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$La(OH)_3$ Hollow Nanostructures with Trapezohedron Morphologies Using a New Kirkendall Diffusion Couple

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A highly symmetric trapezohedron of lanthanum glycolate precursor is converted to hollow $La(OH)_3$ with the same morphology via a simple hydrothermal treatment of the lanthanum glycolate precursor in an alkaline solution. The formation process of the hollow structure is the result of the Kirkendall effect, in which a new diffusion couple, water and lanthanum glycolate, is proposed. This expands the scope of the Kirkendall effect in material fabrication. The hollow $La(OH)_3$ trapezohedron can be further converted into hollow La_2O_3 material by calcinations. The as-prepared $La(OH)_3$ hollow trapezohedron shows excellent ability to remove certain organic pollutants in wastewater.

Introduction

Hollow nanostructures are promising materials for applications in drug delivery, catalysis, lightweight fillers, and photonic crystals, etc.[1−4] A variety of methods have been developed to synthesize hollow structured materials, including hydrothermal treatment,[5−8] high-temperature annealing of solid precursors,[9−12] and in particularly Kirkendall effect based methods, such as oxidation, sulfuration[13] and phosphoration[14,15] of metal nanoparticles. The Kirkendall effect, which originally explains how void space on zinc side is produced when a copper and a zinc metal are pressed against each other at elevated temperature,[16] has been a useful tool for the synthesis of hollow structured materials. The essence of the Kirkendall effect based methods is to choose an appropriate diffusion couple, and during the synthesis, one component is either diffused through the interface or converted to the desired species with higher lattice density, thus leaving the original space void.

Recently, the Kirkendall effect based technique has been expanded beyond two solid materials. Xia et al. synthesized single-crystalline hollow polyhedral nanoboxes of gold using silver nanocubes and $HAuCl_4$ solution as a diffusion couple.[17] Yin et al. produced the hollow nanocrystals of the cobalt oxide and chalcogenides using cobalt nanocrystals and oxygen, sulfur, or selenium as the diffusion couple.[13] Some other hollow nanostructures have been reported using similar designs.[9,18−21] However, so far the diffusion couples are often limited to metals, metal oxides, and gases, and the size of the hollow materials was usually less than 50 nm.

In this study, we tried to expand the Kirkendall effect to a new diffusion couple between a solid and a liquid (i.e. metal glycolate and water as diffusion couple, both of which are inexpensive and nontoxic materials) and produced $La(OH)_3$ hollow structures with trapezohedron morphologies. This hollow nanostructure is several hundreds nanometers in size and consists of $La(OH)_3$ crystalline rods in simple hexagonal phase. Furthermore, a hollow La_2O_3 hollow structure with similar morphology is obtained by calcination. Hollow trapezohedron $La(OH)_3$ exhibits excellent removal ability for organic pollutants.

Experimental Section

Synthesis of lanthanum Glycolate. In a typical procedure, 0.5 g of lanthanum acetate (Alfa Aesar) is added to a mixture of 25 mL of ethylene glycol (Beijing Chemical Reagent Ltd.) and 5 mL of ethanol (Beijing Chemical Reagent Ltd.); the solution is then heated to 150 °C for a certain time to generate cube or trapezohedron lanthanum glycolate. The latter are collected, washed, and dried for preparation of lanthanum hydroxide hollow nanostructures and further characterization.

Synthesis of Lanthanum Hydroxide Hollow Nanostructures. The lanthanum hydroxide hollow nanostructures are synthesized via a hydrolysis process in NaOH aqueous solution. A 50 mg sample of lanthanum glycolate precursor with cube or trapezohedron morphology is mixed with 30 mL of 1 M NaOH (Beijing Chemical Reagent Ltd.) aqueous solution. The mixture is heated in Teflon-lined stainless steel autoclave at 150 °C for 12 h.

Synthesis of Lanthanum Oxide Hollow Nanostructures. Lanthanum oxide hollow nanostructures are synthesized via the calcination of $La(OH)_3$ hollow structures in air at 700 °C for 6 h.

Characterization. The samples are characterized by X-ray diffraction (XRD; D/max-2500), transmission electron microscopy (TEM; JEOL 2010 and 1011), selected area electron diffraction (SAED), scan electron microscopy (SEM; Hitachi S-4300F), and high-resolution TEM (HRTEM).

