides that a two-magnon scattering peak is observed at 1320 cm⁻¹ which rose from the interaction of two magnons created on antiparallel close spin sites.¹⁵



Figure S₄. Typical TEM images of samples obtained at different reaction time with Fe:EG ratio (1:1).



Figure S₅. Schematic illustration of complexation, nucleation and growth process for development of α -Fe₂O₃ superstructures during synthesis process.

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