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Shape-controlled synthesis and characterization of cobalt oxides hollow spheres and octahedra[†]

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We demonstrated that single-crystalline cobalt monoxide (CoO) hollow spheres and octahedra could be selectively synthesized *via* thermal decomposition of cobalt(II) acetylacetonate in 1-octadecene solvent in the presence of oleic acid and oleylamine. The morphologies and sizes of as-prepared CoO nanocrystals could be controlled by adjusting the reaction parameters. Cobalt oxide (Co₃O₄) hollow spheres and octahedra could also be selectively obtained *via* calcination method using corresponding CoO hollow spheres and octahedra as precursors. The morphology, size and structure of the final products were investigated in detail by XRD, SEM, TEM, HRTEM, DSC, TG, and XPS. The results revealed that the electrochemical performance of cobalt oxide hollow spheres is much better than that of cobalt oxide octahedra, which may be related to the degree of crystallinity, size, and morphology of cobalt oxides.

1. Introduction

Inorganic nanocrystals with novel morphologies and desired compositions have drawn immense attention due to their unique morphology- and composition-dependent physicochemical properties and their importance in basic scientific research and potential technology applications.¹⁻³ Cobalt oxides have aroused much more attention in recent years on the basis of their distinctive electronic, magnetic, and catalytic properties and wide variety of practical and potential applications. It is well known that CoO and Co_3O_4 are two especially important forms among the various cobalt oxides based on their distinctive structural features and fascinating properties. Especially, CoO, crystallizing in the rock salt structure, is promising for functional materials owing to their potential applications based on magnetic, catalytic and gas-sensing properties.⁴⁻⁶ Co₃O₄ belongs to the normal spinel crystal structure based on a cubic close packing array of oxide ions, in which Co(II) ions occupy the tetrahedral 8a sites and Co(III) ions occupy the octahedral 16d sites. Co₃O₄ is an important magnetic p-type semiconductor that has been demonstrated to have considerable application in, e.g., heterogeneous catalysts, gas sensors, electrochromic devices, solar energy absorbers, pigments, etc.⁷⁻¹¹

In recent years, considerable effort has been devoted to preparing cobalt oxides nanocrystals with controlled morphology and desired compositions. Several chemical and physicochemical methods have been employed to prepare cobalt oxides nanocrystals, for example, spray pyrolysis,¹² chemical vapor deposition,¹³ sputtering,¹⁴ thermal decomposition,¹⁵ electrospinning technique,¹⁶ electrochemical and sonochemical synthesis.¹⁷ Recently a variety of novel shapes such as cobalt oxides nanocone,¹⁸ nanobelt,¹⁹ nanoring,²⁰ nanocube,²¹ nanofiber,²² nanorod,²³ nanotube²⁴ and multishelled hollow sphere^{25,26} have been reported. However, a few routes have been proposed for the synthesis of pure CoO nanocrystals. As far as we know, CoO nanocrystals have been obtained mainly based on the following two methods: thermal decomposition of metal–surfactant complexes in noncoordinating solvents^{27–29} and controlled oxidization of Co₂(CO)₈ or metallic cobalt nanocrystals.^{30,31}

Herein we demonstrated that single-crystalline CoO hollow spheres and octahedra could be selectively synthesized in large quantities by thermal decomposition of cobalt(II) acetylacetonate $(Co(acac)_2)$ in 1-octadecene solvent in the presence of oleic acid and oleylamine. The morphologies and sizes of as-prepared CoO nanocrystals could be controlled by adjusting the reaction parameters, such as surfactants and reaction atmosphere. In particular, we could obtain CoO nanocrystals via a facile thermolysis method without a protected atmosphere. Co₃O₄ hollow spheres and octahedra could also be obtained via a calcination method using the corresponding CoO as a precursor. The results revealed that the electrochemical performance of hollow spheres is much better compared with that of octahedra, which may be related to the degree of crystallinity, morphology, and particle size of the cobalt oxides. It is worthy to note that the current synthetic strategy can be used to synthesize other metal oxides nanocrystals, and it will have a good prospect in future large-scale applications due to its high yields and simple reaction apparatus.

