

Experimental and Theoretical Investigations on the Magnetic-Field-Induced Variation of Surface Energy of Co_3O_4 Crystal Faces

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Magnetic fields have long been reported to influence the structures and physical properties of materials, such as crystal structures,^[1] electronic properties,^[2] magnetic and mechanical properties.^[3] Based on the interactions between materials and the magnetic fields themselves, there is potential for the design of many devices, including magnetic actuators, and in many systems for the investigation of electron-transport properties.^[4] Although magnetic fields were, for a long time, considered to only have weak influence on the synthesis of materials, recent advances indicate that the real situation is not as previously assumed. It has been found that magnetic fields can induce the assembly of ferromagnetic (FM) nanocrystallites along magnetic lines of force, and also the anisotropic growths of single-crystal materials.^[5] Moreover, materials synthesized under magnetic fields usually exhibit different properties, such as enhanced saturated magnetization and different ions arrangement in the lattice.^[5]

Although it is generally realized that magnetic fields can influence the materials' growth, hitherto the pathways by which they work remain unknown. Theoretical work on the influence of magnetic fields on materials synthesis is rare. In this paper, Co_3O_4 nanoparticles are selected as objects for investigating the effects of external magnetic fields on nanomaterial growth. Experimental results show that external magnetic fields can result in the morphology of Co_3O_4 nanoparticles changing from irregular spheres to nanocubes. Then in the theoretical investigations, the effects of external magnetic fields on the competitive growth between {111} and {100} faces and on the morphology of Co_3O_4 crystals are simulated. It is shown that the energy of both faces decrease

under external magnetic fields; however, the energy of {100} faces decrease more rapidly, so that the energy of the {100} faces is lower than that of {111} faces and the growth rates along {100} and {111} faces are also different. As a result the {100} faces are the growth limiting form.

Co_3O_4 particles are chosen for straightforwardness in discussing the effect of magnetic fields. Since they are not ferromagnetic, interaction between their intrinsic magnetic fields and external magnetic fields can be eliminated. The possibility that the as-formed nuclei assemble by magnetic dipole–dipole interactions and form one-dimensional structure can also be ruled out. The synthesis is based on a recent publication and is further modified.^[6] We denote the samples synthesized in the absence and presence of magnetic fields as S1 and S2, respectively. X-ray diffraction (XRD) patterns of S1 and S2 show that they are pure Co_3O_4 (shown in Figure 1a). The average diameter of particles calculated by Scherrer's equation for both samples are about 15 nm, in accordance with transmission electron microscopy (TEM) observations, indicating these grains are of high-quality single-crystalline particles. TEM images of S1 and S2 (Figure 1b and 1c) show that S2 produces cubes, but S1 produces polyhedra. High-resolution TEM (HRTEM) images of S1 and S2 (Figure 1d and 1e) show crystal-lattice fringes with an interdistance of 4.63 Å, which can be indexed to {111} faces of Co_3O_4 , and lattice fringes with an interdistance of 4.02 Å, which can be indexed to {200} faces. Judging from the angle between lattices and the facets of cubes, nanocubes in S2 are enveloped by six {100} faces.

As indicated by the above results, the application of external magnetic fields results in the morphological transition of Co_3O_4 particles from polyhedra to cubes. In a crystallographic context, the final shape of a crystal can be determined by both kinetic and thermodynamic factors. It has been reported that when kinetics dominate, the Co_3O_4 nanocubes form layer by layer and lots of edges and kinks can be generated on their surfaces.^[7] However, no evidence of kinks and edges have been found in our samples, so the dominant factor may be thermodynamic. Magnetic fields have an influence on the surface energy of Co_3O_4 , and

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Supporting information for this article is available on the WWW
under <http://dx.doi.org/10.1002/chem.201001309>.

