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Controlled Synthesis of Self-Assembled Metal Oxide Hollow Spheres Via Tuning Redox Potentials: Versatile Nanostructured Cobalt Oxides**

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Self-assembly of nanomaterials has attracted a great deal of attention by bridging different areas of science and engineering for design and development of outstanding materials, methodologies, and theories.[1–4] Nanostructured hollow spheres and their related structures are widely considered to possess important applications in drug delivery,[5] high surface area catalysts,[6] high efficiency photodecomposition,[7] and low density batteries or devices. Low-density hollow materials prepared by template-assisted syntheses have been reported,[8,9] however, contamination by residues of templates is difficult to be totally removed.

Cobalt oxides have been used in many applications, such as toxic gas sensors,[10] catalysts,[11–13] magnetic semiconductors,[14,15] and rechargeable battery materials.[4,16–18] With the discovery of significant electrochemical improvements of nickel hydroxide and nickel oxyhydroxide electrodes (NOE) by incorporation of cobalt oxide hydroxide,[17,18] the investigation of cobalt oxide hydroxide (CoOOH) has drawn great research interest in the last decade. The most common preparation of cobalt oxide hydroxide involves precipitation under basic conditions with the presence of oxidizing reagents (NaOCl or H_2O_2). However, CoOOH synthesis in acidic conditions has seldom been studied.

In this work, a one-pot hydrothermal treatment under acidic conditions is reported to directly synthesize nanostructured hollow metal oxides (CoOOH and CeO_2) spheres without adding surfactants or templates. We performed the first work where the net redox potentials were controlled to assist in the formation of hollow structures. An example of utilizing as-synthesized CoOOH as a versatile precursor to produce nanostructured cobalt derivatives was performed as well.

The reaction of cobalt sulfate with ammonium persulfate at 100 °C (**S-100**) produced highly self-assembled CoOOH microspheres with three levels of structure (Fig. 1). The primary structure (1°- structure) is the layered crystal structure of CoOOH with an interlayer spacing of 0.44 nm. The secondary structure (2°- structure) is the CoOOH nanoflakes, which form microspheres by physical stacking. The tertiary structure (3°- structure) shown in Figure 1a is a self-assembled spherical structure with a diameter around 1–2 um. Figure 1b shows that the tertiary structure is self-assembled with an empty core; a physical stacking of CoOOH nanoflakes with a 13–25 nm thickness as shown in Figure 1c. The high resolution transmission electron microscopy (TEM) image of a vertical standing nanoflake (Fig. 1d) shows lattice fringes, identified as (003) based on $d_{003} =$ 0.44 nm, which are parallel to the surface of the nanoflakes so plates crystallize along (003) and are bounded by basal planes of the (001) form. The low magnification TEM images (Fig. 1e) further confirm the formation of hollow cores indicated by arrows in the tertiary structure. After vigorous stirring for three days in aqueous solution, a collapse of the tertiary structure was observed (Fig. 1f), which further confirms that the tertiary structure is constructed primarily by physical stacking without any connection to a common center within the microspheres. The XRD pattern of **S-100** shown in Figure 2a was indexed as CoOOH (JCPDS-07-169). Elemental analysis was performed by energy dispersive X-ray spectroscopy (EDX) to indicate that no sulfur exists in the as-synthesized CoOOH microspheres.

