Hollow Nanoparticles

DOI: 10.1002/anie.200803048

Single-Crystalline Hollow Face-Centered-Cubic Cobalt Nanoparticles from Solid Face-Centered-Cubic Cobalt Oxide Nanoparticles**

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Hollow nanoparticles are of great interest because of their applications in catalysis, nanoelectronics, photonics, drug delivery system, nanoreactors, lubrication, and chemical storage.[1–5] Various known hollow spheres include those composed of carbon,[6] polymers,[7] metals,[8–12] and inorganic materials.[13–16] Diverse synthetic methods have been developed to prepare these hollow nanoparticles, such as removal of the templating core,[11] galvanic replacement,[12] and through the Kirkendall effect.[15]

Cobalt exhibits hexagonal closed-packed (hcp Co) and face-centered cubic (fcc Co) structures in the bulk, and a metastable cubic structure labeled ε-Co in the nanometer range.[17] Cobalt nanostructures have been widely studied because of their potential applications, mainly in ultrahigh-density magnetic storage.[18] However, reports on hollow cobalt nanoparticles are very limited thus far,[8,9] although they are interesting materials in terms of their unusual magnetic domains and quantum properties.

We herein report that fcc Co hollow nanoparallelepipeds have been prepared by thermolysis of fcc CoO solid nanoparallelepipeds in oleylamine ($C_{18}H_{35}NH_2$). The fcc CoO solid nanoparallelepipeds, surprisingly, are reduced by the oleylamine surfactant to form fcc Co hollow nanoparallelepipeds. This new phenomenon could signify an important methodology to produce constituent metal (M) hollow nanoparticles from metal oxide (MO) solid nanoparticles.

In our previous work, we reported phase- and size-controlled syntheses of hexagonal and cubic CoO nanocrystals (hcp CoO and fcc CoO).[19] The fcc CoO solid nanoparallelepipeds in oleylamine undergoes reduction at high temperatures (270–290 °C) to transform into hollow nanoparallelepipeds composed of cubic metallic Co (fcc Co). Figure 1 shows the evolution of the morphology of fcc Co hollow nanoparallelepipeds with time (a→d) when a slurry of fcc CoO solid nanoparallelepipeds in oleylamine is heated at 290 °C for 2 h and then subjected to thermal treatment at 270 °C for 1 h. The HRTEM image of each nanoparallelepiped is shown as an inset in Figure 1. The expanded HRTEM images in Figure S1 (see the Supporting Information) reveal that the observed lattice spacing of fcc CoO is estimated to be 2.18 Å ((200) plane for a and b) and that of fcc Co to be 2.04 Å ((111) plane for c and d), which represents a highly crystalline nature and a well-defined morphology of both nanomaterials. The dark-field TEM image in Figure S2 clearly indicates the hollow nature of the fcc Co nanoparallelepipeds. The selected area electron diffraction (SAED) pattern of the fcc Co nanoparallelepipeds given as an inset in Figure S2 is consistent with the cubic cobalt structure featur-

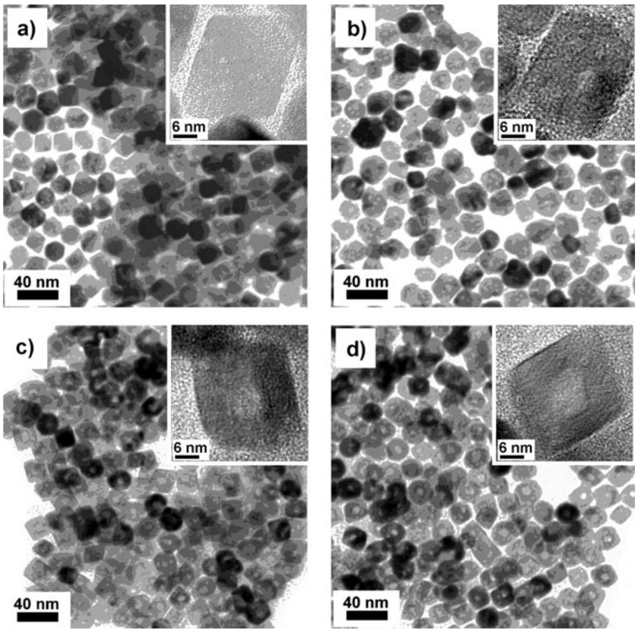

Figure 1. Evolution of fcc Co hollow nanoparallelepipeds with time. a) TEM image of fcc CoO nanoparallelepipeds. b,c) TEM images of nanoparallelepipeds after heating fcc CoO at 290 °C for b) 1 h and c) 2 h; d) TEM image of fcc Co nanoparallelepipeds prepared after heating fcc CoO at 290 °C for 2 h and then at 270 °C for 1 h. A HRTEM image of each of the hollow nanoparallelepipeds is shown as an inset.

