Interfacial Reaction-Directed Synthesis of Ce–Mn Binary Oxide Nanotubes and Their Applications in CO Oxidation and Water Treatment

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Interfacial oxidation–reduction reaction is herein developed to prepare hollow binary oxide nanostructures. Ce–Mn nanotubes are fabricated by treating Ce(OH)CO$_3$ templates with KMnO$_4$ aqueous solution, where MnO$_4$$^-$ is reduced to manganese oxide and the Ce$^{3+}$ in Ce(OH)CO$_3$ is simultaneously oxidized to form cerium oxide, followed by selective wash with HNO$_3$. The resulting Ce–Mn binary oxide nanotubes exhibit high catalytic activity towards CO oxidation and show significant adsorption capacity of Congo red. Moreover, guided by the same interfacial-reaction principle, binary oxide hollow nanostructures with different shapes and compositions are synthesized. Specifically, hollow Ce–Mn binary oxide cubes, and Co-Mn and Ce-Fe binary oxide hollow nanostructures are achieved by changing the shape of the Ce(OH)CO$_3$ templates from rods to cubes, by changing the templates from Ce(OH)CO$_3$ nanorods to Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$ nanowires, and by replacing the oxidant of KMnO$_4$ with another strong one, K$_2$FeO$_4$, respectively. This work is expected to open a new, simple avenue for the general synthesis of hollow binary oxide nanostructures.

1. Introduction

Transition-metal oxide nanotubes represent a promising class of materials due to their potential applications (e.g. catalysis, ferroelectric, lithium storage, and gas sensors). Among a wealth of studies on the fabrication of nanotubes, template-assisted synthesis based on interfacial reaction is an effective approach, where the templates are normally designed to chemically react with given reactants following various pathways, such as ion exchange and Kirkendall diffusion, and the residual templates often need to be removed later on. Therefore, in this approach the selection of appropriate templates is critical not only for the formation of hollow structures, but also for their chemical purity. To be more specific, the templates should be easily removed by either washing or calcination without causing the collapse of the shell. So far, most nanotubes synthesized by this approach are single metal oxides despite the consistently irregular morphology of Ce–Mn binary oxide nanoparticles achieved from these methods, high temperature (400–800 °C) calcination is a necessary step in these routes. Therefore, both simplifying synthesis strategies and controlling the morphology of the Ce–Mn binary oxide are areas of interest for further enhancing their widespread applications.

In previous work, we chose Ce(OH)CO$_3$ nanorods as template and successfully fabricated CeO$_2$ nanotubes and CePO$_4$:Tb nanotubes through different interfacial reactions. Thanks to the unique feature of Ce(OH)CO$_3$, the template can be easily removed by acid wash or calcination. Moreover, the outward diffusion of Ce$^{3+}$ ions in the template is faster than the inward diffusion of OH$^-$ ions from solution during the reaction of Ce$^{3+}$ with NaOH solution, which is responsible for the formation of Kirkendall-type voids in the CeO$_2$ nanotubes. Last but not least, the solubility product constants of Ce(OH)$_3$ and CePO$_4$ are smaller than that of Ce(OH)CO$_3$, which is a key factor for transforming Ce(OH)CO$_3$ into CeO$_2$ and CePO$_4$. It should be noted that there are no valence changes (i.e. no oxidation–reduction reactions are involved) for the participating species in these specific interfacial reactions. Considering the reduction ability of Ce (III), these highly interesting Ce(OH)CO$_3$ nanorod templates may be further employed in the interfacial oxidation–reduction reactions with oxidizing agents to form binary oxide nanotubes. As a matter of fact, the interfacial oxidation–reduction...
reaction has recently been explored for the synthesis of hollow structures or binary oxides \[26–28\]. For example, hollow MnO\(_2\) structures were prepared by the interfacial reaction between KMnO\(_4\) and MnCO\(_3\) oxidation–reduction pairs, followed by the removal of unreacted MnCO\(_3\) \[27\]. Co\(_3\)O\(_4\)@MnO\(_2\) core@shell arrays were also synthesized under the guidance of the interfacial oxidation–reduction reaction, \[28\], where the authors deposited a carbon layer on pre-synthesized Co\(_3\)O\(_4\) nanowires as templates, followed by oxidation–reduction between the deposited carbon layer and KMnO\(_4\). The introduction of the carbon layer is crucial to the oxidation–reduction reaction; without carbon, no MnO\(_2\) can be observed on the Co\(_3\)O\(_4\) nanowire surface. In both examples introduced above, KMnO\(_4\) is reduced to MnO\(_2\), either by MnCO\(_3\) or by C. Taking both the strong oxidation ability of KMnO\(_4\) and reduction ability of Ce(III) into account, it is expected that Ce–Mn binary oxide nanotubes can be synthesized by the interfacial oxidation–reduction reaction between KMnO\(_4\) and Ce(OH)CO\(_3\) nanorods under certain conditions.