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The synthesis uses commercially available reagents: cobalt(II) acetylacetonate (Co(acac)₂, analytical grade, 99%, ACROS), trioctylphosphine oxide (TOPO, analytical grade, 99%, ACROS), 1-octadecene (ODE, technical grade, 90%, ACROS), oleic acid (OA, chemical grade, SCRC), oleylamine (OAm, technical grade, approximate C₁₈-content 80–90%, ACROS), hexadecyl trimethyl ammonium bromide (CTAB), polyvinyl pyrrolidone (PVP) and sodium dodecyl sulfate (SDS) were of analytical grade and used without any further purification.

All the reactions were conducted in a three-neck flask equipped with a stirring and heating attachment. In a typical reaction, 0.2571 g Co(acac)₂ (1 mmol) and 0.0364 g CTAB (0.1 mmol) were dissolved into 20 mL ODE with 4 mmol OA and 10 mmol OAm. The reaction mixture was degassed for 20 min at room temperature using high purity gas of nitrogen. The solution was heated up to 260 °C with approximately 8 °C min⁻¹ under vigorous stirring. At the beginning of the reaction, a balloon was used to seal the system and buffer the high pressure generated during the reaction. After heating under reflux for 2 h, the solution was then cooled to room temperature, and a mixture of alcohol and hexane was added to the solution to yield a waxy precipitate, which was separated by centrifugation. Finally, the products were dried in an oven at room temperature. The resulting precipitate was found to be re-dispersible in many organic solvents, such as n-hexane and chloroform. Shape control of the products can be achieved by adjusting some of the parameters, such as the surfactants and reaction atmosphere.

2.1 Characterization

The obtained products were characterized on a D/max2550 VB + X-ray powder diffractometer (XRD) with Cu-K α radiation ($\lambda = 1.54178$ Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The size and morphology of asprepared products were determined at 20 kV by a XL30 S-FEG scanning electron microscope (SEM) and at 160 kV by a JEM-200CX transmission electron microscope (TEM) and a JEOL JEM-2010F high-resolution transmission electron microscope (HRTEM). Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) were carried out with a NETZSCH STA-449C simultaneous TG-DTA/DSC apparatus at a heating rate of 10 K min⁻¹ in flowing air. X-ray photoelectron spectroscopy (XPS) data were acquired on a VG ECA-LAB MK2. Sintering process was conducted in box-type resistance furnace (SX-4-10).

In order to evaluate the electrochemical characteristics, electrodes were fabricated using the powder by mixing 80 wt% active materials, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone. The resultant slurries were spread on aluminum foil substrates. After coating, the electrodes were pressed and dried at 120 °C under vacuum for 12 h and then pressed between two stainless steel plates at 1 MPa. Prior to cell assembling, the electrodes with area of 0.64 cm² were dried at 120 °C for 4 h under vacuum. The testing cells had a typical two-electrode construction using a polypropylene microporous sheet as the separator, and 1 M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl

carbonate (DMC) (1 : 1, v/v) was used as the electrolyte. A pure lithium foil was used as the counter electrode and the samples under test were used as the working electrode during electrochemical measurements. All cells were assembled in an argon-filled glove box. The electrode capacity was measured by a galvano-static charge–discharge experiment with a current density of 200 mA g⁻¹ at a potential between 0 and 2.5 V.

