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Shear Disassembly of Hierarchical Superparamagnetic Fe_3O_4 Hollow Nanoparticle Necklace Chains

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Supplementary Information

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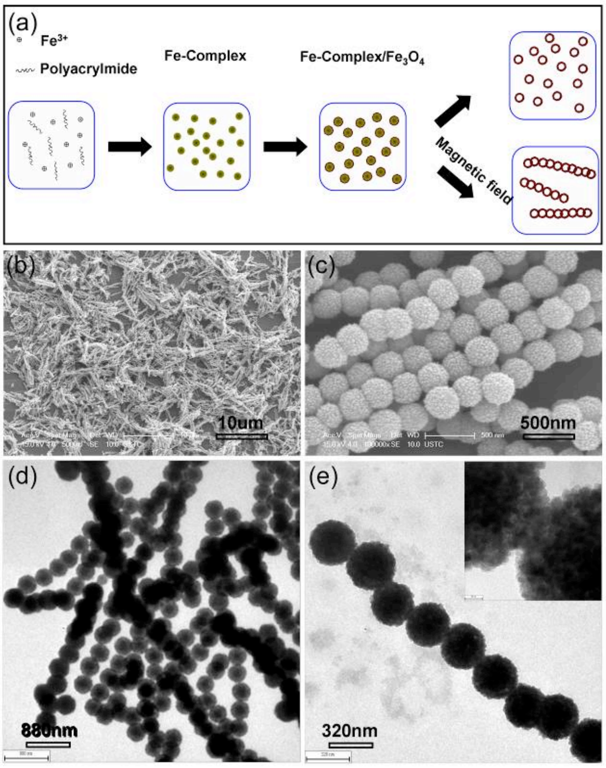

Figure S1. The scheme (a), SEM (b,c), and TEM (d,e) images of the Fe_3O_4 chains based on hollow nanospheres. Figure S1b shows typical SEM images of the as-prepared chains for a reaction of 5 h, which indicates as short chains. These short chains possess non-uniform length ranging from one to tens of micrometers. The higher magnification image (Figure S1c) indicates that these short chains were assembled by uniform spheres, exhibiting a necklace-like morphology. The average width is about 350 nm which is the same as the diameters of the Fe_3O_4 hollow nanospheres. The TEM images (Figure S1d) also show the standard bundle structure of the Fe_3O_4 chains, whereas the chains are presumably held together by supramolecular hydrogen-bond interactions between their polyacrylamide surfaces. It was reported that by directly applying a magnetic field, the synthesized Fe_3O_4 nanospheres could be physically attached with each other to form chain-like morphology. However, a visible inter-particle space was found between the peripheries of Fe_3O_4 hollow spheres. Herein, inter-particle spaces are not observed (Figure S1e), revealing that the chains were covalently connected and the Fe_3O_4 crystals of the surfaces of two hollow spheres were overlapped. These chains were found to be stable even after a high-intensity ultrasonic treatment, proving that the Fe_3O_4 hollow spheres were tightly connected but not through a surface reversible and physical self-assembly.

