Manipulating the dimensional assembly pattern and crystalline structures of iron oxide nanostructures with a functional polyolefin†

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Controlled crystalline structures (α- and γ-phase) and assembly patterns (1-D, 2-D and 3-D) were achieved in the synthesized iron oxide (Fe₂O₃) nanoparticles (NPs) using polymeric surfactant-polypropylene grafted maleic anhydride (PP-g-MA) with different concentrations. In addition, the change of the crystalline structure from the α- and γ-phase also led to the significantly increased saturation magnetization and coercivity.

Assembling Fe₂O₃ NPs into well-defined hierarchical patterns has been extensively studied for the fabrication of functional materials with unique properties. Usually, the bottom-up method by thermal-decomposition of an organometallic precursor like Fe(CO)₅, with the aid of different surfactants is one of the most powerful methods to obtain 3-dimensional (3-D) patterns assembled from the building block nanostructures with well-defined particle size and shape. For ferrimagnetic Fe₂O₃ (maghemite) NPs, their inherent magnetic dipole attractions and van der Waals forces are usually the driving forces to enable the self-assembled construction at the nano-scale. Though the assembly of well defined 1-D, 2-D and 3-D nanostructures has been reported, the imperative hard template aided or magnetic field induced assembly is time consuming and costly in most cases. Besides, the co-existence of two crystalline structures is usually observed during the synthesis due to the abundance in crystalline structures of magnetic iron or cobalt NPs and low energy requirement to form the stacking fault (which eventually cause the change of stacking sequence and crystalline structure). It is well acknowledged that surfactants with different capping tips and structures played important roles in tuning the particle size and shape during the synthesis of magnetic NPs via the typical bottom up methods. The surfactants are thus speculated to be vital in controlling the assembly patterns of the bottom-up formed magnetic colloidal NPs since the assembly of these magnetic NPs will be affected by the parameters including the surfactant concentration, bonding strength and molecular chain length.

Previously, we have used a specialized polypropylene grafted with maleic anhydride (PP-g-MA, structure shown in Scheme S1†) to synthesize either mono-disperse hollow α-Fe₂O₃ NPs or magnetic γ-Fe₂O₃ nanochains through a facile bottom up method. However, only 3-D assembly patterns were observed upon drying the as-obtained colloids into solids. Other than the traditionally used small molecular weight surfactants like fatty acids, the polymeric surfactant PP-g-MA has its own advantages including a long tail chain length besides the strong bonding strength onto the surface of magnetic NPs. This in turn offers a larger steric hindrance than that of small molecular weight fatty acids to magnetic colloidal NPs in solution. The bonding density on the surface of the magnetic NPs by the long tail chain length of PP-g-MA can be easily controlled, which would favor the manipulation of crystalline structures for magnetic nanostructures in addition to the control of morphology and assembly patterns. However, the control over both the assembly patterns and the crystalline structures simultaneously is still obscure.

In the present work, by using a commercial PP-g-MA with a specific chemical structure (Scheme S2†) as a stabilizer and surfactant, Fe₂O₃ NPs with a tunable size, assembly pattern, crystalline structure and magnetic properties were synthesized.
by a facile bottom up approach, i.e. thermo-decomposing Fe(CO)$_3$ in xylene with the aid of different PP-g-MA concentrations (%). The commercial PP-g-MA here will provide denser bonding ligands to the synthesized particle surfaces compared with the other PP-g-MA used before. The multi-MA groups on the backbone of PP-g-MA here would favor the assembly pattern control during the in situ bottom up synthesis of magnetic NPs due to the strong steric hindrance force from the PP tails and coordination strength from the MA heads. Specifically, by controlling the PP-g-MA:Fe(CO)$_3$ weight ratio, we demonstrate for the first time the synthesis of stable (1) 2-D flat microstructures (consisting of mono-disperse α-Fe$_2$O$_3$ NPs as building blocks), (2) 3-D porous microstructures (consisting of α- and γ-Fe$_2$O$_3$ NPs as building blocks), and (3) 1-D γ-Fe$_2$O$_3$ nanochains (consisting of γ-Fe$_2$O$_3$ NPs as building blocks). The crystalline structure evolved from the thermally stable α- to less stable γ-phase was achieved by lowering PP-g-MA % to a certain critical point. In addition, the magnetization was found to increase from 4.2 to 70.4 emu g$^{-1}$ in association with the changes of the crystalline structures and assembly patterns.