3. Results and discussion

Fig. 1A shows the low-magnification TEM image of CoO obtained by using 0.1 mmol CTAB in the presence of oleic acid and oleylamine at 260 °C for 2 h under a nitrogen environment. We found that the product mainly consisted of hollow spheres with an outer diameter of about 250 nm and wall thickness of about 50 nm. The remarkable contrast between the shells and centers indicates the hollow nature of the spheres. More details of structure can be obtained from a further magnified image, as shown in Fig. 1B. The surfaces of hollow spheres are rough with some flocculates. High-resolution TEM provided further insight into the structures of as-prepared products. Fig. 1C shows the HRTEM image of the area marked in Fig. 1B. The lattice spacing is calculated to be 0.21 nm, corresponding to d-spacing of (200) crystal plane of cubic CoO, which further confirmed its single-crystalline structure. The inset of Fig. 1C is the fast Fourier transform (FFT) image of the HRTEM result. Fig. 1D shows the XRD pattern of as-prepared CoO hollow spheres. All diffraction peaks can be readily indexed to a pure cubic structure with lattice constant a = 4.263 Å, well consistent with the standard PDF database (JCPDS file no. 65-2902). Diffraction peaks of the sample are sharp and narrow, indicative of a relatively good crystallinity.



Fig. 1 (A) Low-magnification TEM image of CoO hollow spheres obtained by using 0.1 mmol CTAB in the presence of oleic acid and oleylamine at 260 °C for 2 h under a nitrogen environment; (B) high-magnification TEM image of CoO hollow spheres; (C) HRTEM image of the area marked by the square in figure (B); (D) XRD pattern of CoO hollow spheres. The inset of (C) is the fast Fourier transform image.

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Generally, the chemical and physical properties of inorganic materials are directly related to their morphology, size, and phase composition. Therefore, it is very important to tailor their electronic, magnetic and optical properties through the morphology and shape control of the final products. Fig. 2A shows the lowmagnification SEM image of CoO nanocrystals prepared by using 0.1 mmol CTAB in the presence of oleic acid and oleylamine at 260 °C for 2 h without a protected atmosphere. The products comprise large quantities of CoO octahedra. More details of the structure can be obtained from a further magnified image, as shown in Fig. 2B, from which uniform CoO octahedra with the size of about 150 nm and edge length of 80-120 nm can be seen clearly. Fig. 2C is the representative TEM image of CoO octahedra, which clearly shows those octahedral structures from different viewing angles. The inset of Fig. 2C is the HRTEM image taken from individual octahedra. The lattice spacing was calculated to be 0.21 nm, corresponding to the dspacing of (200) crystal plane of cubic CoO. Fig. 2D shows the XRD pattern of as-prepared octahedral CoO nanocrystals. All diffraction peaks can be readily indexed to a pure cubic structure with lattice constant a = 4.274 Å (JCPDS file no. 65-2902), which indicates that cubic CoO phase can be obtained without a protected atmosphere.

The surfactant is also a very important factor influencing the morphology of the final products.³² Fig. 3A and B show the typical SEM and TEM images of as-prepared product obtained by using 0.03 g PVP in the presence of oleic acid and oleyl-amine at 260 °C for 2 h under nitrogen environment. The product is nearly monodisperse and the heterogeneous contrast effect from its TEM image (Fig. 3B) suggests that nanocrystals might have an unsmooth surface. The SEM image confirms this point. On the whole, these quasi-spherical particles have the

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Fig. 2 (A) Low-magnification SEM image of the as-prepared octa-

hedral-like CoO nanocrystals prepared by using 0.1 mmol CTAB in the

presence of oleic acid and oleylamine at 260 °C for 2 h without a pro-

tected atmosphere; (B) high-magnification SEM image of octahedral

CoO nanocrystals selected from (A); (C) TEM image of octahedral CoO

60 70

40 50 2 theta (degree)





Fig. 3 Morphologies of CoO nanocrystals prepared by using different surfactants in the presence of oleic acid and oleylamine at 260 °C for 2 h under a nitrogen environment: SEM image (A) and TEM image (B) of CoO nanocrystals prepared with 0.03 g PVP; SEM image (C) of CoO nanocrystals prepared with 0.1 mmol TOPO; TEM image (D) of CoO nanocrystals prepared with 0.1 mmol SDS.

trends of polyhedra. However, it is worth noting that in our previous research with a similar reaction system, PVP is a more favorable surfactant for the dispersity of nanoparticles.³³ In particular, when 0.1 mmol TOPO was employed as surfactant to control morphology of product, CoO nanocrystals with octahedral structures can be obtained, as shown in Fig. 3C. SEM image shows that the majority morphology of as-prepared CoO nanocrystals is octahedra. The edge-length of octahedral CoO is about 80 nm. Fig. 3D is the TEM image of CoO nanocrystals prepared by using 0.1 mmol SDS in the presence of oleic acid and oleylamine at 260 °C for 2 h under nitrogen environment, from which it can be seen that products are composed of irregular monodisperse nanoparticles in the size range of 20–30 nm.