Removal of Dyes in Water. A 10 mg sample of as-prepared lanthanum hydroxide hollow trapezohedron, lanthanum oxide hollow trapezohedron, and commercial lanthanum oxide powder (Beijing Chemical Reagent Ltd.) are added to 15 mL of Congo red (Beijing Chemical Reagent Ltd.) aqueous solution with a concentration of 100 mg/L, respectively. The mixture is magnetically stirred and analyzed via UV−vis to measure Congo red concentration at different time intervals.

Results and Discussion

SEM results (Figure 1a) of the lanthanum glycolate precursor indicate that they are uniform and highly symmetric trapezo-

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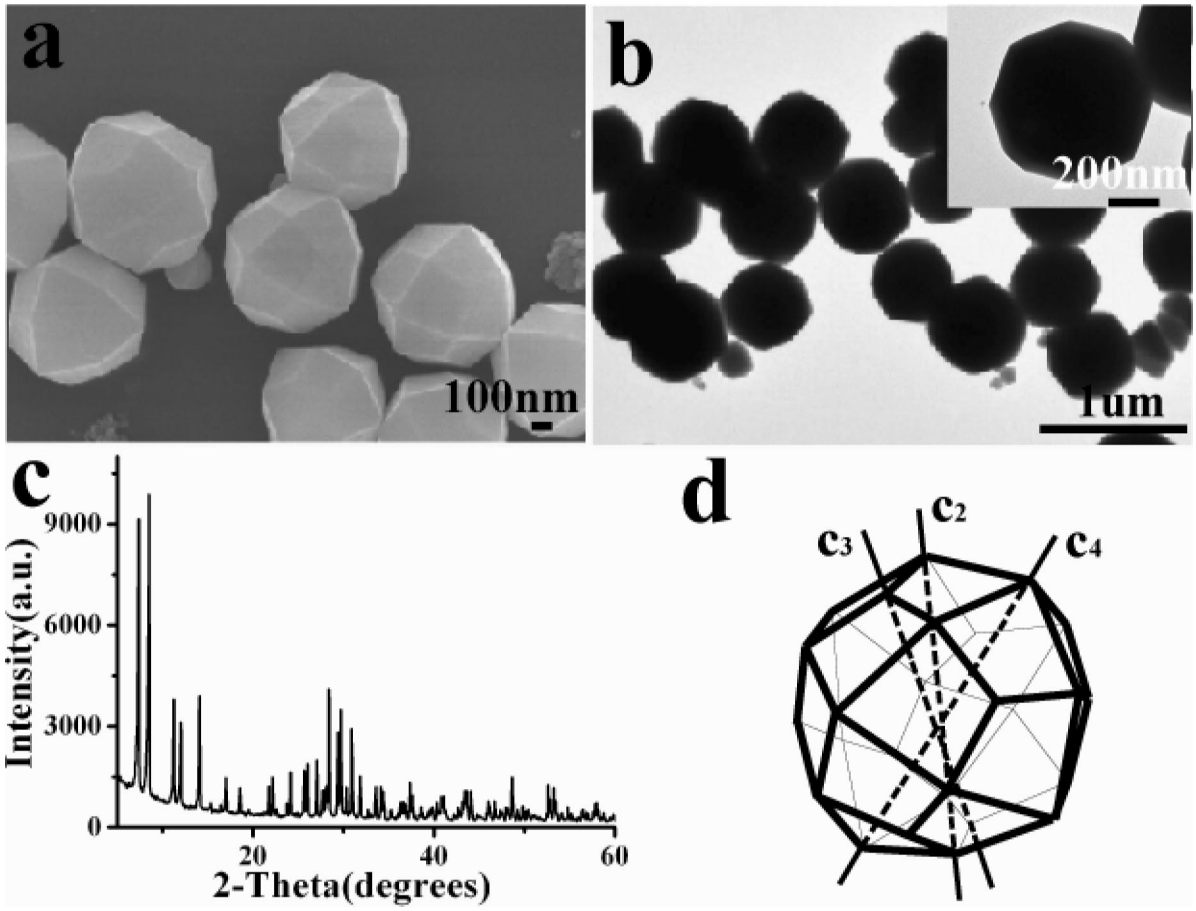