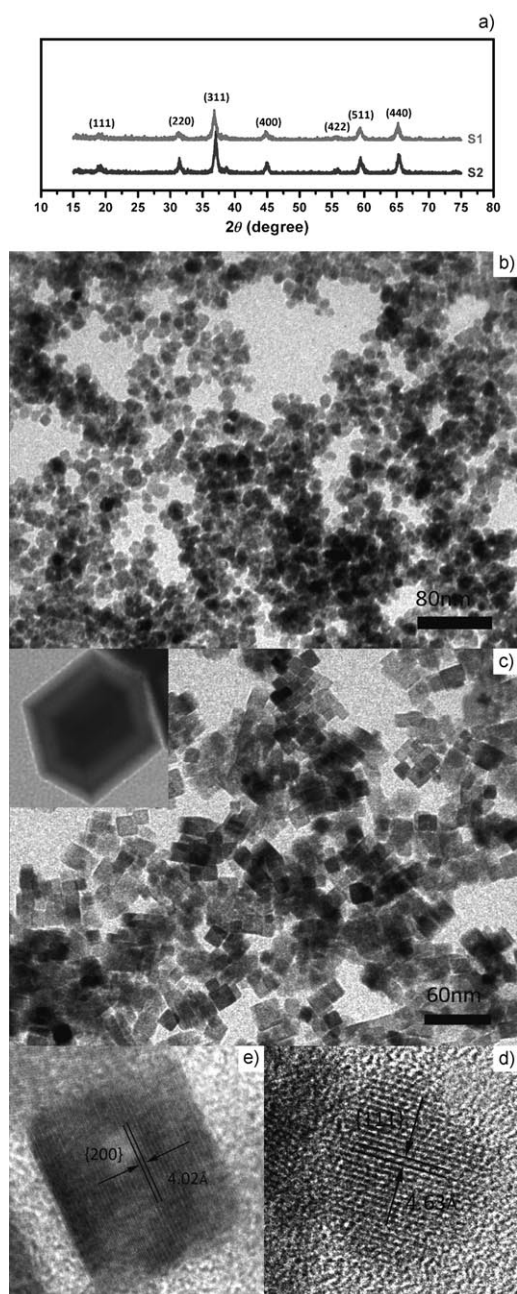


Figure 1. a) XRD patterns of S1 and S2. b) TEM image of S1. c) TEM image of S2 (top left is an enlarged Figure of a single particle which shows a distinct cubic shape). d) HRTEM image of S1. e) HRTEM image of S2.

therefore result in the morphological variation of Co_3O_4 particles.

Wang et al. reported the formation of Fe_3O_4 nanowires under magnetic fields and proposed that magnetic fields may influence the surface energy; He et al. and Hu et al. also reported the magnetic-field-induced formation of ferrosulfide and nickel, respectively;^[5] however, detailed discussions and theoretical evidence about how magnetic fields work were not reported. Moreover, the variations of surface energy are expected to result in regular polyhedral particles,

since a set of surfaces with identical indexes share the similar energy. However, till now, for many ferromagnetic materials, magnetic fields are only reported to bring on one-dimensional wirelike or irregular morphology.^[5] Such disagreements indicate that the pathways by which magnetic field affects the growth process of materials still need to be further investigated.

For certain crystals, when the thermodynamic factors dominate, equilibrium can be reached when the $\sum_j \gamma_j A_j$ is the minimum at constant volume. The γ_j denotes the free energy of surface j , while the A_j is the area of this surface. To calculate the energy of Co_3O_4 {111} and {100} surfaces, periodic slab models for each surface were created, as shown in Figure 2. The application or not of an external

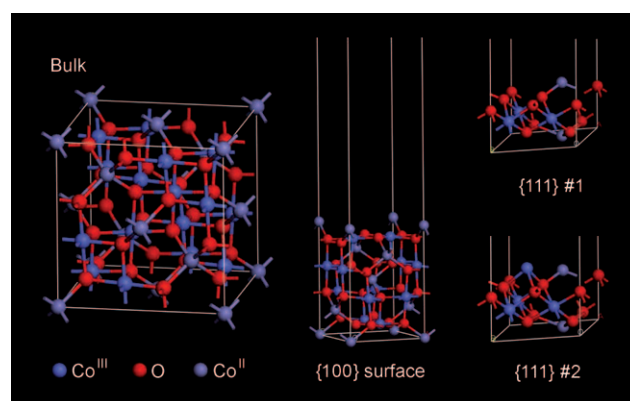


Figure 2. Structures of bulk Co_3O_4 and surface models for Co_3O_4 {100} and {111}.

magnetic field was simulated by using slab models with different configurations, one with a ferromagnetic and the other with a paramagnetic configuration. In the absence of magnetic fields, spins in Co_3O_4 arrange in a disordered manner, which corresponds to a paramagnetic configuration. However, when external magnetic fields are applied, Co_3O_4 particles are magnetized and spins align parallel, corresponding to a ferromagnetic configuration.