It should be mentioned that there was a failure to control the morphology of the products if the reaction was adopted in an air atmosphere. Ammonia release accompanying the reaction provides an anaerobic atmosphere. All of these experimental conditions and phenomena ensured the formation of cobalt monoxide, preventing it from further oxidation. Experimental results suggest that the reaction atmosphere and surfactant CTAB may play important roles in the formation of CoO hollow spheres. As is well-known, most of the methods for preparation of hollow spheres are template-based ones, in which sacrificial templates, either hard or soft ones, are used.^{34,35} We considered that nitrogen gas could help the surfactant CTAB to serve as template, and CoO crystallites deposited along the template surface, resulting in formation of the shells around the CTAB vesicles. Based on the hypothesis above, it is suggested that the amount of CTAB surfactant used should be effective on the formation of CoO hollow spheres (see ESI, Fig. S1A and S1B[†]). When the amount of CTAB increased from 0.5 mmol to 1.0 mmol, CoO spheres with hollow interior and floccular structures can be clearly observed due to the excessive amount of CTAB.

The thermal behavior of CoO nanocrystals oxidized to Co₃O₄ was investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperature range 25–750 °C with the heating rate of 10 °C min⁻¹ in air, as shown in Fig. 4. The gradual mass loss (3.39%) in the range 25-290 °C can be attributed to evaporation of the absorbed organic residues and water species on the CoO surfaces accompanied by a weak broad exothermal peak at 240 °C. With the temperature rising, the obvious gravimetric gain can be seen from Fig. 4. The first rapid mass increase (2.78%) occurred from 290 °C to 320 °C, illustrating quick oxidation of the surface of products. The second mass increase (1.81%) occurred before 445 °C, which was attributed to the further oxidation of CoO. The DSC curve of the sample displayed two exothermal peaks in the gravimetric gain region: one is centered at 290 °C and another at about 380 °C. The total mass increase on the curve was smaller than the theoretical value (7.1%), which may be associated with partial oxidation of CoO in early stage and organic residues.

Co₃O₄ hollow spheres and octahedra could be selectively obtained via calcination method using corresponding CoO hollow spheres and octahedra as precursors. Fig. 5A shows XRD patterns of Co₃O₄ hollow spheres (curve a) and octahedra (curve b) obtained by the calcination of corresponding CoO nanocrystals at 600 °C for 2 h in air. All the reflections in the XRD patterns can be indexed to the pure face-centered-cubic phase (space group: Fd3m (No. 227)) of spinel cobalt oxide with lattice constant a = 8.085 Å (JCPDS file no. 78–1969). No impurity peaks were observed, which indicates that cubic CoO was completely converted into the spinel structure Co₃O₄. The low-magnification SEM image of Co3O4 hollow spheres is shown in Fig. 5B and the high-magnification SEM image inset in Fig. 5B further shows the spheres with a hollow interior. Fig. 5C and D are low- and high-magnification SEM images of Co₃O₄ octahedra, respectively. The morphology analysis of Co₃O₄ hollow spheres and octahedra reveals the perfect inheritance from corresponding CoO nanocrystals.