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[**] This work was supported by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD; KRF-2005-201-C00021) and by the Nano R&D Program (grant 2005-02618) of the Korea Science and Engineering Foundation (KOSEF) funded by MEST. This work was also supported in part by the SRC program (grant R11-2005-008-00000-0) of KOSEF through the Center for Intelligent Nano-Bio Materials at Ewha Woman's University. Prof. D. G. Churchill and Prof. H. Ihee of KAIST are acknowledged for proofreading this manuscript and helpful discussion.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803048.

ing strong ring patterns assigned to the (111), (200), (220), and (311) planes.

The XRD pattern of the fcc Co hollow nanoparallelepipeds is shown in Figure 2 e and matches well with that of the standard fcc Co (JCPDS no. 15-0806). Time dependent XRD patterns obtained during thermolysis of fcc CoO in oleylamine provided in Figure 2 reveal that signals due to fcc Co grow with time and fcc CoO is completely consumed at 270–290 °C in 3 h, indicating smooth and complete conversion from fcc CoO solid nanoparallelepipeds to fcc Co hollow nanoparallelepipeds. The fcc Co hollow nanoparallelepipeds as prepared are ferromagnetic and attracted to a magnet, as shown at the bottom right of Figure 2.

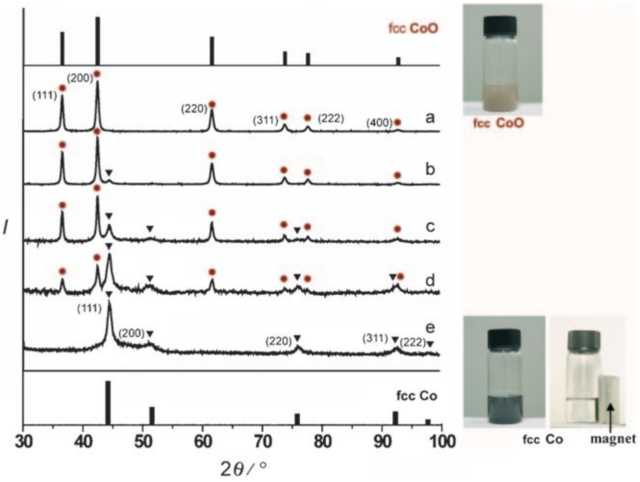


Figure 2. XRD patterns during conversion. a) fcc CoO nanoparallelepipeds; b–d) samples after heating fcc CoO at 290 °C for b) 0.5 h, c) 1 h, and d) 2 h; e) fcc Co nanoparallelepipeds prepared after heating fcc CoO at 290 °C for 2 h and then at 270 °C for 1 h. The brown dots and black triangles represent peaks due to fcc CoO and fcc Co, respectively. The standard XRD patterns for fcc CoO (JCPDS no. 43-1004) and fcc Co (JCPDS no. 15-0806) are shown as a bar diagram at the top and bottom, respectively. The fcc Co hollow nanoparallelepipeds in oleylamine are attracted to a magnet at the right bottom.

The transformation of solid fcc CoO into hollow fcc Co nanoparallelepipeds was originally assumed to occur straightforwardly [Eq. (1)]. Surprisingly, we found that CO and NH_3 are the only gas products that evolve and there was a notable absence of dioxygen: a mixture of $C_{17}H_{34}$ (heptadecene) and $C_{17}H_{32}$ (heptadecadiene) was identified as a third co-product from GC/MS data (Figure S3 a,c). On the basis of the GC/MS data, both olefins consisted of structural isomers because double-bond migration occurred during the transformation. The balanced reaction is now formulated as Equation (2).