Figure 1. SEM image (a) and TEM image (b) for highly symmetric trapezohedron of lanthanum glycolate precursor; (c) XRD pattern for lanthanum glycolate precursor; and (d) the morphology model for trapezohedron.

hedron nanocrystals with a particle size around 700−800 nm. This polyhedron contains 24 faces, 26 vertices, and 48 edges, as shown in the structural model (Figure 1d). Figure 1b shows the TEM result of the lanthanum glycolate precursor. Since the particles are too big (about 800 nm) for TEM beams to penetrate through, their TEM images show the projected polygonal shapes of the particles. The particles look like hexagon or octagon under TEM if the particles are sitting on the 3-fold or 4-fold axis, respectively. The inset of Figure 1b shows an octagonal shaped particle.

The XRD pattern in Figure 1c shows that the lanthanum glycolate trapezohedron is quite crystalline. However, no corresponding JCPDS card file has been found due to its complicated composition and few people have studied its crystal structure. Elemental analysis (La, C, O, H) was performed to learn the chemical composition of the lanthanum glycolate trapezohedron, which can be expressed as $LaC_4H_{10}O_4$. This result suggests that one ethylene glycol is bi-dente associated with the La ion. We are not able to solve the exact crystalline structure of this precursor, as its size is too small (about 700 nm) for single crystal analysis.

After being treated with 1 M NaOH solution, the trapezohedron sample becomes hollow. Figure 2d shows the TEM images of the hollow trapezohedron $La(OH)_3$ particles, showing hollow interiors with characteristic polygonal shapes. The SEM images of $La(OH)_3$ are shown in Figure 2a−c. Unlike the SEM images of the lanthanum glycolate precursor, which shows clear trapezohedron morphology, from the images in Figure 2b, the particles can be barely envisioned as trapezohedrons. The surface of the particles is rough, so that the trapezohedron edges are difficult to identify. However, combining SEM and TEM images, we conclude that the $La(OH)_3$ particles in Figure 2 remain as trapezohedron. Figure 2c and the insert show a broken particle, further confirming their hollow features.

The concentration of NaOH solution is critical. When lanthanum glycolate trapezohedron particles are treated with pure water, discreet nanorods of about 30 nm are produced, while with 6 M NaOH solution, condensed spheres with no hollow interiors are produced. The implication of these findings will be discussed later.

XRD study in Figure 4b shows that the prepared sample is $La(OH)_3$ crystalline with simple hexagonal phase (JCPDS no. 36-1481) and the lattice constants c and a are 3.858 and 6.528 Å, respectively. Figure 4a shows the HRTEM image of a small region of the $La(OH)_3$ hollow trapezohedron, showing parallel lattice fringes. The lattice space is 3.15 Å, consistent with the (101) face of the $La(OH)_3$ crystal. The insert in Figure 4a is the SAED result of the crystal. The discrete and sharp dots prove that the prepared $La(OH)_3$ hollow trapezohedron is composed of single crystals.

To study the formation process of the hollow structure, the products are collected with different time intervals after being treated with 1 M NaOH solution. The TEM images of these samples with 0.5, 2, 4, and 6 h treatments are shown in Figure S1 in the Supporting Information. Treatment for 0.5 h did not generate significant morphology change. After 2 h of hydrothermal treatment, a core−shell structure starts to form. The core becomes smaller and shell becomes thicker with the reaction time increases. Finally a hollow shell is produced after 12 h of hydrothermal treatment. This observation suggests that