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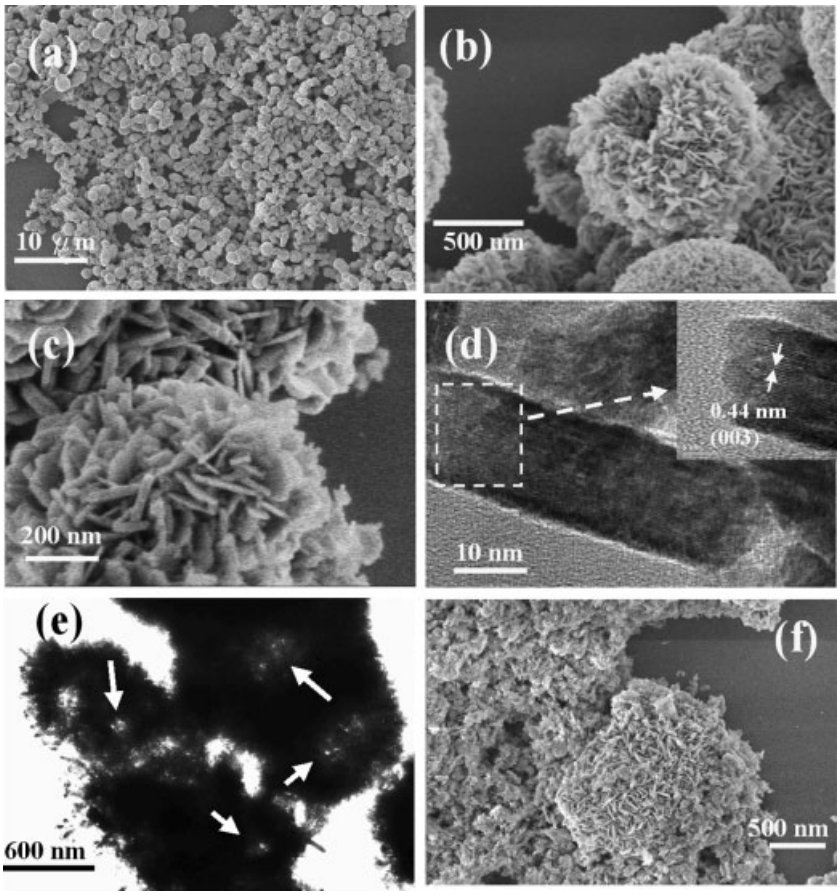


Figure 1. Electron Microscopy images of CoOOH synthesized at 100 °C, **S-100**. (a) Scanning electron microscopy (SEM) images showing a microspherical morphology; (b) exhibiting the tertiary structure with a hollow core; (c) demonstrating the physical stacking of nanoflakes (secondary structure) to build the tertiary structure; (d) HR-TEM image of a vertical standing nanoflake; inset corresponds to the area of white dashed-line square, which shows the (003) lattice fringe is parallel to the surface of nanoflakes; (e) TEM image of hollow cores shown by arrows. The hollow cores appear as lighter regions; (f) collapse of tertiary structure after vigorous stirring for 3 days.

The effectiveness of using **S-100** sample as a precursor to produce cobalt oxide derivatives was examined in this work. After calcination of **S-100** at 450 °C in air, the tertiary structure shown in Figure 3a showed no significant morphology change or collapse even though the crystal structure (primary structure) was transformed from CoOOH to Co_3O_4. The crystal phase transformation has been studied by *in-situ* XRD in air at various temperatures (Fig. 2b). The calcination of CoOOH started from 150 °C to 500 °C at 50 °C intervals. The pattern at 500°C was indexed and characterized as Co_3O_4. The pattern at 150 °C is similar to the XRD patterns at room temperature (Fig. 2a) indicating no crystal structure change from room temperature to 150 °C. The crystal transformation from CoOOH to Co_3O_4 occurred between 250 °C–300 °C, which is consistent with work of Zeng *et al.*[19] In a magnetic study, the Co_3O_4 obtained from the crystal transformation was characterized by antiferromagnetic ordering with a Néel Temperature $T_N \approx 30$ K consistent with earlier work.[20] The temperature dependence of the magnetic susceptibility for the paramagnetic state above the ordering temperature can be fit to the Curie-Weiss law yielding an effective magnetic moment $\mu_{eff} = 3.90 \pm 0.05$ μ_B per formula unit and Curie-Weiss temperature $\theta = -77 \pm 5$K. These results are in excellent agreement with previous work on both bulk Co_3O_4 as well as larger Co_3O_4 nanoparticles, in which all the magnetic contribution is attributed to Co^{2+} ($S = 3/2$) in the tetrahedral (A sites) of the spinel structure. The Co^{3+} (low spin, $S = 0$) in the octahedral (B sites) have no magnetic contribution.[21,22] (see Supporting information).