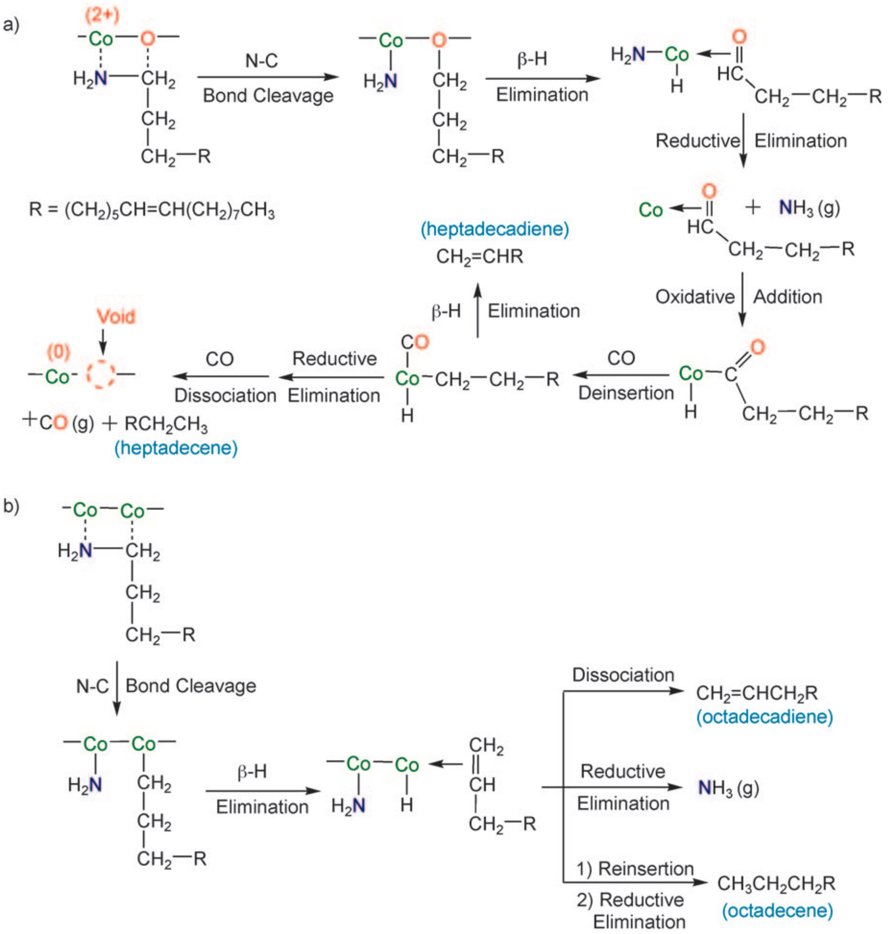
$$\text{solid fcc CoO} \rightarrow \text{hollow fcc Co} + 1/2\,O_2 \tag{1}$$

$$\text{solid fcc CoO} + C_{18}H_{35}NH_2 \rightarrow \text{hollow fcc Co} + CO + NH_3 + C_{17}H_{34} \tag{2}$$

Plausible reaction pathways for the transformation are proposed in Scheme 1 a. Coordination of the amino group on the electropositive cobalt site and interaction of the relatively electropositive α-carbon atom of oleylamine with the oxygen center results in the C−N bond cleavage of oleylamine. This C−N bond cleavage of amines is known in catalytic hydrodenitrogenation reactions.[20] The subsequent reaction sequences are well-documented reactions in organometallic chemistry, such as β-hydride elimination of the alkoxide, oxidative addition of C−H bonds, reductive elimination of NH_3 and $C_{17}H_{34}$, and CO deinsertion and dissociation. The surface heptadecenyl species undergoes β-H elimination to produce the heptadecadiene. Overall, the fcc CoO has been reduced to fcc Co by oleylamine, which is oxidized to afford CO, NH_3, and heptadecene. Voids are formed on the surface of fcc CoO solid nanoparallelepipeds by oxide removal. Octadecene ($C_{18}H_{36}$) and octadecadiene ($C_{18}H_{34}$) were also formed along with heptadecene and heptadecadiene during the conversion of fcc CoO to fcc Co (Figure S3b,d) from the reaction of fcc Co with oleylamine. The deamination of oleylamine followed by β-hydride and reductive eliminations of surface species on fcc Co proposed in Scheme 1 b would produce ammonia and a mixture of octadecene and octadecadiene. This was verified by carrying out a similar reaction of oleylamine with fcc Co in the absence of fcc CoO, which gives only ammonia and a mixture of structural isomers of octadecene and octadecadiene, as shown by GC/MS analysis (Figure S4).