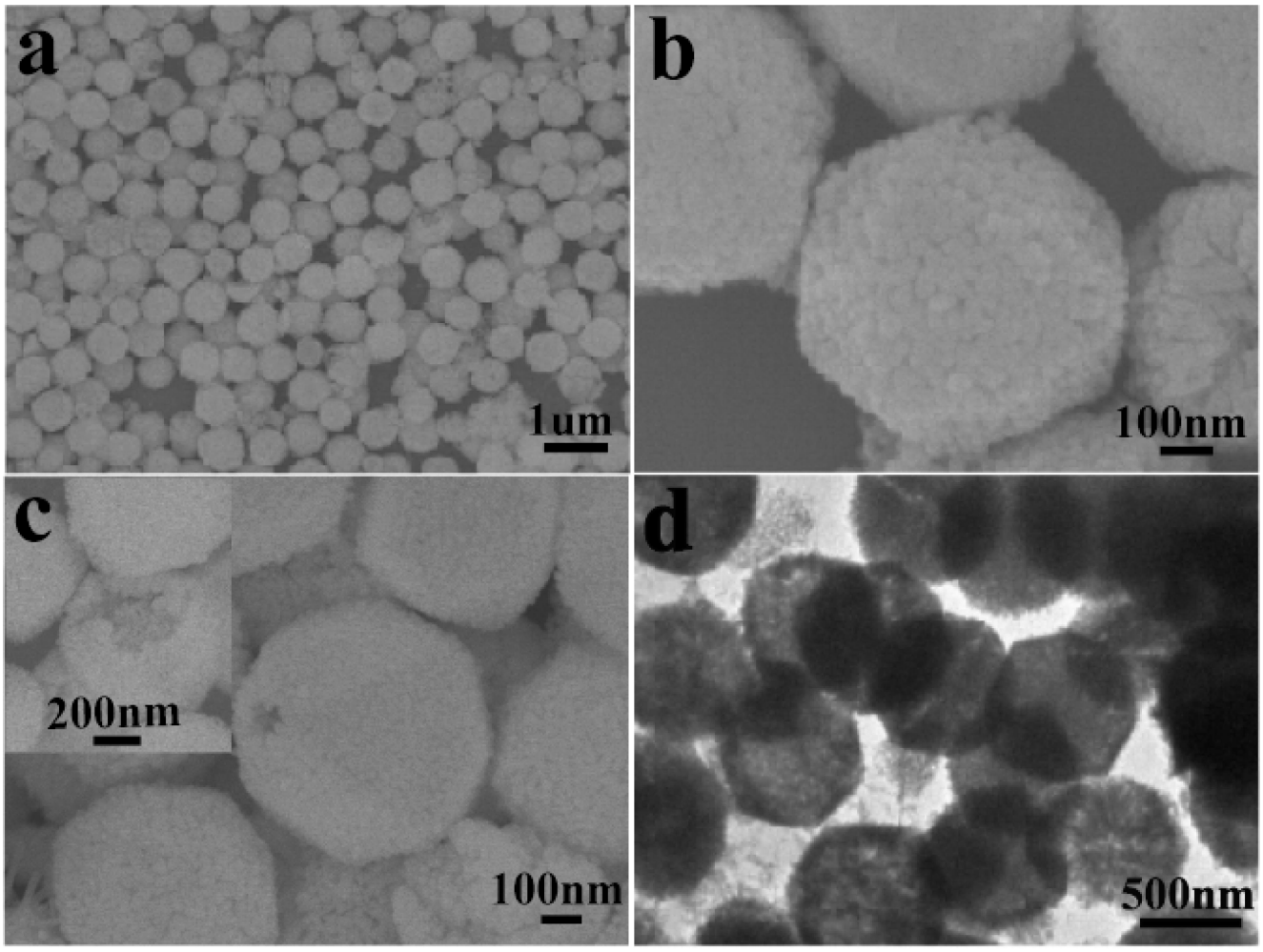


Figure 2. (a) Low-magnification SEM images of $La(OH)_3$ hollow trapezohedron; (b) high-magnification SEM images showing highly symmetric hollow trapezohedron; (c) a cracked nanostructure and a broken one (inset) revealing its hollow feature; and (d) TEM images of the $La(OH)_3$ hollow trapezohedron.