X-ray photoelectron spectroscopy (XPS) is a reliable method for intensive investigation of samples, especially efficient for studying the status of atoms less than 10 nm deep from the





Fig. 5 (A) XRD patterns of inner hollow (curve a) and octahedral (curve b) Co_3O_4 nanocrystals calcined at 600 °C for 2 h using the corresponding CoO nanocrystals as precursor, respectively. (B) Low-magnification SEM image of Co_3O_4 nanocrystals with inner hollow structures calcined at 600 °C for 2 h using CoO hollow spheres as precursor. (C) Low-magnification SEM image of octahedral Co_3O_4 nanocrystals calcined at 600 °C for 2 h using octahedral Co_3O_4 nanocrystals calcined at 600 °C for 2 h using octahedral Co_3O_4 nanocrystals. Inset of (B) is the corresponding high-magnification SEM image of Co_3O_4 hollow spheres.

surface of metastable materials with partially filled valence bands. It was introduced here to evaluate the surface of as-prepared CoO and Co₃O₄ nanocrystals. The full survey spectra of the two samples are just in coherence with each other and are shown in Fig. 6, where each of the main peaks are indexed to O 1s, C 1s and Co 2p regions, confirming the cobalt oxides with nonexistence of impurities. The inserted profile is the binding energy (BE) spectrum for C 1s electrons of CoO sample. A main peak emerged at BE of 284.8 eV, which is the standard BE for amorphous carbon as an inert reference. The surface of the nanomaterials is very vulnerable to being affected by circumstance because of its special immense surface area and high activity. The cubic 3d transition metal Co has a partially filled valence band within which strong electron correlations among the 3d electrons were localized. It is of great importance to study the stability and status of atoms special requirements rising from electrochemical application of cobalt oxides.

CoO and Co₃O₄ have different coupling into the two possible final states giving rise to the main and satellite peaks. It is well known that cobalt series occupy the identical BE region belonging to Co $2p_{1/2}$ and Co $2p_{3/2}$ electrons, but the distinction among many of the cobalt compounds is still vague, as chemical shift of main peaks in XPS spectra of Co 2p electrons in Co²⁺ and Co³⁺ is not obvious enough. The survey spectra for Co 2p region of inner hollow CoO nanocrystals (curve a) prepared using 0.1 mmol CTAB with the molar ratio of OA to OAm 4:10 at 260 °C for 2 h in nitrogen atmosphere and Co₃O₄ nanocrystals (curve b) sintered at 600 °C for 2 h using inner hollow CoO nanocrystals as precursors are shown in Fig. 7. The curves are





Fig. 6 Full survey XPS spectra of CoO (curve a) and Co_3O_4 (curve b) hollow spheres. The inserted profile is the C 1s survey curve.



Fig. 7 Co 2p electron XPS spectra for (a) CoO hollow spheres and (b) Co_3O_4 hollow spheres. Data were acquired with Mg K α radiation and were fitted after removal of a linear background.

fitted by pseudo-Voigt function; the binding energy (BE) values emerged on the fitting lines are listed in Table 1. It was in fact observed that the BE values of the most intense Co photoelectronic peak (Co 2p) did not allow a clear distinction between CoO pure Co (11) and Co_3O_4 Co $^{II}Co ^{III}{}_2O_4.$ The two major peaks appearing in curve a shown in Fig. 7 are at 780.890 eV and 796.773 eV, separated by 15.9 eV, corresponding to the Co $2p_{3/2}$ and Co $2p_{1/2}$ spin–orbit peaks, respectively, of the CoO phase, which are consistent with the supposed BE values of earlier reported literature.^{36,37} Furthermore, two satellites located at approximately 6 eV above the primary binding energy peaks were detected at 786.278 and 802.796 eV, which were used as a fingerprint for the recognition of high-spin Co (II) species in CoO.^{38,39} In addition, the Co 2p spectrum of Co₃O₄ shown in Fig. 7b yields a Co $2p_{3/2}$ peak at 780.591 eV and Co $2p_{1/2}$ peak at 795.935 eV with the corresponding satellites at 784.929 eV and 803.621 eV, respectively, are just in the same shape and are the identical BE of Co $2p_{3/2}$ and Co $2p_{1/2}$ electrons, respectively,

which is in agreement with the literature for Co_3O_4 .^{38,40–42} Unlike in Co(II) compounds, in the low-spin Co(III) compounds, the satellite structure is weak or missing.⁴¹ Co_3O_4 , a mixedvalance oxide, shows a weak satellite structure symptomatic of shake-up from the minor Co(II) component.⁴² The (Co $2p_{1/2}$ – Co $2p_{3/2}$) energy separation is approximately 15.3 eV, which is also identical to that of the pure phase Co_3O_4 in the literature.^{43,44}