Interestingly, the size and shape of the hollow nanoparallelepipeds remain (average lateral dimension: (20 ± 3) nm; average acute angle: (80 ± 8)° for both fcc CoO and fcc Co) throughout the transformation. The spherical voids randomly formed on the surface of fcc CoO nanoparallelepipeds in the early stage of the transformation diffuse into the interior finally to form fcc Co nanoparallelepipeds with a spherical hole with diameter of approximately 7 nm as the reaction proceeds with time (Figures 1 and S1; b: (3.5 ± 1.0) nm; c: (6.0 ± 1.0) nm; d: (7.0 ± 1.0) nm). Fast reduction of fcc CoO by oleylamine at higher temperatures (above 290 °C) resulted in the formation of cracks and destruction of the fcc Co nanoparallelepipeds, suggesting that abrupt evolution of carbon monoxide and ammonia gases produces stresses that leads to cracks and eventual destruction of the nanoparallelepiped structure.

Proposing the definitive pathways for the formation of hollow fcc Co nanoparallelepipeds is not warranted, but it is likely that the hollow fcc Co nanoparallelepipeds would be generated by continuous diffusion of oxides out to the surface void followed by removal as carbon monoxide and simultaneous electron transfer from the surface Co atoms to the inner Co^{2+} ions to form surface Co^{2+} ions and interior Co atoms. This proposal is favored, since both the size and shape of the fcc CoO nanoparallelepipeds are conserved in the hollow fcc Co nanoparallelepipeds. The Co metal layer formed on the surface in the early stage determines the size and shape of the hollow fcc Co nanoparallelepipeds, and the surface voids diffuse into the interior of the nanoparallelepipeds to result in the spherical shaped void, which is entirely due to the loss of oxides. The oxide diffusion is well known in metal oxides at high temperatures.[21] Our observation is in contrast with the Kirkendall effect, in which the out-diffusion



Scheme 1. Proposed reaction pathways: a) reduction of fcc CoO to fcc Co by oleylamine with formation of heptadecene and heptadecadiene; b) conversion of oleylamine into octadecene and octadecadiene by fcc Co.

of one constituent is faster than the in-diffusion of the other, forming either a hollow compound or a hollow solid solution.[15]

The magnetic-field dependence of magnetization for the nanoparallelepipeds shown in Figure 1 was measured by a superconducting quantum interference device (SQUID) magnetometer, and the results are represented in Figure 3. As expected, the fcc CoO nanoparallelepipeds show typical antiferromagnetic behavior[19] (Figure 3a). When the void grows in fcc CoO nanoparallelepipeds, the magnetization contains a ferromagnetic component in addition to the antiferromagnetic behavior (Figure 3b). The ferromagnetic component becomes stronger as the void size increases (Figure 3c), and finally only ferromagnetic behavior is observed (Figure 3d). These magnetic data also demonstrate that fcc CoO is indeed transformed into fcc Co in our unique synthetic method. The saturation magnetization (M_s) of fcc Co nanoparallelepipeds is determined as 36 emu g^{-1} with the magnetic coercivity (H_c) of 120 Oe (Figure 3d). The M_s value roughly accounts for 22 % of the corresponding bulk value (161 emu g^{-1}).[22] The M_s values were commonly reported to be smaller (by 20–25 %) for hollow nanoparticles than those for the bulk.[9,10] The magnetization of the fcc Co hollow nanoparallelepipeds was measured as a function of temperature in the applied field of 100 Oe under field cooling (FC) and zero field cooling (ZFC) conditions (Figure S5). The FC curve is almost temperature independent. The fcc Co hollow nanoparallelepipeds exhibit a superparamagnetic behavior with a shoulder of a blocking temperature T_B around 180–185 K based on the ZFC curve. The large deviation between the FC and ZFC curves can be understood, since a Curie temperature of the bulk Co is 1388 K. The temperature dependence of the ac susceptibility (χ'_{ac}) for fcc Co nanoparallelepipeds was investigated in the range of 785 to 10 kHz excitation frequencies at 10 Oe rms field amplitude (Figure S6). The expanded curves between 150 and 200 K in Figure S6b confirm T_B to be 182 K. This unusual superparamagnetic behavior seems to be attributable to the hollow nature of our fcc Co nanoparallelepipeds (20 nm) and their large surface-to-volume ratio. Note that similar sizes of fcc Co spherical solid nanoparticles were reported to reveal blocking temperatures above room temperature.[23] Reports on the formation of Co hollow nanostructures are very limited with only the following two examples of relatively large sizes as nanostructures. The Co hollow nanospheres (diameter: (660 ± 20) nm, thickness: ca. 40 nm, H_c: 450 Oe) were prepared by calcination of $CoCO_3$-coated polystyrene particles under H_2/N_2 (1:1) at 400 °C.[8] Magnetic chains of Co hollow spheres (M_s: 37.5 emu g^{-1}, 23 % of the bulk value) ranging in size from 480 to 850 nm were formed by the reduction of $[Co(N_2H_4)_3]Cl_2$ in ethylene glycol at 197 °C.[9]

