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,[13] 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 \( e\text{-Co} \) 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 in oleylamine 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 of the hollow nanoparallelepipeds is shown as an inset.
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 2e and matches well with that of the standard fcc Co (JCPDS no. 15-0806). Time dependent 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 NH₃ are the only gas products that evolve and there was a notable absence of dioxygen: a mixture of C₁₇H₃₄ (heptadecene) and CO deinsertion and dissociation. 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 NH₃ and C₁₇H₃₄, 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, NH₃, and heptadecene. Voids are formed on the surface of fcc CoO solid nanoparallelepipeds by oxide removal. Octadecene (C₁₈H₃₆) and octadecadiene (C₁₈H₃₄) 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 1b would produce ammonia and a mixture 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±5)°) 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 high 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 nanoparallelepipeds 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 Co²⁺ ions to form surface Co⁴⁺ 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.[22] Our observation is in contrast with the Kirkendall effect, in which the out-diffusion...
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 CoO nanoparallelepipeds is determined as 36 emug\(^{-1}\) with the magnetic coercivity ($H_c$) of 120 Oe (Figure 3d).\[20\]

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-
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 CaH2. 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 then at 270°C for 1 h. The inset in [d] shows the expanded hysteresis loop.

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 isoformers of heptadecene and octadecene, and the second one with structural isoformers of heptadecadiene and octadecadiene. A similar procedure was followed with fcc Co in the absence of fcc CoO to produce a mixture of structural isoformers 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 CuKα radiation at 40 kV and 120 mA) at KAIST, and TEM (low resolution: Omega EM912 operated at 120 kV, high resolution: Philips F20 Tecnai operated at 200 kV) with selected area electron diffraction (SAED) pattern and energy dispersive analyses of X-ray emission (EDX) at KBAS. Magnetic measurements were performed on SQUID magnetometers (Quantum Design PPMS-9 for dc susceptibility and hysteresis measurements; Quantum Design PPMS-9 for ac susceptibility measurement) at KBAS. 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.

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