One-pot synthesis of size- and morphology-controlled 1-D iron oxide nanochains with manipulated magnetic properties†

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Polypropylene grafted maleic anhydride (PP-MA, 2500 g mole⁻¹) has demonstrated its unique capability to synthesize 1-D ferromagnetic hard (292.7 Oe) γ-Fe₂O₃ nanochains made of ~24 nm nanoparticles vs. PP-MA with 8000 g mole⁻¹ for the synthesis of 1-D ferromagnetic soft (70.5 Oe) γ-Fe₂O₃ nanochains (30 nm) made of flowerlike nanoparticles.

Self-assembly of 1-dimensional (1-D) hierarchical nanostructures with magnetic colloidal nanoparticles (NPs) as building blocks represents a powerful versatile bottom-up method to obtain multifunctional nano-materials with unique properties. The inherent magnetic dipole–dipole interactions and the van der Waals forces of the ferromagnetic NPs are usually the driving forces to enable the self-assembly construction at the nano-scale.

Though the assembly of well-defined 1-D iron (oxide) nano-chains has been reported, the imperative hard template aided or magnetic field induced assembly is time consuming and costly in most cases. Recently, we have successfully used a plastic additive – polypropylene grafted with two maleic anhydride (PP-g-MA, structure shown in ESI† Scheme S1), to synthesize mono-dispersed hollow hematite colloidal NPs through a facile bottom up method. In addition, without an external magnetic field, the self-assembled 1-D maghemite (γ-Fe₂O₃) nanochains consisting of spherical NP building blocks with very high coercivity (Hc, 518 Oe) were achieved by simply lowering the PP-g-MA concentration. However, it is impossible to tune the building block structures of the obtained nanochains by varying the PP-g-MA concentration. Several other PP-g-MAs (chemical structures shown in Scheme S2, ESI†) have been studied; however, none of them has shown the capability to manipulate the morphology of the obtained Fe₂O₃ NPs.

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capping strength from different drying the colloids. Chains remain intact during the formation of nanocomposites from thermal-decomposition of Fe(CO)₅.²¹ The further assembly of these of flower-shape NPs grown from the highly concentrated nuclei upon lower steric hindrance from the coordinating PP-MA backbones. When the MA group in PP-MA can be tightly chemisorbed onto the magnetic enhanced repulsive forces against these magnetically attractive NPs head-to-tail NP arrangement, in which the strong attractive magnetic dipolar forces overcome the repulsive forces from PP-MA backbones. Meanwhile, the density of PP-MA adsorbing on the obtained NPs can also be increased upon increasing the PP-MA concentration; hence, enhanced repulsive forces against these magnetically attractive NPs can be achieved while maintaining all other reaction parameters. In this case, the disassembly of the nano-chain structure with separated magnetic NPs could be realized, also different morphologies will be achieved with different concentrations of PP-MA.

Upon increasing the concentration of PP-MA (Mₙ ≈ 8000) from 0.25 to 0.50 g in thermal-decomposition of 3.50 g Fe(CO)₅ in 100 mL xylene, partially assembled nanochains (Fig. S4a, ESI†) and partially separated flower-shape NPs (“intermediate”) comprising of 3-leaf (marked in triangle area) and 4-leaf (marked in square) shape “aggregates” were observed, Fig. 3a. The SAED patterns confirm that these NPs were also pure γ-Fe₂O₃ (Fig. S4b, ESI†). This “intermediate” other than the 1-D nanochain was also clearly observed by SEM, Fig. S5 (ESI†). When using 0.50 g PP-MA (Mₙ ≈ 2500) in decomposing 3.50 g Fe(CO)₅ in 100 mL xylene, mono-dispersed core–shell NPs were observed, Fig. 3b. Strong rings in SAED patterns (Fig. S6a, ESI†) correspond to (311), (400) and (440) planes of γ-Fe₂O₃ (PDF#39-1346),¹⁷ and (104) and (300) planes of α-Fe₂O₃ (PDF#33-0664). The HRTEM image (Fig. S6b, ESI†) clearly demonstrates the core–shell structure, and a shell lattice fringe of the α-Fe₂O₃ (300) plane with a spacing of 1.45 Å. This suggests that a γ-Fe₂O₃ core–α-Fe₂O₃ shell structure was formed with stronger capping strength from PP-MA (Mₙ ≈ 2500). Upon the generation and growth of small nuclei from thermal-decomposition of Fe(CO)₅, iron colloidal NPs coordinated by PP-MA were not chemically stable under ambient conditions and oxidation took place on these particle surfaces and were converted to γ-Fe₂O₃.¹² While maintaining the same PP-MA concentration during the synthesis, decreasing the Mₙ of PP-MA from 8000 to 2500 obviously resulted in an increase of the MA coordinating density. Therefore, the more stable α-Fe₂O₃ shell formed on the surface of the γ-Fe₂O₃ core is probably due to the
chains (30 nm in diameter) have higher saturation magnetization (\(H_c\)) greater than 200 Oe, which is similar to the surface disorder of \(γ\)-Fe\(_2\)O\(_3\). These observations clearly demonstrate the capability of PP-MA in synthesizing stable magnetic Fe\(_2\)O\(_3\) NPs with tunable particle size, composition, shape and self-assembly morphology. Changing the PP-MA molecular weights in turn controls the balance of the overall net force between the attractive and repulsive forces, which is believed to intrigue these aforementioned differences. Scheme S4 (ESI†) depicts the proposed mechanisms in detail.