In conclusion, we have prepared single-crystalline fcc Co hollow nanoparallelepipeds with a spherical shaped void from fcc CoO solid nanoparallelepipeds, surprisingly, by reduction with oleylamine. The void is formed by fast out-diffusion of the oxides followed by removal as carbon monoxide and reduction of Co^{2+} to Co induced by oleylamine oxidation. The shape and size of the fcc Co nanoparallelepipeds are completely retained during conversion and are entirely dependent on those of the fcc CoO nanoparallelepipeds. Reduction of metal oxides by amine to form metals, to the best of our knowledge, is not previously known. The single-crystalline fcc Co hollow nanoparallelepipeds show unusual superparamagnetic behavior with $T_B = 182$ K (average lateral dimension: (20 ± 3) nm; average acute angle: (80 ± 8)°; diameter of the void: (7.0 ± 1.0) nm) as a result of the hollow nature and large surface-to-volume ratio. Our finding promises a new methodology for the preparation of metal hollow nano-

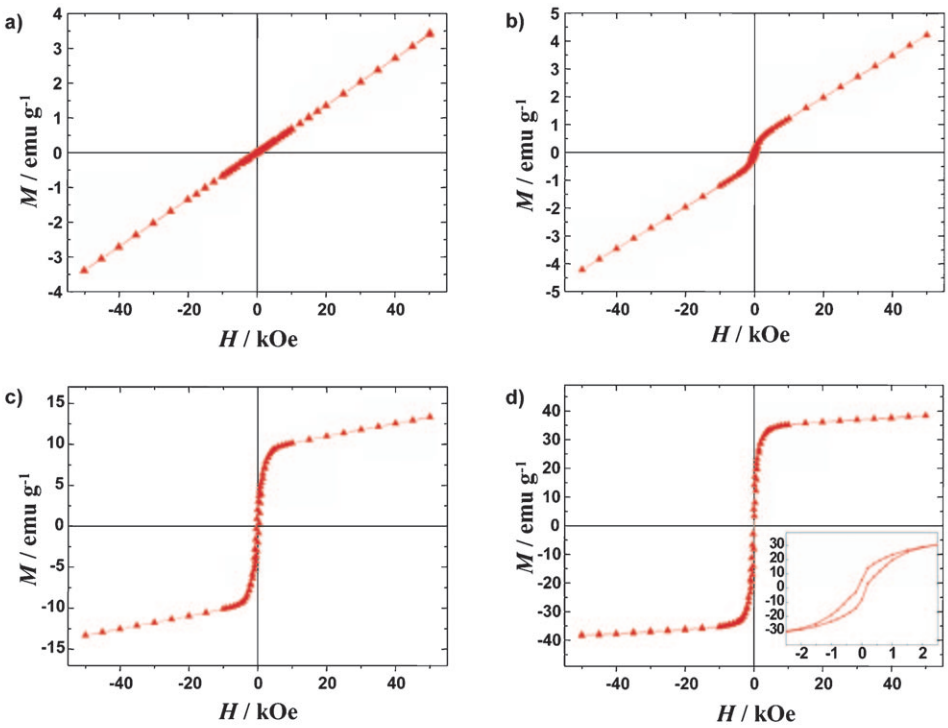


Figure 3. Magnetic-field dependence of magnetization measured at 300 K. a) fcc CoO; b,c) samples after heating fcc CoO at 290 °C for b) 0.5 h and c) 1 h; and d) after heating fcc CoO at 290 °C for 2 h and then at 270 °C for 1 h. The inset in (d) shows the expanded hysteresis loop.

structures from metal oxide nanomaterials in the presence of oleylamine by a one-pot solution reaction.