The electrochemical performances of as-prepared CoO and Co₃O₄ with different morphologies, hollow spheres and octahedral structures, were investigated. Fig. 8 gives the typical first discharge curves of Li-CoO and Li-Co₃O₄ cells made by CoO and Co₃O₄ with inner-hollow (filled squares) and octahedral structures (empty circles), between 0 and 2.5 V at a current density of 200 mA g⁻¹. Generally speaking, nanocrystals with an inner-hollow structure have higher capacity than octahedra, whether CoO or Co₃O₄. Fig. 8A shows that inner-hollow CoO nanocrystals have an initial discharge capacity as high as 510.8 mAh g^{-1} , and 116.6 mAh g^{-1} after 50 cycles. Octahedral ones have an initial discharge of at 291.7 mAh g^{-1} and 29.7 mAh g^{-1} after 50 cycles. The discharge curves of Co₃O₄ hollow spheres electrode shown in Fig. 8B indicated that the discharge voltage decreased sharply from 2.5 V to the discharge plateau located in the range of 1.0-0.8 V at the first discharge cycle. The initial capacity of as-prepared Co₃O₄ hollow spheres reaches 601.2 mAh g^{-1} . The Co₃O₄ hollow spheres electrode demonstrates a stable reversible lithium storage capacity of 165.9 mAh g^{-1} within 50 cycles. Obviously, metal oxide nanocrystals with different morphologies have different lithium storage capacity, and the reason for this difference is complicated, just as many literature reports have mentioned.^{45,46} The higher discharge capacity of hollow spheres may be attributed to their unique morphology. The inner hollow structure is favorable for increasing the interface area between electrode and electrolyte, which can result in a higher diffusion rate and faster electrode kinetics, and also can increase the usage factor of the active component of the electrode.47 However, the discharge capacity of octahedral Co₃O₄ electrode was close to zero, indicating its poor electrode kinetics.

4. Conclusion

In summary, CoO hollow spheres and octahedra can be selectively synthesized *via* thermal decomposition of cobalt(II) acetylacetonate in 1-octadecene solution using oleic acid and oleylamine as capping ligands. The morphologies and sizes of as-prepared CoO nanocrystals can be controlled by adjusting the reaction parameters. This simple and reliable synthetic strategy may be carried out to synthesize other metal oxides nanocrystals. Furthermore, Co₃O₄ hollow spheres and octahedra can be obtained by the calcination of corresponding CoO hollow spheres and octahedra at 600 °C for 2 h. The electrochemical performance of cobalt oxide hollow spheres is much better than that of cobalt oxide octahedra. These cobalt oxide hollow spheres and octahedra can also be expected to bring new opportunities for further fundamental research, as well as for technological applications in catalysts, solid-state sensors, and as anode materials in Li-ion rechargeable batteries.

Samples	Co 2p _{3/2} (eV)	Satellite (eV)	Co 2p _{1/2}	Satellite (eV)
CoO (this work)	780.890	786.278	796.773	802.796
Co_3O_4 (this work)	780.591	784.929	795.935	803.621
CoO	780.0–780.919 ^{38,41}	785.339	796.0–796.519 ^{39–41}	802.639
Co ₃ O ₄	779.5, 780.743	787.945	794.5, 795.038	803.045

Table 1 XPS peak positions (BE in eV) obtained for CoO and Co₃O₄ hollow spheres compared with the literature values



Fig. 8 The first discharge curves of the Li–CoO (A) and Li–Co₃O₄ (B) cells made by CoO and Co₃O₄ with different morphologies, hollow spheres (filled squares) and octahedral structures (empty circles), at a current density of 200 mA g^{-1} . Inset: cycle performance of Li-profiles of the cells at a current density of 200 mA g^{-1} at room temperature.

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