Besides these unique morphological evolution observations, different magnetic properties were also observed. Materials with coercivity (\(H_c\)) greater than 200 Oe are defined as ferromagnetic hard; while those with \(H_c\) smaller than 200 Oe are defined as ferromagnetic soft.\(^{23,24}\) Room temperature magnetic properties reveal that the \(γ\)-Fe\(_2\)O\(_3\) nanochains (30 nm in diameter) have higher saturation magnetization (\(M_s\)) than Fe\(_2\)O\(_3\) nanochains (24 nm in diameter), Fig. 4. More importantly, the \(H_c\) of 30 nm \(γ\)-Fe\(_2\)O\(_3\) nanochains is about 70.5 Oe, reflecting a ferromagnetic soft material; while the \(H_c\) of 24 nm \(γ\)-Fe\(_2\)O\(_3\) nanochains is 292.7 Oe, corresponding to a ferromagnetic hard material. It can be concluded that the magnetic properties such as coercivity (ferromagnetic soft vs. hard) of thus synthesized 1-D nanochains can be easily controlled by only changing the molecular weight of PP-MA. Comparing the as-synthesized 24 nm diameter 1-D \(γ\)-Fe\(_2\)O\(_3\) nanochains (Fig. 1c) with their 30 nm counterparts (Fig. 1a), it is found that the smaller diameter nanochain structure led to a higher aspect ratio, in which the further resulting higher nanomaterials can significantly increase the coercivity.\(^{25}\) Details regarding these magnetic properties are provided in ESI†. For the “intermediate”-flower shape NPs and the core–shell NPs (Fig. 3), the room temperature magnetic property results (Fig. S7, ESI†) reveal a much lower saturation magnetization (\(M_s\), 9.3 emu g\(^{-1}\)) for the core–shell NPs formed in PP-MA (\(M_s\) ≈ 2500) than the flower shape \(γ\)-Fe\(_2\)O\(_3\) NPs formed in PP-MA (\(M_s\) ≈ 8000), which also confirmed the existence of the antiferromagnetic \(α\)-Fe\(_2\)O\(_3\) shell.

In summary, we have demonstrated an extremely facile one-pot bottom up approach to synthesize well defined 1-D \(γ\)-Fe\(_2\)O\(_3\) nanochains with easily controlled building block configurations (single vs. flower shape NPs), self-assembly morphologies towards the further manipulation of magnetic properties (ferromagnetic soft vs. hard). PP-MA with appropriate MA grafting density and reaction concentration is of key importance to achieve these evolved different 1-D \(γ\)-Fe\(_2\)O\(_3\) nanochains. The merits of this colloidal synthesis approach including gram-level production and mild conditions can be used for the self-assembly of other 1-D magnetic nanomaterials with tailored magnetic properties for a variety of applications such as high-density magnetic storage, sensors and environmental remediation.\(^{26}\)

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References