In this paper, we report the simple and robust preparation of Ce–Mn binary oxide nanotubes by employing Ce(OH)CO\(_3\) nanorods as templates, which directly react with KMnO\(_4\) aqueous solution and do not require any additional “intermediate” layers (such as carbon) to finish the oxidation–reduction reaction. The resulting Ce–Mn binary oxide nanotubes exhibit high catalytic activity towards CO oxidation and exhibit significant adsorption capacity of Congo red. Moreover, guided by the same interfacial-reaction principle, hollow Ce–Mn binary oxide cubes are also achieved by utilizing Ce(OH)CO\(_3\) cubes as templates. Although the focus herein is on the Ce–Mn binary oxide, we also demonstrate that this method can be easily extended to fabricate other hollow binary oxide nanocomposites, such as Co–Mn and Ce–Fe binary oxides, when suitable templates and oxidation/reduction pairs are chosen (Scheme 1).

2. Results and Discussion

X-ray photoelectron spectroscopy (XPS) was first used to examine the valence states of Ce and Mn after the interfacial reaction.

As shown in Figure 1a, the as-prepared sample (the solid black line) and Ce(OH)CO\(_3\) nanorods (dotted gray line) show quite different Ce 3d XPS patterns. Four peaks U, U\(_1\), V and V\(_1\), characteristic of Ce(III), are clearly present in the Ce(OH)CO\(_3\) nanorods, while six peaks labeled U, U\(_2\), U\(_3\), V, V\(_2\) and V\(_3\), characteristic of Ce(IV), \[29\] are observed in the as-prepared sample, indicating the oxidation of Ce(III) during the interfacial reaction. In the case of Mn 2p spectrum, an intense peak of Mn 2p\(_{3/2}\) around 643 eV suggests that Mn(IV) is dominant species in the as-prepared sample (Figure 1b). \[18\] The XPS results provide strong evidence that an interfacial oxidation-reduction reaction takes place between the KMnO\(_4\) and Ce(OH)CO\(_3\) nanorods. This was further confirmed by Raman spectroscopy measurements (Figure 1c), where two peaks are clearly present in the Raman spectrum of the as-prepared sample. The peak centered at \(\sim 458\) cm\(^{-1}\) is due to the symmetric breathing mode of oxygen atoms around cerium ions in the cubic-phase cerium oxide, while the other peak centered at \(633\) cm\(^{-1}\) is characteristic of the Mn-O stretching mode of manganese oxides. \[10\] The co-existence of Ce and Mn in the as-prepared sample was also supported by Energy Dispersive Spectroscopy (EDS) measurements, which yields the stoichiometry value of Ce: Mn \(\cong 0.4:0.6\) (Figure S1). X-ray Diffraction (XRD) characterization was conducted to study the crystalline structure of the Ce–Mn binary oxide. Only a very weak, broad peak was observed in the as-prepared sample (Figure S2), denoting the lack of any significant “long-range” crystalline order. The remarkable increase of diffraction peaks is clearly visible after treating the sample at an elevated temperature of \(200\) °C for \(2\) h. No characteristic diffraction peaks of manganese oxides and Ce(OH)CO\(_3\) nanorods are present and all diffraction peaks can be well indexed to CeO\(_2\) (ICPDS81-0792). This is consistent with previous reports concerning the structure features of MnO\(_2\)-CeO\(_2\) binary oxide. \[18–20\] All these results consistently demonstrate that the Ce–Mn binary oxide is formed via the