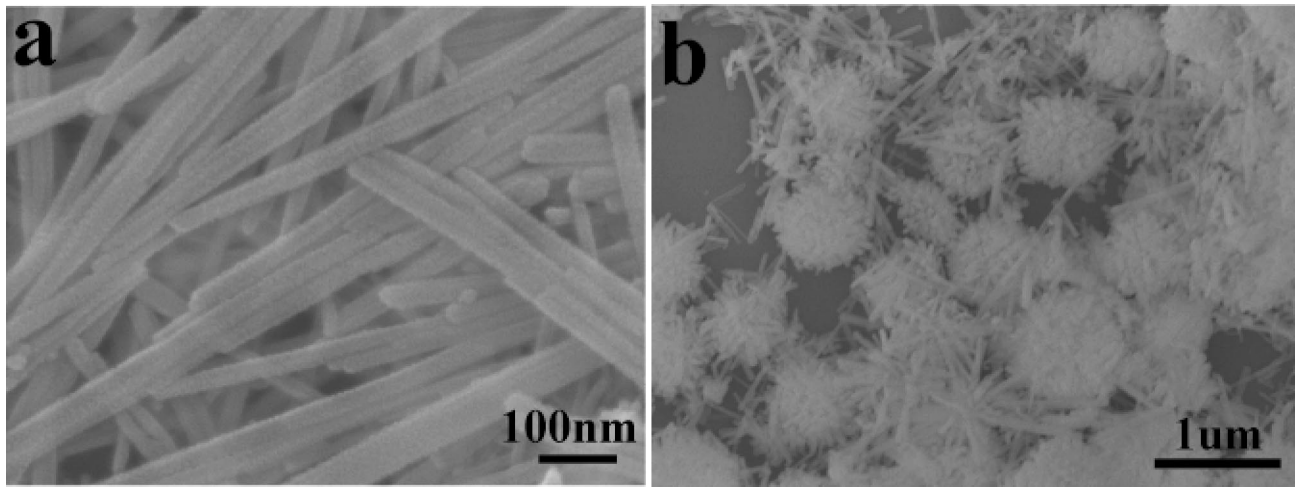


Figure 3. SEM image of $La(OH)_3$ (a) nanorods prepared in pure water and (b) condensed nanosphere mixture prepared in 6 M aqueous NaOH solution.

the process is similar to a Kirkendall process, in that the interior components diffuse outward to the interface, resulting in a hollow interior.

In a control experiment, we dispersed 50 mg of lanthanum glycolate into 30 mL of pure water. After 12 h of hydrothermal treatment, a mass of cracked nanorods was obtained. The SEM result (Figure 3a) shows that these nanorods have a diameter and length about 30 and 200−800 nm, respectively. XRD study (Figure S2, Supporting Information) suggests that they are also $La(OH)_3$ in simple hexagonal phase, though the crystallinity is quite poor.

In other control experiments, we also treated lanthanum glycolate in 0.1, 2, and 6 mol/L NaOH aqueous solution under otherwise identical conditions. Similar hollow trapezohedron