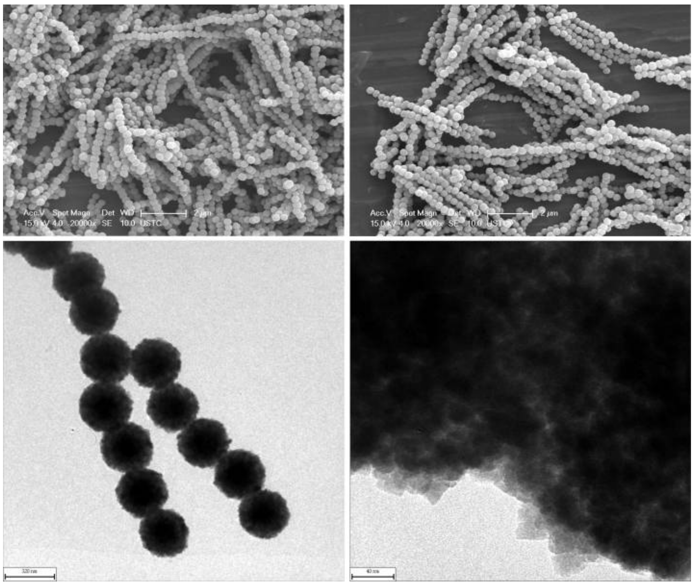

Figure S2. SEM and TEM images of the partially hollow Fe_3O_4 chains reacted for 5 h. Moreover, a pale interfacial interior is clearly observed between the shell and the inner core of the Fe_3O_4 nanospheres, which indicating the as-prepared chain exhibits a yolk-like nanostructure. In consideration that the Fe_3O_4 chains were transformed from the Fe-Complex, the inner core is considered to be the non-reacted Fe-Complex because these Fe_3O_4 chains were synthesized at a short time (5 h, and this product was defined as partially-hollow spheres, Figure S2). With increasing reaction time to 12 h, the structure of the Fe_3O_4 chains product changes significantly while the chain nanostructure retained (Figure S3). Firstly, the size of the Fe_3O_4 hollow nanospheres sharply decreased to 200 nm. Secondly, the Fe_3O_4 nanospheres in the chains present a typical hollow nanostructure. Here, the Fe_3O_4 chains were transformed from the Fe-Complex. The crystallization of the ultrasmall Fe_3O_4 nanoparticles may reduce the volume of the precursor, thus the more matured Fe_3O_4 hollow spheres resulted in a smaller particle size. Simultaneously, the length of the Fe_3O_4 chains became shorter. When all Fe-Complex precursors were consumed, the secondary structure—Fe_3O_4 chains would be stabilized. Therefore, obvious change was not observed for the Fe_3O_4 chains prepared at 24 h. During the above synthesis, the same magnetic were present throughout the synthetic processes for the Fe_3O_4 chains (Figure 3c). Without applying the magnetic field, Fe_3O_4 hollow nanospheres were obtained (Figure 3d) as the sole product.

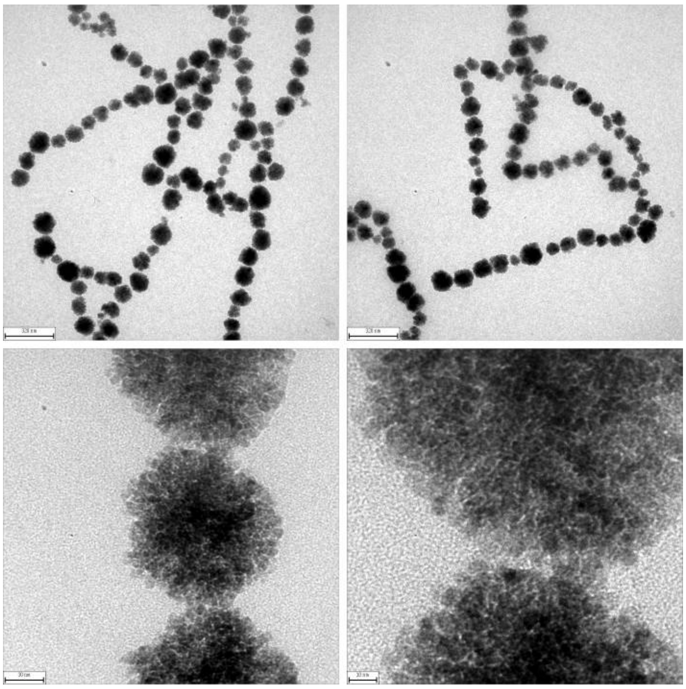

Figure S3. TEM images of the Fe_3O_4 chains based on non-hollow nanospheres at different magnifications.

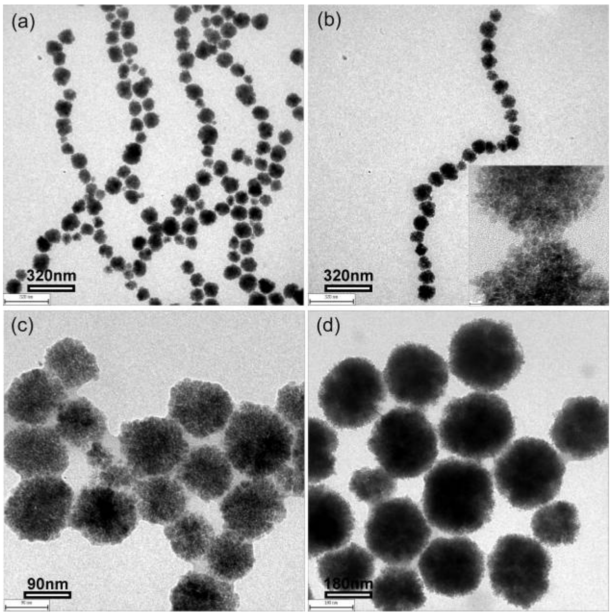

Figure S4. TEM images of the Fe_3O_4 non-hollow nanospheres synthesized with (a,b) and without (c) the magnetic field and large Fe_3O_4 non-hollow spheres (d) with magnetic field.