The formation of a 2-D flat microstructure was found (scanning electron microscopy, SEM, Fig. 1a) when thermo-decomposing 3.5 g Fe(CO)$_3$ in refluxing xylene with the aid of high PP-g-MA %, i.e., 1.0 g PP-g-MA in 100 mL xylene. It is clear from the enlarged SEM image (Fig. 1b) that the 2-D sheet structure consisted of homogeneously distributed NPs. Mono-disperse NPs with average particle size of about 8.4 nm were further confirmed from transmission electron microscopy (TEM) image (Fig. S1a, ES†). Furthermore, strong ring patterns from the selected area electron diffraction (SAED) patterns in Fig. S2a† were indexed to (104), (110), (113), (018) and (300) planes of α-Fe$_2$O$_3$ (PDF# 33-0664); meanwhile, a measured lattice spacing of 2.5 Å (high-resolution (HR)-TEM images shown in Fig. S2b†) was indexed to the (110) plane of α-Fe$_2$O$_3$ (PDF# 33-0664). The X-ray diffraction (XRD) pattern (Fig. S3a†) further confirmed the sole existence of α-phase Fe$_2$O$_3$ in the 2-D sheet structure as evidenced by the characteristic peaks corresponding to (012), (104), (110), (116), (214), (125), (1010), and (306) diffraction planes (α-Fe$_2$O$_3$, PDF# 33-0664).

The formation of 3-D porous micro-spheres was observed (Fig. 1c) when decreasing the PP-g-MA % from 1.0 to 0.5 g per 100 mL xylene. Meanwhile, the micro-spheres made of uniform spherical NPs can be found in the enlarged SEM image (Fig. 1d); and TEM image in Fig. S1b† further revealed partially interconnected chain-like structures with lots of isolated particles (average particle size of ∼11.1 nm). The XRD pattern of the porous micro-sphere assembly showed different crystalline structures: besides the (012), (104), (110), and (024) planes of α-phase Fe$_2$O$_3$, the (311), (222), and (400) planes of γ-Fe$_2$O$_3$ (PDF# 39-1346) were also observed (Fig. S3b†), suggesting the co-existence of the α- and γ-phase Fe$_2$O$_3$ in the as-obtained porous micro-spheres. When further decreasing the PP-g-MA % to 0.25 g in 100 mL xylene, relatively compressed porous micro-spheres were observed, Fig. 1e. Similarly, the well distributed NPs as the building blocks for these compressed porous micro-spheres were observed from the HR-SEM image, Fig. 1f. The TEM image (Fig. S1c†) further displayed the inter-connected chain-like structures with a few dissociated NPs (average particle size of 12.6 nm). Further changes in the XRD pattern were observed in the compressed micro-spheres assembly: besides the (104) and (110) planes of α-phase Fe$_2$O$_3$, (311), (222), (400), (422), (511), (441), and (533) planes of γ-Fe$_2$O$_3$ (PDF# 39-1346) were also observed (Fig. S3c†), indicating the existence of more γ- than the α-phase Fe$_2$O$_3$ in the as-obtained compressed porous micro-spheres.