Details of the calculations are based on previous studies,^[8] and are listed in Supporting Information. Then the surface energies of Co_3O_4 in the presence and absence of external magnetic fields were calculated. When magnetic fields are absent, the energy of {100}, {111}#1, {111}#2 surfaces are 1.849, 1.645, and 1.638 Jm^{-2} , respectively. The energy of {100} faces is higher than that of {111} faces. However, when magnetic fields are applied, the energy of {100}, {111}#1, {111}#2 faces change to 1.326, 1.429 and 1.447 Jm^{-2} , respectively, and the energy of {100} faces becomes lower than that of {111} faces.

For Co_3O_4 nanoparticles with a spinel structure, their final morphology is often determined by the competitive growth of {111} and {100} faces.^[9] The preferred growth of {100} faces results in the formation of octahedra, while the preferred growth of {111} faces leads to the formation of cubes.

According to the calculated results, it can be found that the energy of {100} faces decreases more rapidly than that of {111} faces and thus {100} faces replace {111} faces, as faces with relatively lower energy, when external magnetic fields are applied. This is in perfect accordance with experimental results, and explains the preferred formation of nanocubes under external magnetic fields. During their growth, Co_3O_4 nanoparticles move and rotate in the reaction system, and there is no preferential orientation for the specific facets relative to the magnetic field. However, if the moving and rotating rates are fast enough and also taking the relaxation time of spins into account, statistically speaking, spins arrange parallel to the magnetic fields. Thus the magnetization process is not necessarily influenced. The decrease of surface energy may be explained by that the magnetic-ordered structures are more stable than the magnetic-disordered structures. For instance, Co_3O_4 becomes antiferromagnetic near absolute zero. In our experiment, external magnetic fields help to stabilize Co_3O_4 in a low-energy ferromagnetic configuration, but if they are absent, Co_3O_4 would be ferromagnetic due to thermal agitation.^[10]

To investigate the effect of magnetic field strength, two 0.12 T NdFeB magnets were used instead in a control experiment. We found that the obtained Co_3O_4 nanoparticles were still perfect cubes, as shown in Supporting Information. This makes sense, because a relatively weak magnetic field may still magnetize the particles and therefore influence their surface energy. To extend our findings to other materials, we examine the growth of NiCo_2O_4 nanoparticles under magnetic fields. As shown in Supporting Information, particles synthesized in the absence of magnetic fields are octahedra; in contrast to the irregular polyhedra or spheres obtained in the presence of magnetic fields. This may also be explained by the magnetic-field-induced variation of surface energy. Without fields, the energy of {111} faces is much lower and the formation of octahedra is energy-favorable; but when fields are applied, the energy of {100} faces drops and polyhedra form as a result of competitive growth between {100} and {111} faces.

In summary, we report about an experimental and theoretical investigation on the magnetic-field-induced morphological variation of Co_3O_4 particles. It is found that the application of magnetic fields leads to the formation of Co_3O_4 nanocubes. Theoretical calculations further indicate that the variation of surface energy under external magnetic fields is the major reason. Compared to other chemical methods, using magnetic fields to realize morphological control has unique advantages of being surfactant-free, environment-friendly, and simple. With the use of stronger fields, external

magnetic fields are expected to be more widely used in the synthesis of other materials with different magnetic properties. Our findings not only help in the understanding of the interactions between magnetic fields and materials, but also have instructional implications for future investigations on the synthesis of materials under magnetic fields.

Experimental Section

$\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and 25% ammonia of analytical grade were used without further purification. $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (0.50 g) was first dissolved in a mixed solvent of distilled water (10 mL) and ethanol (15 mL). Then ammonia (2.5 mL) was added dropwise under stirring. After stirring for another 20 min, the mixture was transferred into a 50 mL Teflon autoclave with two 0.2 Tesla cylindrical NdFeB magnets placed above and below. The autoclave was sealed tightly and maintained at 170 °C for 3 h. In a control experiment, a similar autoclave without magnets was used instead, and all the other reaction conditions were similar. After the reaction, the extra solution was discarded. The solid product was washed by distilled water and ethanol repeatedly and then dried in an oven at 60 °C.

Keywords: ab initio calculations • magnetic properties • morphological control • surface energy

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Received: May 14, 2010
Published online: September 8, 2010