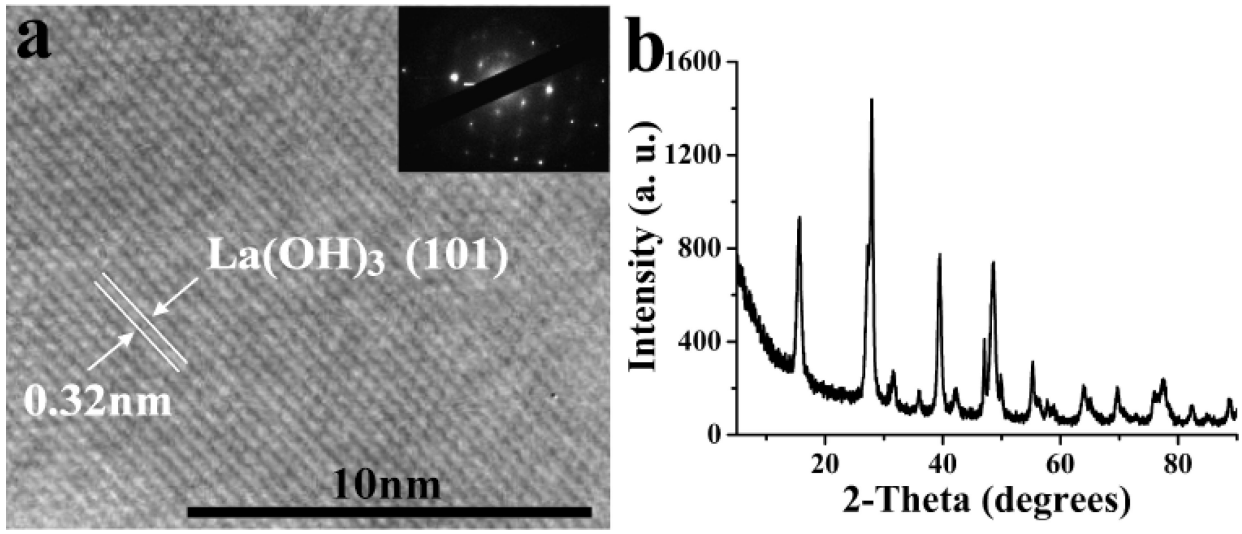


Figure 4. (a) HRTEM image and (b) XRD pattern for as-prepared $La(OH)_3$ hollow trapezohedron. The inset in the HRTEM image is the SAED result.

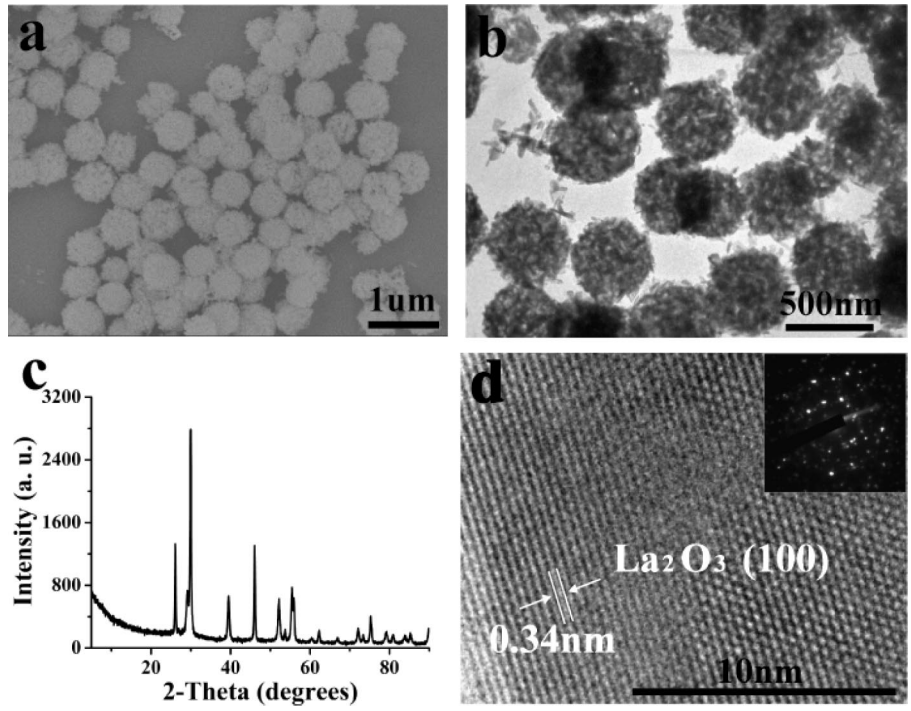


Figure 5. (a) SEM image of La_2O_3 hollow nanoporous spheres formed via calcination of $La(OH)_3$ hollow trapezohedron in air at 700 °C for 6 h. (b) TEM image of La_2O_3 hollow nanoporous spheres. (c) XRD pattern. (d) HRTEM and the inset SAED image show that the pure La_2O_3 is a single crystal in a simple hexagonal phase.

nanostructures are synthesized with 0.1 and 2 mol/L NaOH solution. However, condensed particles are produced with 6 M NaOH solution (Figure 3b). These results suggest that the formation of these morphologies is a kinetic controlled Kirkendall process. A moderate hydrolysis rate is the key factor in producing hollow structures.