The formation of 1-D fully assembled nanochains was observed (SEM images in Fig. 1g and h) when the lowest PP-g-MA % was used, i.e., 0.125 g per 100 mL xylene. Other than the mono-disperse NPs shown in TEM image in Fig. 2a, Fig. 2b further confirmed the sole existence of nanochain structures without any isolated particles (average chain diameter is about 28.6 nm, measured from Fig. S4†). Meanwhile, strong ring patterns from the SAED patterns in Fig. S2c† were indexed to...
that the mono-disperse Fe$_2$O$_3$ NPs in a 2-D sheet assembly strengths from decrease by 8 times, indicative of different coordination when the surfactant PP-$\text{g}$-MA concentration decreased by 8 times, indicative of different coordination strengths from different PP-$\text{g}$-MA %.

The room temperature magnetic properties further revealed that the mono-disperse Fe$_2$O$_3$ NPs in a 2-D sheet assembly pattern did not reach the saturation magnetization even in the applied field of 30 kOe, Fig. S5a†. The extrapolated saturation magnetization ($M_s$) is 4.2 emu g$^{-1}$ (Fig. 3a). This agrees well with the characteristic anti-ferromagnetic behavior of Fe$_2$O$_3$.$^{35,36}$ Moreover, a super-paramagnetic behavior for the mono-disperse Fe$_2$O$_3$ NPs in the 2-D sheet assembly pattern was also confirmed by the lack of a magnetic hysteresis loop with negligible coercivity ($H_c$ of 8.7 Oe, less than 10 Oe, Fig. S5a†). For the Fe$_2$O$_3$ NPs assembled into 3-D porous micro-spheres, $M_s$ of 11.1 emu g$^{-1}$ and $H_c$ of 7.4 Oe (Fig. 3b and S5b†) were observed. As for the Fe$_2$O$_3$ NPs assembled into the 3-D compressed micro-spheres, further increases in both $M_s$ (16.0 emu g$^{-1}$) and $H_c$ (18.0 Oe) were observed (Fig. 3c and S5c†), suggesting a soft ferromagnetic behavior (materials with $H_c$ greater than 200 Oe are defined as hard ferromagnetic; and soft ferromagnetic has $H_c$ smaller than 200 Oe).$^{29,37,38}$ Nonetheless, significantly increased $M_s$ (70.4 emu g$^{-1}$) and $H_c$ (525.0 Oe) were observed for the 1-D γ-Fe$_2$O$_3$ nanochains (Fig. 3d), which was indicative of a hard ferromagnetic behavior. Obviously, the magnetic properties of all the Fe$_2$O$_3$ NPs are correlated with their crystalline structures, because the characteristic anti-ferromagnetic behavior of α-Fe$_2$O$_3$ leads to weak $M_s$ and the ferromagnetic behavior of γ-Fe$_2$O$_3$ results in strong $M_s$. As confirmed from XRD and SAED results, only α-Fe$_2$O$_3$ was formed when the highest surfactant concentration was used (1.0 g PP-$\text{g}$-MA in 100 mL xylene). However, γ-Fe$_2$O$_3$ was found co-existing with α-Fe$_2$O$_3$ when decreasing the surfactant concentration (0.5 g PP-$\text{g}$-MA); and increase of γ-Fe$_2$O$_3$ percentage was observed when decreasing the PP-$\text{g}$-MA % further to 0.25 g. Finally, the sole-existence of γ-Fe$_2$O$_3$ was reached by using the lowest PP-$\text{g}$-MA % (0.125 g).