nanotubes can be identified (indicated by circles). As shown in Figure 2a, the TEM image of the Ce–Mn binary oxide nanotubes, where some open wall thickness of around 40 nm. Figure 2b presents a typical SEM image of the Ce–Mn binary oxide nanotubes, where some open nanotubes can be identified (indicated by circles). As shown in Figure 2c, the as-prepared nanotubes reveal a rather rough surface morphology with fluffy-like nanostructures, which is in contrast to the smooth surface of the Ce(OH)CO$_3$ template (Figure S3). Most of the nanotubes have diameters of 300–350 nm, with typical wall thickness of around 40 nm. Figure 2b presents a typical SEM image of the Ce–Mn binary oxide nanotubes, where some open nanotubes can be identified (indicated by circles). As shown in Figure 2c, the as-prepared nanotubes reveal a rather rough surface morphology with fluffy-like nanostructures, which is in clear contrast to the smooth surface of the Ce(OH)CO$_3$ template. These “fluffs” are loosely connected, similar to those of hollow MnO$_2$ and Co$_3$O$_4$@MnO$_2$ core@shell nanowires prepared from reduction-oxidation interfacial reactions, where the “fluffs” were indexed to MnO$_2$. In our work, the EDS analysis focusing on the “fluff” exhibits the coexistence of Mn and Ce elements. However, due to the low crystallinity of the “fluff”, it is difficult to characterize their structure in detail from either high Resolution TEM (HRTEM) image or Selected Area Electron Diffraction (SAED) (Figure S4). Nonetheless, after a slight heat treatment at 200 °C for 2 h, high-intensity diffraction rings appear in the SAED with the entire pattern well indexed to a cubic phase of CeO$_2$ (Figure 2d). HRTEM characterization reveals that the surface morphology of the nanotubes also changes after such heat treatment. The “fluffs” disappear and both the inner and outer walls of the nanotubes are mainly composed of small nanoparticles (Figure 2e, f). Most of them are 2–3 nm in dimensions and highly crystalline, randomly oriented with each other. The interlayer spacing is measured to be ∼0.32 nm, which could be indexed well to the (111) crystal planes of the cubic CeO$_2$ structure. Since catalytic performance highly depends on the structure stability of catalysts that is normally enhanced with crystallization, catalytic properties were only studied for the heat-treated samples.

To further investigate the elemental distribution of Ce and Mn in the nanotubes, scanning transmission electron microscopy (STEM)–energy-dispersive X-ray (EDX) line scans were conducted on an individual nanotube (Figure S5). Both Ce and Mn show bimodal distributions with their maxima located in the edge part, while their minima in the center. Corresponding high angle annular Dark field (HAADF)-STEM image and elemental maps are shown in Figure 3. We observe that Ce, Mn and O are uniformly distributed in the wall of this representative nanotube. Such uniform distribution of Ce and Mn is beneficial to strengthen the interaction between Ce and Mn, if any, in the binary oxide.[27]

When the Ce(OH)CO$_3$ nanorods are mixed with KMnO$_4$ aqueous solution, there is a liquid-solid interface reaction between the Ce(OH)CO$_3$ nanorods and MnO$_4$$^-$ ions in a basic solution (pH 8). We observe that Ce, Mn and O are uniformly distributed in the wall of this representative nanotube. Such uniform distribution of Ce and Mn is beneficial to strengthen the interaction between Ce and Mn, if any, in the binary oxide.[27]