Lanthanum glycolate undergo hydrolysis during the hydrothermal treatment. The lattice density of $La(OH)_3$ is higher than that of lanthanum glycolate, so that if, after hydrolysis, the morphology and size of $La(OH)_3$ is the same as those of the lanthanum glycolate, a hollow interior must be formed. This is the case when NaOH solutions with moderate concentrations are used in hydrolysis. The rate of hydrolysis is determined by the OH^- concentration. OH^- in solution reacts with surface lanthanum glycolate to form initial $La(OH)_3$, which covers the surface of the trapezohedron. Since $La(OH)_3$ is crystalline, and tends to grow into rod-like morphology, under moderate OH^-

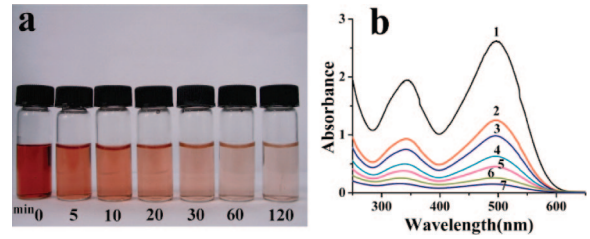


Figure 6. (a) Photo images of absorption of Congo red at different times by $La(OH)_3$ hollow nanostructures; (b) absorption spectra of a solution of Congo red (100 mg/L, 15 mL) in the presence of $La(OH)_3$ hollow trapezohedron (10 mg) at different time intervals: (1) 0, (2) 5, (3) 10, (4) 20, (5) 30, (6) 60, (7) 120 min, respectively.

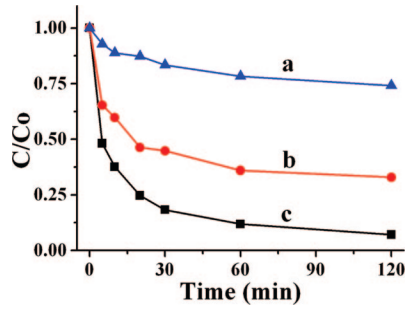
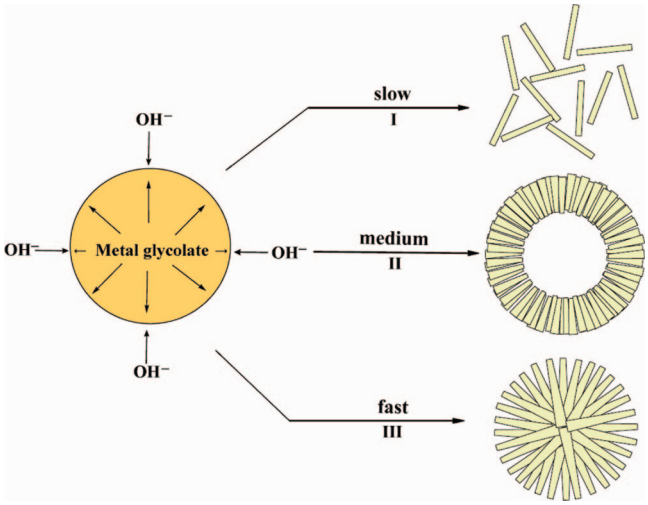


Figure 7. Adsorption rate of the azo-dye Congo red on (a) commercial La_2O_3, (b) La_2O_3 hollow particles, and (c) $La(OH)_3$ hollow trapezohedron.

SCHEME 1: Schematic Illustration of the Formation Process of $La(OH)_3$ Hollow Nanostructures[a]



[a] Dispersed $La(OH)_3$ nanorods (I), hollow nanostructures (II), and condensed nanostructure (III) are obtained under different hydrolysis rate.

concentration and moderate hydrolysis rate, the $La(OH)_3$ nanorods form a close packed assembly that covers the precursor particle and becomes the steady interface between water and lanthanum glycolate.

The interface preserves the morphology of the product, and blocks the direct contact of water and lanthanum glycolate. To further hydrolysis reaction, an inward flow of OH^- and an outward flow of lanthanum glycolate are necessary. Due to the faster diffusion rate of outward lanthanum glycolate, a hollow trapezohedron nanostructure is formed. This is the Kirkendall effect.

The critical factor in this Kirkendall process is a steady $La(OH)_3$ interface, which allows steady diffusion of OH^- and lanthanum glycolate. If the OH^- concentration is too low, as in pure water, the hydrolysis rate is also too low, resulting in larger $La(OH)_3$ nanorods that cannot form a close packed interface. Water can penetrate into the interior of the lanthanum glycolate, resulting in isolated $La(OH)_3$ nanorods shown in Figure 3a.

