**Probing the multi-step crystallization dynamics of micelle templated nanoparticles: structural evolution of single crystalline γ-Fe₂O₃**

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The following supplementary details are available free of charge.

- Calculation of the single domain and paramagnetic size limits.
- Raman spectra for KBr substrate used for background subtraction.
- Selected area electron diffraction and electron energy loss spectra of iron oxide nanoparticles.
- Comparison of selected area electron diffraction, x-ray diffraction and Raman spectroscopy for iron oxide nanoparticles.
- XPS data for loaded micelles and iron oxide nanoparticles.
- Raman spectra for control experiments with solvents, precursors, and homopolymers.
- Table of expected Raman peaks for PS, HP2VP, PS-b-P2VP and o-xylene.
- Raman spectra of different loading conditions

**SI1 Calculation of the single domain and paramagnetic size limits**

The existence of magnetic domain walls is governed by the competition between the magnetostatic energy (\(E_m\)), which is proportional to the particle volume (\(E_m \sim V\)), and the domain wall energy (\(E_{dw}\)), which is proportional to the interface area of the domain (\(E_{dw} \sim S\)). When the particle size decreases beyond a certain threshold, the single domain configuration is energetically favourable. This single domain limit, related to several anisotropic energy terms, normally exists in the region from several tens to hundreds of nanometers, depending on the saturation magnetization (\(M_s\))\(^2\). The single domain critical diameter (\(D_{\text{single}}\)) for spherical magnetic nanoparticles could be estimated by the following equation:\(^3\)

\[
D_{\text{single}} \approx 36 \frac{\sqrt{AK_{\text{eff}}}}{\mu_0 M_s^2}
\]  

(1)

where \(A\) is the exchange constant, \(K_{\text{eff}}\) is the effective anisotropy constant, \(\mu_0\) is the vacuum permeability and \(M_s\) is saturation magnetization.

Below this limit, under an external magnetic field, the nanoparticle array would be magnetized such that all the magnetic moments share the similar magnitude as \(M_s\), causing high frequency magnetization reversal, which results in zero net magnetization during a typical measurement. Hence, the nanoparticles could exhibit superparamagnetic features without spontaneous magnetization reversal can be estimated to be at around 12 nm.

With further decreasing size, the superparamagnetic limit would be reached at a point where the thermal energy \(K_BT\) (25.7 meV) overcomes \(E_a\), causing a spontaneous magnetization reversal. The relaxation time for magnetization reversal is expressed by the Neel-Brown expression as follows:\(^2\)\(^3\)\(^11\)

\[
\tau = \tau_0 \exp \left( \frac{K_{\text{eff}}V}{K_BT} \right)
\]  

(3)

where \(\tau_0\) is typically in the range between \(10^{-11}\) and \(10^{-9}\) s. Since the \(K_{\text{eff}}\) of \(\gamma\)-Fe₂O₃ is known\(^3\), the critical diameter that causes the spontaneous magnetization reversal can be estimated to be at around 12 nm.

Below this limit, the \(\tau\) shares the similar magnitude as \(\tau_0\), causing high frequency magnetization reversal, which results in zero net magnetization during a typical measurement. Hence, the nanoparticles could exhibit superparamagnetic features without \(H_c\) while maintaining a decent value of \(M_s\). On the other hand, when the \(\tau_m\) is longer than \(\tau\), the magnetization reversal cannot finish within the measurement period and thus is called the "block state"\(^6\). When \(\tau_m = \tau\), the corresponding temperature is defined as the blocking temperature (\(T_B\)). According to equation\(^3\) \(T_B\) goes down with smaller size nanoparticles, offering the ability to obtain superparamagnetism under a large temperature window.
Figure SI1 Raman spectra of KBr for background subtraction and unsubtracted P4824 empty micelles coated KBr.

Figure SI2 TEM micrograph of iron oxide nanoparticles with Fe and O elemental maps determined by energy selective filtering of the energy loss spectrum (EELS). Overlays of image, Fe and O maps show excellent correspondence. The loss spectra contain no features other that Fe and O from the particles, and N from the support grid. The lack of C and Cl signals suggest complete removal of the polymeric micelles and complete conversion of the FeCl$_3$. 
Figure S13 Comparison of XRD, SAD and Raman characterization for iron oxide nanoparticles after 600 °C annealing under N2. (a) XRD spectrum of thick drop-cast film of nanoparticles on Si with 2h and 4h (two steps @ 2h each) annealing. Blue and green indicates crystallographic planes corresponding to α-Fe2O3 and γ-Fe2O3 phases, respectively. (b) TEM micrograph with selected area for electron diffraction, the electron diffraction pattern, and the line intensity profile of spin coated nanoparticle film with 2h annealing. Spacing observed correspond to γ-Fe2O3. (c) Raman spectrum of nanoparticles on KBr with 2h annealing. Blue and green indicates vibrational modes corresponding to α-Fe2O3 and γ-Fe2O3 phases, respectively.

The XPS spectra were generated by a monochromated Al Ka source (Thermo K-Alpha) with a photon energy of 1486.6 eV at a pass energy of 100.00 eV and 25.00 eV for wide range survey scans and high resolution individual core level scans. The spot size was 400 mm2. The XPS spectra was analyzed with the Thermo Avantage software tool using the Smart background correction option, which is based on the Shirley background correction method. The peaks were then fitted with Gaussian-Lorentzian functions.