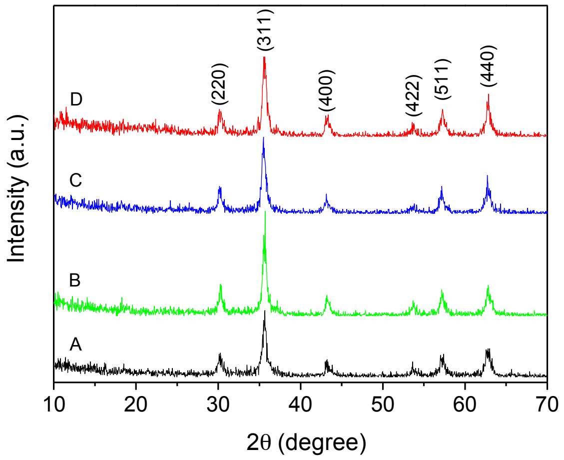

Figure S5. XRD diffraction patterns of the Fe_3O_4 chains based on hollow nanospheres synthesized at different times: 5 h (A), 12 h (B), 24 h (D), and the hollow nanospheres (C). The as-prepared Fe_3O_4 hollow nanospheres and their chains possessed the same crystal structure which had been characterized by XRD. Figure 4A shows the XRD pattern of the Fe_3O_4 chains which were synthesized for a 5 h reaction. All sharp signals were indexed as the face-centered cubic magnetite phase (JCPDS no. 79-0419) with the lattice constants of $a = 8.38$ Å. Prolonged reactions did not influence the crystal structure of the final products, thus they show the same XRD patterns. The Fe_3O_4 grain size of all products is similar. The Fe_3O_4 chains based on partially hollow nanospheres showed similar diffraction patterns with slightly reduced peak intensity.

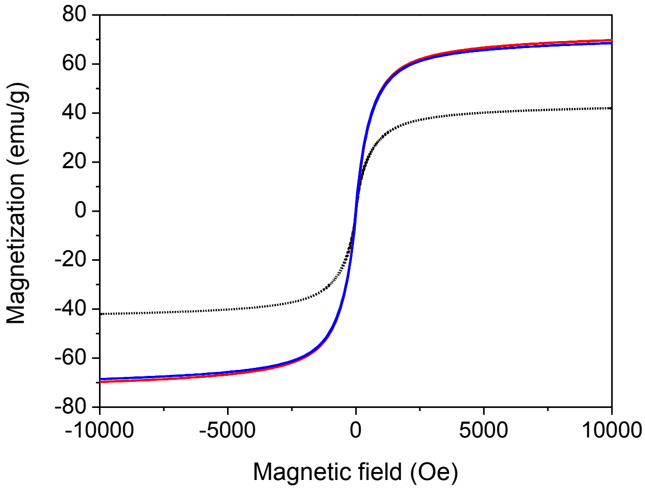

Figure S6. *M-H* curves of the Fe_3O_4 chains based on hollow nanospheres reacted for 5 h (black), 12 h (red), and the hollow nanospheres reacted for 12 h (blue).

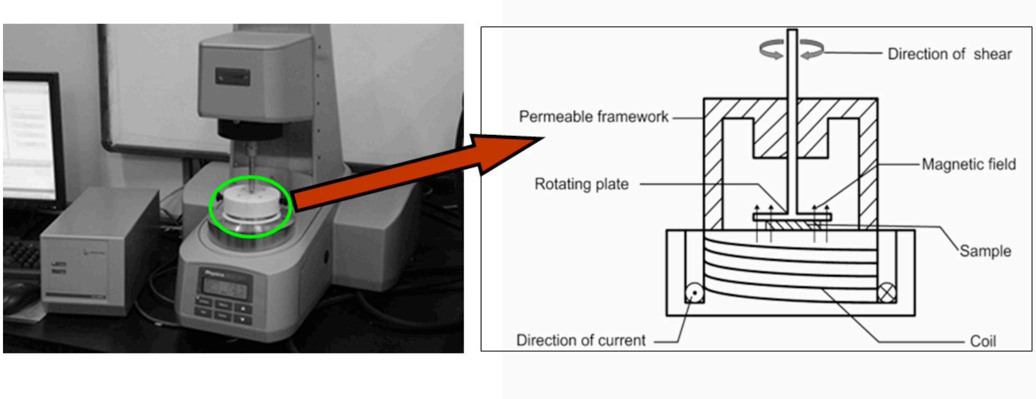

Figure S7. Picture of the magnetorheometer (Physica MCR 301, Anton Paar Co. Austria) and the principle scheme of characterization.