Both the formation of the uniformly distributed cerium and manganese oxides and the segmented voids can be explained as follows. In the herein discussed Ce(OH)CO$_3$–KMnO$_4$ system, once MnO$_4$$^-$ ions oxidize Ce(III) ions slowly dissociated from the Ce(OH)CO$_3$ nanorods (equation 1), MnO$_4$$^-$ is reduced to manganese oxide (equation 2), and the Ce(III) is simultaneously oxidized to form CeO$_2$ (equations 3 and 4). Both types of oxide particles are nucletated and synthesized at ultra-small sizes and are in close contact with each other, forming an intimate mixture. The whole process is similar to the redox-precipitation reaction reported by Arena et al.[21] In that scenario, MnO$_4$$^-$ ions were mixed with Ce$^{3+}$ and Mn$^{2+}$ ions in a basic solution (pH=8) to...
attain a mixture of MnO$_2$ and CeO$_2$ species at the atomic level. In our case, although the pH value of the initial reaction solution was set at $\sim 7$, it gradually increased to $\sim 9$ after reaction due to the release of OH$^-$ ions from the slow dissociation of the Ce(OH)CO$_3$ nanorods (equation 1) and the reduction reaction of the MnO$_4^-$ ions (equation 2). The newly formed oxides cover the surface, preventing a direct chemical reaction between MnO$_4^-$ in solution and Ce$^{3+}$ in the Ce(OH)CO$_3$ nanorods. Further reaction relies on the diffusion of Ce$^{3+}$ and/or MnO$_4^-$ through the outer wall. Due to the different ionic radii of Ce$^{3+}$ and MnO$_4^-$, the outward diffusion of Ce$^{3+}$ in the Ce(OH)CO$_3$ nanorods is faster than the inward diffusion of MnO$_4^-$ from solution.$^{[10]}$ A net outflow of Ce$^{3+}$ ions through the outer wall results in the opposite transport of lattice vacancies and eventually the formation of the segmented voids.

We anticipate that this method can be extended to prepare hollow structures with different shapes and compositions, provided suitable templates and oxidants can be identified. For example, hollow Ce–Mn cubes can be obtained when solid Ce(OH)CO$_3$ cubes are used as template (Figure 6a,b). When Ce(OH)CO$_3$ nanorod templates are replaced by Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$ nanowires, the Co(II) in the Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$ is expected to be oxidized by KMnO$_4$ since Co has variable valency. As shown in Figure S6, after 6 days of the interfacial reaction between Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$ and KMnO$_4$ at room temperature, hollow structures are clearly observed in the TEM image. As mentioned in the paper, the Kirkendall diffusion is responsible for the initial formation of the hollow structure owing to the outward diffusion of Co$^{2+}$ in the Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$ nanowires is faster than inward diffusion of MnO$_4^-$ ions from solution. Once calcined for decomposition of the residual Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$, the sample is transformed into porous Co-Mn binary oxide nanotubes (Figure 6c). The voids aroused by the Kirkendall diffusion and the vacancies resulted from gas release during the calcinations process are possibly responsible for the final porous structures. Another example is the generation of Ce-Fe binary oxide nanotubes when K$_2$FeO$_4$ (a strong oxidizing agent) is engaged to react with the Ce(OH)CO$_3$ nanorods (Figure 6d). FeO$_4^{2-}$ ions are reduced to Fe$^{3+}$ ions, which are easily hydrolyzed in solution to form Fe(OH)$_3$. The dehydration of Fe(OH)$_3$ during subsequent heat treating process (drying) results in the formation of iron oxide. The Ce$^{3+}$ is oxidized to form CeO$_2$ simultaneously, as discussed above.

Figure 4. TEM images of the as-prepared Ce–Mn binary oxide products after different reaction time: (a) 1, (b) 3, (c) 4, and (d) 6 days without heat treatment. Scale bar: 500 nm.

Figure 5. TEM images of typical nanorods with segmented voids without acid and heat treatments and relevant chemical equations.