A second set of experiment was performed to produce battery material, $LiCoO_2$, by using as-synthesized CoOOH as the precursor. A mixture of 0.1 g CoOOH (**S-100**) and LiOH solution (2.3 M) was reacted by hydrothermal treatment at 130 °C for 3 d. The XRD of product shown in Figure 2c corresponds to $LiCoO_2$ (JCPDS-16-0427). The SEM image (Fig. 3b) shows that the thickness of the flakes, 2°- structure, still remained in the nano-scale range (13–25 nm); no significant change was observed except a slight distortion of the tertiary structure of microspheres was observed. A recent study reported that the thickness of $LiCoO_2$ material within 15–30 nm exhibits an outstanding high rate capacity in lithium-ion rechargeable batteries.[23] The electrochemical activity was tested by O_2 reduction using cyclic voltammetry. Both CoOOH and $LiCoO_2$ electrodes have higher O_2 reduction current than other metal oxide materials used as electrodes in lithium-air batteries.[24] The nanostructured $LiCoO_2$ electrode shows about a 40% higher O_2 reduction current than CoOOH (see Supporting Information). These results demonstrate that the nanostructured CoOOH and $LiCoO_2$ are good candidates as battery electrode materials. A charge/discharge study of as-synthesized $LiCoO_2$ is still under investigation.

These above two synthetic experiments demonstrate that CoOOH can be used as a versatile precursor to produce nanostructured microspheres of cobalt oxide derivatives, such as Co_3O_4 and $LiCoO_2$ (Scheme 1). More importantly, this concept may be generalized to prepare and design various functional nanostructured metal oxides of controlled shapes or sizes from corresponding preformed metal oxide hydroxide precursors.

Various reaction temperatures, including 100 °C, 120 °C (**S-120**), 180 °C (**S-180**), and 250 °C (**S-250**), were applied in this work to study temperature effects on the self-assembly of

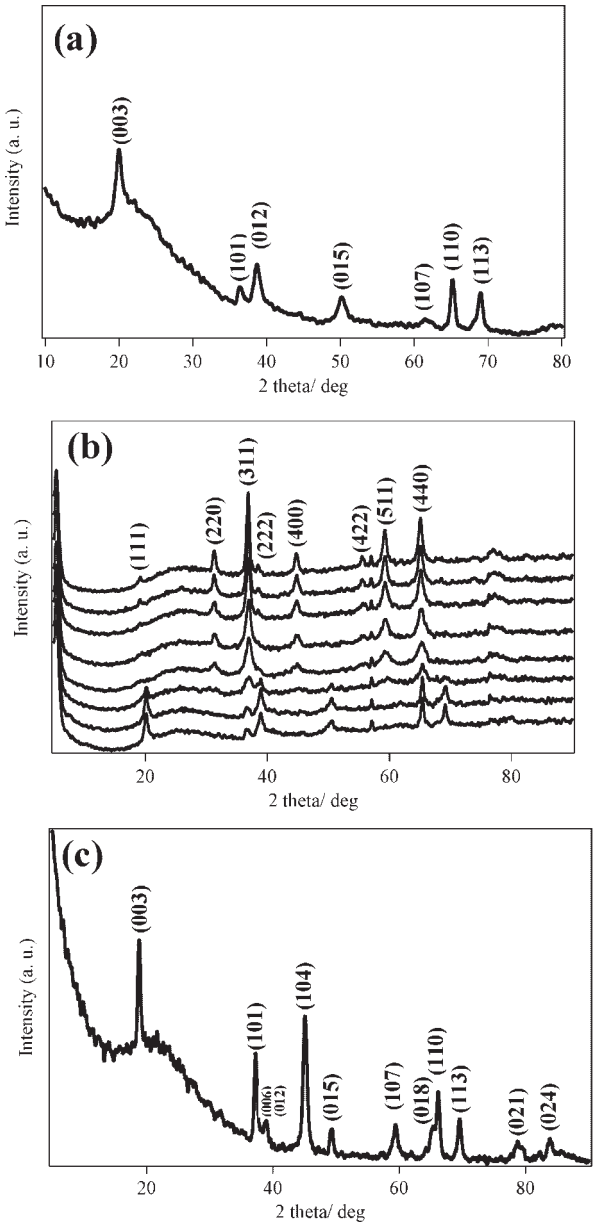


Figure 2. (a) The XRD pattern of CoOOH synthesized at 100 °C (**S-100**); (b) the *in-situ* XRD in air from 150 °C to 500 °C at 50 °C intervals (from bottom to top); a one hour heating stage was performed before each scan; (c) the XRD of $LiCoO_2$ obtained from hydrothermal treatment of **S-100** with LiOH solution.

cobalt oxide hydroxide (supporting information). The results show that the self-assembly of tertiary structure can be obtained at 120 °C but not higher than 180 °C. The SEM images show that only separated particles can be observed in **S-180** and **S-250**. This temperature-dependent self-assembly allows selective synthesis of self-assembled CoOOH microspheres or separated particles by changing temperatures, which could be useful to further study the effects of self-assembly and hollow structures of materials as shown below in studies of catalytic activity.