The XPS Fe2p spectra of the Fe$_2$O$_3$ nanostructures were studied in order to confirm their chemical environment. The Fe2p spectra of the NPs in the 2-D sheet assembly pattern (Fig. S6a†) depict two intensive peaks at Fe2p$_{3/2}$ (711.0 eV) and Fe2p$_{1/2}$ (723.4 eV) with two satellite peaks around each peak, which are in good agreement with the previously reported α-Fe$_2$O$_3$.$^{35}$ Meanwhile, the XPS Fe2p spectra of the Fe$_2$O$_3$ NPs with micro-sphere assembly patterns also show two intensive peaks at Fe2p$_{3/2}$ (709.6 eV) and Fe2p$_{1/2}$ (722.7 eV) with two satellite peaks around each peak, Fig. S6b and c†, indicating the existence of α-Fe$_2$O$_3$. Therefore, α-Fe$_2$O$_3$ exists in these three Fe$_2$O$_3$ NPs synthesized with PP-$\text{g}$-MA % of 1.0, 0.5, to 0.25 g per 100 mL xylene. On further decreasing PP-$\text{g}$-MA % to 0.125 g per 100 mL xylene, only one satellite peak around Fe2p$_{1/2}$ (Fig. S6d†) can be observed for the Fe$_2$O$_3$ nanochain, indicating the γ-Fe$_2$O$_3$ characteristics without any α-Fe$_2$O$_3$. This further confirms the sole-existence of γ-Fe$_2$O$_3$ in the 1-D nanochains.$^{30}$

Upon heating in the solvent xylene, Fe(CO)$_5$ underwent thermal decomposition reactions and released carbon monoxide, then finally formed the metallic Fe NPs.$^{39,40}$ Under the open air synthesis conditions, the formed Fe NPs experienced oxidation and changed to Fe$_2$O$_3$ with different crystalline phases, i.e., α-Fe$_2$O$_3$ was formed with the highest surfactant concentration while γ-Fe$_2$O$_3$ was formed with the lowest surfactant concentration. In the meantime, carboxylate bonding between the Fe$_2$O$_3$ surface and the adsorbed PP-$\text{g}$-MA was formed as evidenced by: (1) the peak shift in XPS O1s spectra, (2) the formation of carboxylate peak in XPS C1s spectra (Fig. S7a and b†), and (3) a disappearance of the carbonyl bonding in association with the formation of symmetric stretching vibration of carboxylate from FT-IR spectra.

![Fig. 2 TEM images of (a) monodisperse Fe$_2$O$_3$ NPs; and (b) self-assembled 1-D Fe$_2$O$_3$ nanochain. Reaction conditions: thermo-decomposing 3.5 g Fe(CO)$_5$ in (a) 1.0 and (b) 0.125 g PP-$\text{g}$-MA in mL xylene.](image1)

![Fig. 3 Room temperature hysteresis loops of: (a) monodisperse, (b) intermediate, (c) self-assembled chain-like Fe$_2$O$_3$ NPs, and (d) 1-D Fe$_2$O$_3$ nanochain.](image2)
A wet chemistry method is usually reported to synthesize size and shape controlled NPs. It is well acknowledged that modulating of the crystal growth parameters including the type and amount of capping ligands and growth time are of great significance to the size and shape control. Here, PP-MMA is able to coordinate the particle growth by providing strong bonding to control the size and direct the crystalline structure evolution. With the highest PP-MMA % in solution, the Fe₃O₃ NPs can be tightly “wrapped” within PP-MMA, leading to the smallest Fe₂O₃ NPs (∼8.4 nm). When reducing to the lowest PP-MMA concentration in solution, the weakest coordination strength on the surface of thus formed Fe₃O₃ NPs resulted in largest NPs (∼28.6 nm). However, when thermo-decomposing Fe(CO)₅ within the regular PP, the physically adsorbed PP chain on the NPs only provided a weak coordination. So, the regular PP cannot control the particle growth as evidenced by the random agglomeration shown in TEM and SEM images (Fig. S9f).