Figure 6. TEM images of (a) Ce(OH)CO$_3$ cube templates and (b) as-prepared hollow Ce–Mn binary oxide cubes without further heat-treatment. (c) Co-Mn binary oxide and (d) Ce-Fe binary oxide hollow structures. Inset in (b) is a magnified hollow cube.
The ultra-small crystallite size of the nanoparticles in the nanotubes and the hollow structure together lead to a high specific surface area (~202 m²/g), which definitely also contributes to the better performance of the nanotubes. Last but not least, the hollow structure enables the better contact of catalytically active particles with the gas molecules due to the existence of the interior space and penetrable wall, which is also beneficial for gas-phase reactions.

In addition, hollow structures with high surface area have also emerged as an attractive platform for water treatment (e.g. the removal of Congo red). The binary oxide nanotubes developed herein are found to exhibit significant adsorption capacity of Congo red (Figure 8). The estimated adsorption capacity of Congo red at 10 min is about 100 mg g⁻¹ for Ce–Mn binary oxide nanotubes, 24 mg g⁻¹ for CeO₂ nanotubes, 21 mg g⁻¹ for commercial MnO₂ and 7 mg g⁻¹ for commercial CeO₂. It is interesting to note that the CeO₂ nanotubes with the similar cavity prepared from the same Ce(OH)₂CO₃ template exhibit considerably inferior adsorption performance in comparison to Ce–Mn binary oxide nanotubes. Brunauer-Emmett-Teller (BET) measurements show that the specific surface area of the Ce–Mn binary oxide nanotubes (inset in Figure b) is far higher than that of the CeO₂ nanotubes (~74 m²/g) even though they have the similar tubular structures. The higher surface area of Ce–Mn binary oxide nanotubes might be ascribed to smaller crystallite size (~2 nm) and much rougher surface in comparison to that of CeO₂ nanotubes (crystallite size, ~6 nm).

3. Conclusions

In summary, Ce–Mn binary oxide nanotubes were successfully fabricated by easily reacting the Ce(OH)₂CO₃ nanorods with KMnO₄ aqueous solution, followed by selective wash with HNO₃. Since the reaction can be carried out at mild conditions,
it should be straightforward to scale up the entire process for high-volume production of the Ce–Mn binary oxide nanotubes. Due to the strong interaction between CeO$_2$ and MnO$_2$ in the Ce–Mn binary oxide and the high specific surface area, the Ce–Mn binary oxide nanotubes exhibit high catalytic activity towards CO oxidation in comparison with both commercially available CeO$_2$ and MnO$_2$ particles and their physical mixture. In addition, the nanotubes display excellent adsorption performance when used to remove a common organic waste of Congo red from water, suggesting their potential application in water treatment. This work also represents the first demonstration of an interfacial oxidation–reduction reaction-engaged process capable of generating binary oxide hollow nanostructures with different shapes and compositions from the solution phase.

4. Experimental Section

Materials: Cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O), cobalt (II) chloride hexahydrate (CoCl$_2$·6H$_2$O), urea (NH$_2$CONH$_2$), potassium permanganate (KMnO$_4$), potassium ferrate (K$_2$FeO$_4$), sodium hydroxide (NaOH), nitric acid (HNO$_3$) and acetic acid (CH$_3$COOH) were purchased from Sigma-Aldrich and used without further purification. Water was purified by a Millipore Ultrapure water system and has a resistivity of 18.2 MΩ·cm at 25 °C.

Synthesis of Ce(OH)CO$_3$ templates: In a typical experiment, Ce(NO$_3$)$_3$·6H$_2$O (4 mmol) and urea (24 mmol) were added to water (80 mL) under vigorous magnetic stirring at 80 °C for 24 h. The obtained powder sample was centrifuged, washed with distilled water and dried.[23]

Synthesis Ce(OH)CO$_3$ cube-like templates and Ce(OH)$_2$Co$_{2.35}$Cl$_{0.20}$(OH)$_{1.10}$ nanowire templates: These two types of templates were synthesized by simple hydrothermal methods. For Ce(OH)CO$_3$ cube-like templates, Ce(NO$_3$)$_3$·6H$_2$O (0.05 M) solution and CO(NH$_2$)$_2$ (0.1 M) solution were mixed, then hydrothermally reacted at 160 °C for 1 h.[15] In the case of Ce(OH)$_2$Co$_{2.35}$Cl$_{0.20}$(OH)$_{1.10}$ nanowires, CoCl$_2$·6H$_2$O (5 mmol) and CO(NH$_2$)$_2$ (5 mmol) were dissolved in 40 mL of water and heated at 100 °C for 12 h.[16]

