

Abstract

This research focuses on the investigation of shaped Fe_3O_4 and $\text{FePt@Fe}_3\text{O}_4$ core-shell nanoparticles (NPs), especially on the shape control, core-shell structure and their potential applications. The dissertation contains three main issues, including the shape-controlled synthesis of Fe_3O_4 NPs, the shape-controlled synthesis of $\text{FePt@Fe}_3\text{O}_4$ core-shell NPs, and the special features and potential applications of the above two kinds of shaped NPs.

The first part describes the shape evolution, formation mechanism, and shape-induced assembly of Fe_3O_4 NPs. The hot-injection method was first used to synthesize the shaped Fe_3O_4 NPs. By injecting the Fe precursor into the hot reaction solution at 290 °C with controllable injecting rate, the monomer concentration can be easily adjusted. It was found that the final shape of Fe_3O_4 NPs was dominated by the surface energy of each plane and monomer concentration. At lower monomer concentration caused by the injecting rate of 10 mL/h, the limited monomers preferentially grow on the high energy planes. Therefore, the lowest energy {100} planes become the terminated planes resulting in cubic Fe_3O_4 NPs. Furthermore, when the injecting rate becomes 20 mL/h, the increased monomer concentration can alter the relative growth rates of {100}, {110} and {111} planes, and the rhombicuboctahedral Fe_3O_4 NPs with the main terminated planes of {100} and {110} were obtained. Both cubic and rhombicuboctahedral Fe_3O_4 NPs have similar size of 16 nm, and can be self-assembled into crystallographic orientation-ordered superlattice on TEM grids and textured-like assembly on Si substrates.

The second part of dissertation contains the shape-controlled synthesis of core-shell structured FePt@Fe₃O₄ NPs by using the hot-injecting method and seed-mediated growth. The final shape of FePt@Fe₃O₄ NPs was dominated by the growth condition of Fe₃O₄ shell. Noteworthily, our method has the advantage that the shaped cores are unnecessary to synthesize shaped core-shell NPs. Additionally, HRTEM images further verified that the epitaxial relationship between FePt core and Fe₃O₄ shell is not necessarily, which indicates the similar lattice constants between core and shell materials are not required. The above results indicated the hot-injecting method combined with seed-mediated growth has fewer requirements in synthesizing the metal core-Fe₃O₄ shell NPs. The various and desired core materials can be substituted to extend their applications.

The last part is the investigation of the special features and potential applications of shaped Fe₃O₄ and FePt@Fe₃O₄ NPs, including the cation site occupancies and MRI applications. The cation site occupancies of Fe₃O₄ NPs measured by XMCD are strongly affected by their shapes. For the cubic Fe₃O₄ NPs, more ferric ions, Fe³⁺, occupied the octahedral sites. However, for the rhombicuboctahedral Fe₃O₄ NPs, the cation site occupancies are closer to the bulk Fe₃O₄. The cation site occupancies should be affected by the surface-to-volume ratio of NPs or by their terminated planes. These results may help to study the catalytic abilities of Fe₃O₄ NPs. Finally, we also demonstrate that superparamagnetic FePt@Fe₃O₄ nanocubes show a high r_2 relaxivity and significantly enhanced MRI contrast, which is attributable to the high magnetization of the FePt core. In addition, the self-assembly of FePt@Fe₃O₄ nanocubes may become the potential multispectral MRI agent.

摘要

本論文主要著重於四氧化三鐵和鐵鉑-四氧化三鐵核殼結構磁性奈米微粒之合成、形狀控制、鑑定、與其應用之研究。

首先，我們利用高溫注入前驅物的方法來製備四氧化三鐵的奈米微粒，注射時的反應溶液溫度為 290 °C。我們發現溶液中鐵單體的濃度會影響著四氧化三鐵奈米微粒的形狀。當前驅物注射速度只有 10 mL/h 時，所還原出的有限鐵單體將優先成長於具有較高能量的晶面，而造成具有最低能量的{100}晶面變成主要外露面，最終得到立方體形的奈米微粒。然而，當注射速度增加到 20 mL/h 時，增加的鐵單體濃度會改變各主要晶面的相對成長速率。因此原本具有第二低能量的{110}晶面，也和{100}晶面一樣變成了主要外露面之一，最後形成了削菱截角立方體(Rhombicuboctahedron)。在我們的實驗中，這兩種四氧化三鐵奈米微粒的粒徑大約都在 16 奈米左右，並且都可以在 TEM 銅網上和矽基板上自組裝成具有優選晶體方向的奈米微粒超晶格結構。

第二部分的研究主要是製備具由核殼結構的鐵鉑-四氧化三鐵奈米立方體。我們利用上述之高溫注入前驅物的方法搭配晶種成長法，來製備具有球形鐵鉑核和立方體形四氧化三鐵殼的複合式磁性奈米微粒。此複合式奈米微粒的最終形狀主要取決於四氧化三鐵殼的成長

條件。並且經由 HRTEM 的分析可得知，鐵鉑核和四氧化三鐵殼並不需具備磊晶成長關係，此結果表示內核的材料並不需要具備與外殼四氧化三鐵相近之晶體常數。因此，不同材料的核可被選用來製備具有核殼結構的四氧化三鐵奈米立方體，以增進其應用價值。

最後一部分則是探討四氧化三鐵和鐵鉑-四氧化三鐵奈米立方體的特性和前瞻應用。我們利用 XMCD 來量測鐵離子在四氧化三鐵內不同位置的分佈情形。在立方體形的四氧化三鐵奈米微粒內，我們發現三價鐵離子佔有八面體位置的比率比一般四氧化三鐵塊材還來的高。然而，在削菱截角立方體形的四氧化三鐵奈米微粒內，其鐵離子在不同位置上的分佈情形就比較接近於四氧化三鐵塊材。此鐵離子分佈位置的不同可能是由於這兩種形狀的奈米微粒具有不同的比表面積和外露面所致，此結果也將有助於進一步研究四氧化三鐵的催化特性。最後，我們也發現鐵鉑-四氧化三鐵奈米微粒能顯著地增強 MRI 影像對比，並且效果優於目前市售之影像顯影劑，此顯著效果應歸因於鐵鉑核的高單位磁化量。另外具有自組裝排列的鐵鉑-四氧化三鐵奈米立方體有機會成為前瞻性多頻譜的影像增強劑。