In contrast, with high NaOH concentration, the OH^- inward diffusion rate is higher than the outward diffusion of lanthanum glycolate. This is opposite to the desired Kirkendall effect. The result is a condensed particle with solid interior and shrunk volume. Indeed, the size of the particles in Figure 3b is about 650 nm, significantly smaller than that of the original lanthanum glycolate particles (800 nm). This is a kinetically controlled process and only the appropriate dynamics can favor the desired Kirkendall effect and lead to a highly symmetric $La(OH)_3$ hollow trapezohedron.

The Kirkendall effect observed in this work is different from those in the work of Xia[17] or Yin.[13] In those works, diffusion couples consisted of metal nanospheres and gases, and the hollow products are also in the nanometer range. A steady interface is readily maintained in these cases. As $La(OH)_3$ hollow structures in this work are several hundred nanometers, thus maintaining a steady interface between lanthanum glycolate and aqueous solution is more diffucult, as surface tension resulting from lattice density difference will usually crack the interface. In this work, the interface is indeed cracked, the final hollow structure consists of nanorods. Under the right condition, the nanorods aligned perpendicular to the surface of the original lanthanum glycolate precursor, thus the final hollow structures retain the trapezohedron morphology of the precursor.

When the $La(OH)_3$ hollow trapezohedron were calcined in air at 700 °C, La_2O_3 hollow particles were obtained. The trapezohedron morphology is even harder to identify (Figure 5a,b). However, their TEM images maintain clear polygonal shapes, suggesting that they are likely still trapezohedrons with hollow interiors. Figure 5c shows an XRD pattern of pure La_2O_3; all peaks can be indexed as the simple hexagonal phase (JCPDS card file no 74-2430) of La_2O_3. HRTEM data in Figure 5d also confirm the crystalline structure of La_2O_3.

In a control experiment, we calcined the lanthanum glycolate precursor directly, and particles with rough surface were produced. As shown in Figure S3 in the Supporting Information, these particles have an average size of about 500 nm. The TEM result (see in Figure S4 in the Supporting Information) indicates that they were condensed particles with solid interior. Thus using air and lanthanum glycolate as a diffusion couple is not working.

$La(OH)_3$ is often used in light emissions[22,23] and biological labeling.[24,25] The 4f orbit, which is lack of electrons, provides a strong affinity for electron-rich organics,[26,27] thus they may be very useful as adsorbents for organic wastes. Herein, we use the $La(OH)_3$ hollow trapezohedron as adsorbent to remove Congo red, a common azo-dye in the textile industry. When the initial concentration of Congo red in water solution is 100 mg/L, 10 mg of $La(OH)_3$ hollow trapezohedron could remove about 93% of the Congo red from 15 mL of solution, as shown by the photo and UV/vis absorption curves at different time in Figure 6, panels a and b, respectively. The adsorption capacity of the $La(OH)_3$ hollow trapezohedron for Congo red is about 140 mg/g.

Hollow La_2O_3 nanostructures were also tested for removing Congo red in water solution. As shown in Figure 7, though the hollow La_2O_3 nanostructures has a higher adsorption capacity than commercial La_2O_3 (surface area 13 m^2/g), it has less removal ability than the $La(OH)_3$ hollow trapezohedron. This might be ascribed to the smaller surface area (37 m^2/g) of hollow La_2O_3 nanostructures than the that of $La(OH)_3$ hollow trapezohedron (67 m^2/g).

Conclusion

In summary, a Kirkendall effect based method is developed to fabricate hollow structured materials. Lanthanum glycolate crystals with morphologies ranging from cube to trapezohedron have been successfully synthesized in ethylene glycol/ethanol mixture; and lanthanum hydroxide hollow nanostructures with the same morphologies were prepared via a hydrothermal process. The formation of hollow structures is attributed to the Kirkendall effect. After calcinations of lanthanum hydroxide, lanthanum oxide nanoporous hollow structures were also

obtained. These materials exhibit excellent ability to remove organic pollutants in water.

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Supporting Information Available: TEM images of $La(OH)_3$ hydrothermal treated for different times in 30 mL of 1 mol/L NaOH solution at 150 °C; XRD pattern of $La(OH)_3$ nanorods hydrothermally treated in 30 mL of pure water; and the SEM and TEM images of La_2O_3 particles prepared via calcinations of lanthanum glycolate precursor directly at 700 °C for 6 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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