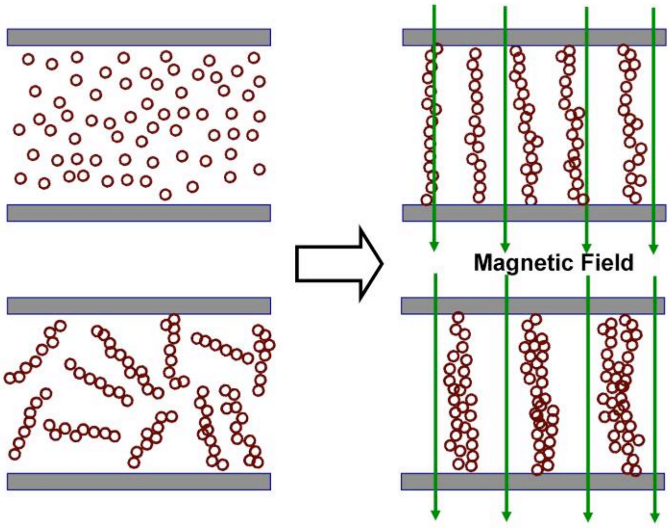

Figure S8. Schematic illustration of the assembled bundle wire-like structure in the superparamagnetic fluids.

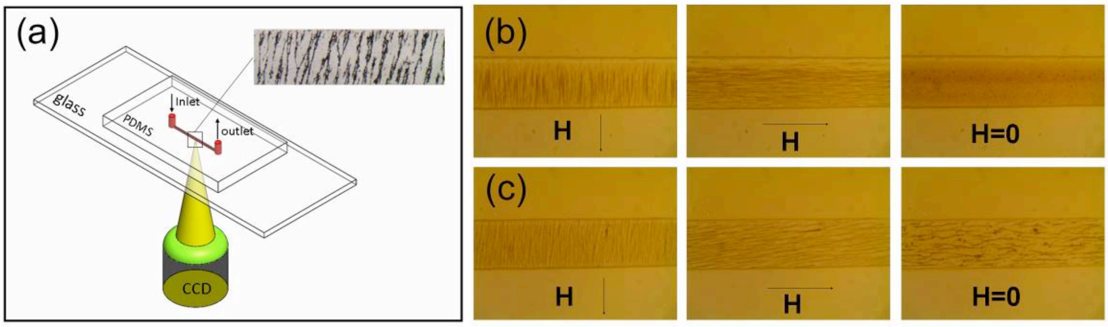

Figure S9. Schematic diagram of PDMS chip fabricated by soft lithography (a) and the flow behavior of the hollow nanospheres (b) and chains (c) based superparamagnetic fluids at different directions of magnetic field. A microfluidic channel was prepared for further investigating the flow characteristics of the as-prepared superparamagnetic fluids. A polydimethysiloxane chip with a specific pattern was fabricated by the soft-lithography method, which is schematically shown in Figure S9a. The superparamagnetic fluids continuously flow from inlet to outlet of the microfluidic apparatus. A magnetic field generated by an electromagnet was applied either perpendicular or parallel to the channel while a CCD camera was monitored *in situ* the structural change of the fluids. Here, the magnetic fluids composed of Fe_3O_4 chains and hollow nanospheres with the same concentrations were slowly injected to the microchannel for investigation. In Figure S9b, it was observed that the hollow nanospheres also assembled to form bundle wire-like structures by applying a perpendicular magnetic field. By comparing the studies between hollow nanospheres (Figure S9b) and chains (Figure S9c) with and without magnetic field at two different directions of magnetic fields, interestingly, the bundle wires assembled by the chains are less dense and filled with gaps (Figure S9c). These bundle wires could be observed at the edges of the upper and lower walls of the channel while the hollow nanospheres could not. By changing the direction of the magnetic field from perpendicular to parallel, the superparamagnetic fluids demonstrate much longer bundle wire-like structures. By withdrawing the magnetic field (Figures S9b and S9c, H=0), the two superparamagnetic fluids exhibit definitely different flowing behavior. The bundle wire-like structures in the hollow nanosphere-based fluid disappear quickly and redispersed as a homogenous solution. The superparamagnetic fluid based on Fe_3O_4 chains surprisingly kept a structurally relaxed form of some curving wires (Figure S9c, H=0). Clearly, the bundle wire-like structure formed by the chains is more stable than that of the hollow nanosphere. Therefore, they express higher magnetorheological effects than the hollow nanospheres are reasonable, which agreed well with the rheological analysis.