Even though lattice constants, unit cell symmetry, and number of atoms in the cell are significantly different between the hexagonal α- and cubic γ-Fe₂O₃, the α- to γ-Fe₂O₃ conversion also involves the sheaving of oxygen layers from AB to ABC.⁴⁴

The ⁵⁷Fe Mössbauer spectra results (Fig. S10f) further suggest that the chemical environments of the as-prepared Fe₃O₃ NPs affected by the PP-MMA % also contribute to the change of different crystalline structures. Specifically, the more distorted oxygen environment might contribute to the possible defects formed when reducing the PP-MMA %, which would cause the defect/vacancy induced phase transition.⁴⁵ Hence, re-arrangement of the stacking sequence of the Fe₂O₃ NPs by low PP-MMA % further led to the change of crystalline structures from α- to γ-phase. In addition, the specific gravity of α-Fe₂O₃ (5.26) is higher than that of γ-Fe₂O₃ (4.86), which further supports our results that the stronger surfactant coordination strength led to denser α-Fe₂O₃. This is also consistent with the fact that the α-Fe₂O₃ is thermodynamically more stable than γ-Fe₂O₃,⁴⁶ where α-Fe₂O₃ formed in the highest PP-MMA % with strongest bonding strength coordinated onto the Fe₂O₃ surface. Another possible reason is that, with low PP-MMA coordination strength, γ-Fe₂O₃ preferentially nucleates due to the fact of its defective spinel polymorph.⁴⁷

The main reason for the assembly of different patterns is the huge difference in magnetic properties, which is caused by different crystalline structures of Fe₂O₃ NPs. In addition, higher PP-MMA can result in lower saturation magnetization (Mₛ) due to the higher tendency of magnetically disordered surface layer and the surface canting formed in stronger coordination on the particle surface.²³ Thermogravimetric analysis (TGA) data shown in Fig. S11f demonstrated slightly lower final residues for all the prepared Fe₂O₃ samples, indicating that Fe(CO)₅ may experience a slight evaporation during the thermal decomposition. However, the residue trend from TGA results clearly showed that the low PP-MMA concentration led to the high Fe₂O₃ percentage. And the highest Fe₂O₃ NP percentage (80.7%) formed in 0.125 g PP-MMA with the measured Mₛ of 70.4 emu g⁻¹-composites can be converted into ~86.7 emu g⁻¹-Fe₂O₃ NPs (70.4/80.7%); which agrees well with the commonly reported Mₛ of γ-Fe₂O₃. Therefore, the 1-D γ-Fe₂O₃ nanochains were formed due to the strong magnetic attraction forces that overcome the weakest repulsive forces (from the lowest PP-MMA %).⁴⁸ As for the 2-D weak magnetic α-Fe₂O₃ structure formed in the highest PP-MMA %, it is primarily due to the weak magnetic attraction forces (anti-ferromagnetic α-Fe₂O₃) overcome by the most intensive PP-MMA repulsive forces. And the 3-D porous macro-structure is caused by the stronger magnetic forces balanced by the repulsive force from the surfactant PP-MMA with intermediate concentrations.

Conclusions

To summarize, we have successfully synthesized magnetic Fe₂O₃ NPs with controllable sizes, crystalline structures, assembly patterns and magnetic properties with the aid of commercially available PP-MMA. The coordination strength by PP-MMA controls the surface oxygen vacancy/defect, nuclei density, and defect distortion induced stacking sequence re-arrangement: stronger coordination strength (from higher PP-MMA%) favors to form thermo-dynamically stable α-Fe₂O₃ and the lower PP-MMA% tends to lead to the less stable γ-Fe₂O₃ NPs. Compared with the high temperature solid state thermal treatment, this low temperature solution method provides energy saving alternatives for control over the Fe₂O₃
crystalline structure. With a high yield (at gram scale) and the availability as an industrial polymer additive, the scale up of well controlled magnetic nanostructures by using PP-g-MA with the polyolefin family, it can easily integrate into fabricating magnetic polyolefin based nanocomposites with well-defined magnetic nanostructures. The assembly patterns such as 1-D magnetic nanochains and the porous micro-spheres consisting of magnetic NPs as building blocks are ideal for fabricating lightweight polymer nanocomposites toward environmental remediation and microwave absorption.\textsuperscript{52–54}

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Notes and references