Experimental Section

[Co(acac)$_3$] (99.99 + %, Aldrich; acac = acetylacetonate) was used without further purification. Oleylamine (70 %, Aldrich) was purified by vacuum distillation over CaH$_2$. All other reagents from commercial sources were used without further purification. All reactions were carried out under an argon atmosphere.

Synthesis of fcc Co hollow nanoparallelepipeds: A green slurry of [Co(acac)$_3$] (0.10 g, 0.28 mmol) in neat oleylamine (9.24 mL) was heated at 135 °C for 5 min. Immediately after dissolution, the reaction mixture was flash-heated to 200 °C. After the solution was stirred at 200 °C for 1 h, hexagonal pyramid-shaped hcp CoO nanocrystals with side edge lengths of (47 ± 4.6) nm and basal edge length of (24 ± 2.4) nm were obtained as a green suspension. The green suspension was heated at 240 °C for 1 h to afford fcc CoO nanoparallelepipeds as a brown suspension. The resulting brown suspension of fcc CoO nanoparallelepipeds was heated at 290 °C for 2 h and 270 °C for 1 h to produce a black suspension. The black fcc Co hollow nanoparallelepipeds were separated by centrifugation and purified by washing with ethanol.

Analyses of gas products and hydrocarbons: The evolved gases CO and NH$_3$ were analyzed during conversion of fcc CoO into fcc Co by using gas analyzers Greenline MK2 (Eurotron) and VRAE PGM-7840 (RAE Systems Inc.), respectively. The GC/MS data were obtained with a GC/MS apparatus equipped with Agilent Technologies 6890N Network GC System, 5973 Network Mass Selective Detector, 7683 Series Injector, and G1701 DAMSD Chemstation. All of the hydrocarbon mixtures were analyzed by GC/MS on a fused silica capillary column (HP35MS 30 m × 0.25 mm, 0.25 μm). After the conversion into fcc CoO was complete, the reaction mixture was centrifuged. The supernatant was distilled under vacuum at 180 °C, and the distillate was purified by column chromatography using pentane as an eluent (silica gel GF254, type 60, E. Merck) to give two fractions, the first eluate with a mixture of structural isomers of heptadecene and octadecene, and the second one with structural isomers of heptadecadiene and octadecadiene. A similar procedure was followed with fcc Co in the absence of fcc CoO to produce a mixture of structural isomers of octadecene for the first eluate and of octadecadiene for the second eluate.

As-prepared fcc Co hollow nanoparallelepipeds were characterized by XRD (Rigaku D/MAX-RB diffractometer using graphite-monochromatized Cu$_{K\alpha}$ radiation at 40 kV and 120 mA) at KAIST and TEM (low resolution: Omega EM912 operated at 120 kV; high resolution: Philips F20Tecnai operated at 200 kV) with selected area electron diffraction (SAED) pattern and energy dispersive analyses of X-ray emission (EDX) at KBSI. Magnetic measurements were performed on SQUID magnetometers (Quantum Design MPMS-7 for dc susceptibility and hysteresis measurements; Quantum Design PPMS-9 for ac susceptibility measurement) at KBSI. The ac and dc susceptibilities as well as the hysteresis measurements were recorded for powdered samples of nanoparallelepipeds in a gelatin capsule. An ac field amplitude of 10 Oe rms was applied for the ac susceptibility measurement. The temperature was varied between 5 and 350 K according to a zero field cooling/field cooling (ZFC/FC) procedure at 100 Oe, and the hysteretic loops were obtained in a magnetic field varying from +5 to −5 T.

Received: June 25, 2008
Revised: September 8, 2008

Keywords: cobalt oxide · cobalt · hollow nanoparticles · magnetic properties · nanostructures

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