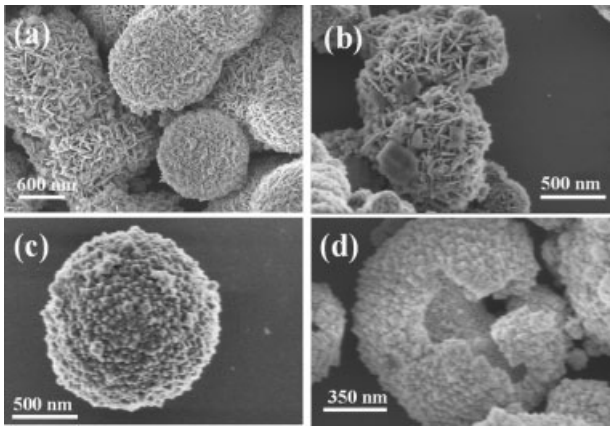
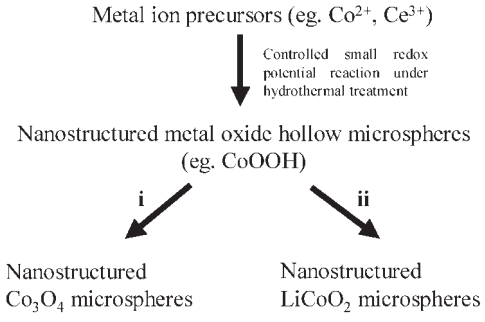


Figure 3. SEM images of (a) Co_3O_4 obtained after calcination of **S-100** at 450 °C for 1 h; (b) $LiCoO_2$ obtained from hydrothermal treatment of **S-100** with LiOH solution; (c) CeO_2 hollow microsphere and (d) a broken sphere demonstrating the hollow structure of CeO_2 spheres.

The catalytic activity tests of three samples, **S-100**, **S-180** and Co_3O_4 obtained after 450 °C calcination of **S-100**, were examined for the oxidation of cumene with tertiary butyl hydroperoxide (TBHP) as the source of oxygen (Table 1). Cobalt oxide based catalysts are widely used for oxidation of hydrocarbons.[25] Self-assembled **S-100** showed the highest 42% conversion; **S-180** and Co_3O_4 microspheres afforded 17% and 9% conversion, respectively. Compared with separated particles (**S-180**), the hollow structure microspheres with finer particles (**S-100**) exhibited a significant improvement of catalytic activity. Acetophenone was the only product observed in all cases, indicating an outstanding selectivity to acetophenone. The results are summarized in Table 1. These data show that the oxidation states of cobalt and the surface areas of the tested samples may play key roles in their catalytic activity. The conversions are comparable to similar substrate oxidation protocols in the vapor and liquid phase with cobalt based zeolites.[26,27]



Scheme 1. Summary procedure of producing metal oxide hollow spheres and their derivatives. For the CoOOH hollow spheres, (i) is a calcination at 450 °C and (ii) is a hydrothermal treatment with LiOH solution.

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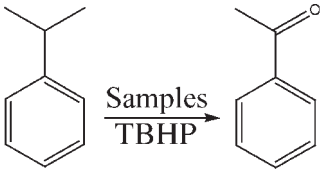
Table 1. Oxidation of cumene with cobalt oxides with TBHP [a].



Samples	Morphology [c]	Surface area [$m^2\ g^{-1}$]	Conversion [b] [%]	Oxidation number
CoOOH (**S-100**)	3°- structure	53.5	42	3
CoOOH (**S-180**)	Separated particles	20.5	17	3
Co_3O_4	3°- structure	52.4	9	2.7

[a] Reaction conditions: 1 mmol of cumene, 5 mmol TBHP, 10 mL acetonitrile as solvent, 70 °C, 24 h. [b] Product identification and quantification by GC-MS. [c] Morphology observation by SEM.