Figure S14 XPS survey scans of thick drop-cast film of iron chloride micelles on Si (top panel) and after oxygen plasma etching for 6h and annealed at 600°C in N2 for 2h (bottom panel).
The survey spectra of a thick drop-cast film of iron chloride loaded micelles on Si and its consequential treatment by oxygen plasma etching for 6h and annealing at 600°C in N₂ for 2h are presented in Figure [SI4]. The peaks in the survey scans are identified and clearly show the removal of the polymeric micelle and evolution of the iron oxide. The most dramatic change is observed with the Cl₂s peak due to the polymeric micelles, which decreases after treatment (though some adventitious C remains); the Cl₂p, identified as chloride in the iron salt has also decreased substantially, as can be confirmed from the high resolution scan in Figure [SI5(a)]. The O1s changes substantially after the oxidation of iron chloride salt in Figure [SI5(b)], which can be deconvoluted into constituent components. The dominant peak (blue curve) in the O1s envelope in both scans can be attributed to water content (at 532.4eV) in the highly hygroscopic iron chloride samples, as well as resulting from the native oxide of the Si substrate at 532eV. The green curve at 529.7eV in the O1s envelope corresponds to the oxide (O²⁻), which can be assigned to Fe₂O₃ and Fe₂O₅ in both γ- and α- forms. The remaining peak at 531.4eV belongs to the hydroxyl (OH⁻) group for which the peak position is also indistinguishable for Fe₂O₅, γ- and α- Fe₂O₃. It is therefore, difficult to infer the iron oxidation from the XPS O1s spectrum.

The high-resolution scans of Fe 2p₃/2 are also shown in Figure [SI6] in attempt to distinguish the form of iron oxides (bottom panel) from iron chloride (top panel). The Fe 2p₃/2 envelope can be deconvoluted into several multiplets from Fe²⁺ and Fe³⁺ following the parameters provided by Grosvenor et al. The multiplet splitting fits, including the pre-peak, surface peaks and satellites, are marked in Figure [SI6]. Grosvenor et al. demonstrated a rigorous Fe 2p₃/2 peak fitting analysis of Fe₂O₃, FeCl₃ and Fe₂O₅ in their work. However, they have also remarked on the similarity of peaks used to fit the envelope in all the aforesaid iron species, making an unambiguous assignment difficult. From the high-resolution spectra in Figure [SI6] it is possible to conclude that there may be mixed phases of iron oxides in the sample, with assignment to any of the possible iron phases. The satellite shift does suggest the formation of oxides from chlorides.
SI4  Raman spectra for control experiments

Figure S17 Raman spectra of pristine precursors, solvent and polymers used for control experiments.

Table S11 Table of expected Raman peaks for PS, HP2VP, PS-b-P2VP and o-xylene

<table>
<thead>
<tr>
<th>PS</th>
<th>HP2VP</th>
<th>PS-b-P2VP</th>
<th>o-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>998 (vs)</td>
<td>1056 (s)</td>
<td>1000 (vs)-symmetric ring breathing</td>
<td>585 (m)</td>
</tr>
<tr>
<td>1032 (m)</td>
<td>1030 (m)-CH in-plane bending</td>
<td>737 (vs)</td>
<td>737 (vs)</td>
</tr>
<tr>
<td>1585 (sh)</td>
<td>1583 (m)-pyridine ring</td>
<td>1055 (s)</td>
<td>1584 (w)</td>
</tr>
<tr>
<td>1596 (m)</td>
<td>1602 (m)-polystyrene ring</td>
<td>1255 (s)</td>
<td>1610 (m)</td>
</tr>
</tbody>
</table>

*vs: very strong, s: strong, m: medium, w: weak, sh: shoulder.

SI5  Estimation of the percentage of $\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ from Raman spectra

Due to the presence of features from both the $\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ phases in the same spectrum, we used the intensity ratio of the $A_{1g}$ peak of $\gamma$-Fe$_2$O$_3$ ($\sim$ 550-800 cm$^{-1}$) against the $A_{1g}$ of $\alpha$-Fe$_2$O$_3$ ($\sim$ 150-300 cm$^{-1}$) to make a semi-quantitative estimate of the percentage of each phase, following a modified approach similar to that by Bersani et al.$^{[23]}$ and Choupra et al.$^{[24]}$. As Raman is more sensitive to the $\alpha$-Fe$_2$O$_3$ phase, this is probably an underestimation of the amount of $\gamma$-Fe$_2$O$_3$ present in the samples. Though the Raman analysis was not correlated to the XRD data, it was used here to provide a semi-quantitative analysis of the relative abundance of each phase.

To calculate the intensity, the area of the $A_{1g}$ of the $\alpha$ phase and the area of the $A_{1g}$ of the $\gamma$ phase were approximated using the rectangle approximation with widths of approximations as small as 2 cm$^{-1}$.

The area intensity ratio of $\gamma$ phase to $\alpha$ phase was given by $\Sigma = \frac{I_{\gamma}}{I_{\alpha}}$.

The percentage of $\gamma$ phase to $\alpha$ phase was given by $\%\gamma = \frac{\Sigma}{\Sigma + 1} \times 100$.

Following this approach, the $\%\gamma$ of the nanoparticles resulting from the conditions shown in Figure S18(b) would be $\sim$90% (88%) for the micelle loaded FeCl$_3$ condition, and 0% for the unprotected FeCl$_3$ condition.
SI6 Comparison of Raman spectra for different loading conditions

![Raman spectra comparison](image)

**Figure SI8** (a) Raman spectra of the FeCl₃ loaded PS-P2VP micelles with different loading ratios (b) Iron oxide nanoparticles produced with 600°C annealing under N₂ for 2h with and without micelles.

**References**