The redox potential of $S_2O_8^{2-}/SO_4^{2-}$ (2.01 V) is slightly larger than Co^{2+}/Co^{3+} (1.808 V), which gives a net potential of 0.202 V (Supporting Information). A small net redox potential was intentionally designed to reduce the reaction and nucleation rate to limit the particle size of cobalt oxide hydroxide particles.[28] The generality of this concept was tested by applying the same procedure to a non transition metal oxide, cerium oxide. The net redox potential between Ce^{3+}/Ce^{4+} and $S_2O_8^{2-}/SO_4^{2-}$ is 0.29 V, which is close to 0.202 V between Co^{2+}/Co^{3+} and $S_2O_8^{2-}/SO_4^{2-}$. The SEM and XRD results (Fig. 3 and Fig. S-4) show that nanostructured hollow cerium oxide microspheres can be successfully produced, demonstrating the potential of this concept as a general route to prepare hollow metal oxide microspheres. The detailed formation mechanism of hollow microspheres is still under investigation. A reviewer has suggested that the formation of hollow structures could be obtained without redox transformations during hydrothermal treatment, indicating that small redox potential factors may not be involved in the formation of hollow structures.[29] A noticeable temperature effect has shown that the CoOOH particles with diameters larger than a certain size (ca. 200 nm, **S-180** and **S-250**) do not prefer to form microspheres (Supporting Information). Based on these experimental observations, we agree with the reviewer that convectional processes or microbubbles may occur during the hydrothermal synthesis; and size-controlled one dimensional nanoflakes (CoOOH) or three dimensional nanoparticles (CeO_2) ≤ 50 nm by redox potential control have a suitable size to interact with microbubbles or convectional processes to generate curvature, and thus assist the formation of hollow nanostructures of spherical shape.[30] The hollow assembly may also be spherical in shape due to surface tension properties.[6]

A schematic illustration of our work is given in Scheme 1. In summary, a general method to produce self-assembled metal oxides with hollow structures was successfully developed by controlling the net redox potentials. No templates were needed, thus avoiding contamination of resides of templates. In the cobalt oxide hydroxide case, the nanostructured CoOOH hollow spheres are versatile precursors for nanomaterials of cobalt oxide derivatives, and also possess excellent catalytic activity. Metallic cobalt microspheres with strong magnetic moments can also be produced from nanostructured CoOOH hollow spheres via reduction with hydrazine. Continuing research of applying the template-free and controlled net redox potential syntheses to other metal oxides and their derivatives will be focused on further understanding and controlling the crystal growth of metal oxide nanomaterials.

Experimental

Synthesis: The CoOOH was prepared from a redox reaction between $CoSO_4$ and $(NH_4)_2S_2O_8$ under hydrothermal treatment. The mixture of 1.48 mmol of $CoSO_4 \cdot 7H_2O$ and 0.74 mmol of $(NH_4)_2S_2O_8$ was dissolved in 13 mL of deionized (DI) water to form a clear solution, which was then transferred to a 23 mL Teflon-lined autoclave. The reaction temperatures were varied from 100 °C to 250 °C for 3 d. The resulting brown slurry was washed several times with DI water and then dried in an oven at 100 °C for 24 h. The synthesis of CeO_2 from $Ce(NO_3)_3 \cdot 6H_2O$ was following the same procedure as above at 180 °C reaction temperature.

Characterization: XRD measurements were carried out using a Scintag PDS 2000 diffractometer with a CuKα X-ray source. Field-emission scanning electron microscopy (FE-SEM) studies were performed using a Zeiss DSM 982 Gemini FESEM with a Schottky emitter operating at 2 kV with a beam current of 1 μA. Powder specimens were dispersed in ethanol. Transmission electron microscopy (TEM) images were obtained in a Philips EM420 operating at 120 kV and JEOL JEM 2010 FasTEM at 200 kV. BET surface area measurements were obtained in a Micromeritics ASAP 2010 system. Magnetic measurements were carried out using a Quantum Design MPMS SQUID magnetometer for temperatures 10 K $\leq T \leq$ 300 K and applied fields 0 kOe $\leq H \leq$ 50 kOe. The electrodes for cyclic voltammetry were prepared by mixing samples with carbon powder in a 1:1 ratio. Five drops of 25 wt % PTFE were added after suspending the mixture in water. A 1 cm × 1 cm XR 72 carbon paper was coated with the prepared suspension and waiting until dry to obtain electrodes.

The cyclic voltammetry tests were performed with a CHI 430 Electrochemical Workstation with 50 mV s^{-1} in 1.0 M KOH solution.

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