Synthesis of Ce–Mn Binary Oxide Nanotubes: Ce(OH)CO$_3$ powder (5 g) was mixed with K$_2$MnO$_4$ (60 mL, 0.025 M) aqueous solution. After stirring 10 min, the mixture was kept still for 6 days. Finally, the sample was removed and washed by HNO$_3$ (1 M) thoroughly to remove unreacted templates, and dried at 60 °C.

Synthesis of Hollow Ce–Mn Cubes and Co–Mn, Ce–Fe Composites: For the preparation of Ce–Mn binary oxide nanocubes, Ce(OH)CO$_3$ nanocubes (50 mg) were mixed with K$_2$MnO$_4$ (30 mg, 0.5 mM) aqueous solution. After stirring 10 min, the mixture was kept still for 6 days. Finally, the sample was washed by HNO$_3$ (1 M) thoroughly to remove unreacted templates, and dried at 60 °C. While for the preparation of hollow Co–Mn, Co$_2$CO$_3$Cl$_{2.35}$(OH)$_{1.10}$ (50 mg) was dispersed in water (30 mL), followed by the addition of K$_2$MnO$_4$ (2.5 mL, 0.05 M). Then, the mixture was kept still for 9 days before washing by water thoroughly. Finally, the sample was calcined at 350 °C for 4 h. For the preparation of hollow Ce–Fe, Ce(OH)CO$_3$ powder (300 mg) was mixed with K$_2$FeO$_4$ (30 mL, 0.025 M) aqueous solution. After stirring 10 min, the mixture was kept still for 6 days. Finally, the sample was washed, and then washed by acetic acid thoroughly to remove unreacted templates, and dried at 60 °C.

Materials Characterization: The samples were characterized by powder XRD (Bruker D8 Advance) with Cu-Kα radiation, SEM (JSM-6700F), TEM (JEM-2100) equipped with an EDS. Micro-Raman measurements were taken with an RM 1000 Rennishaw Raman microscope system equipped with a laser at 514 nm, a Leica microscope and an electrically refrigerated CCD camera. Brunauer-Emmett-Teller surface area measurements were performed for the catalysts with a Quantachrome Instruments Autosorb-1. UV-vis adsorption spectra were measured on a Cary 5000 UV-Vis-NIR spectrophotometer (Varian). XPS spectra were taken using a VG Escalab 220-iXL equipped with a twin anode X-ray source.

CO Oxidation: Catalytic activity was measured using a continuous flow fixed-bed microreactor at atmospheric pressure. In a typical experiment, the system was first purged with high-purity N$_2$ gas and then a gas mixture of CO$_2$/N$_2$ (1:10) was introduced into the reactor which contained 50 mg of the Ce–Mn binary oxide nanotubes. Gases were analyzed with an online infrared gas analyzer (Gasboard-3121, China Wuhan Cubic Co.) which simultaneously detects CO and CO$_2$ with a resolution of 10 ppm. The results were further confirmed with a Shimadzu gas chromatograph (GC-14C). For the purpose of comparison, the CO oxidation tests were also run on commercial MnO$_2$ and CeO$_2$ particles, as well as their physical mixture under exactly same conditions. MnO$_2$ particles (mean size ~10 μm) and CeO$_2$ particles (mean size ~0.5 μm) were ordered from Sigma-Aldrich and used without further purification.

Water Treatment Experiment: The adsorbent sample (20 mg) was added to Congo red (Sigma-Aldrich, 99%) solution (20 ml, 100 mg/L) under stirring. UV-Vis absorption spectra were recorded at different intervals to monitor the process. CeO$_2$ nanotubes were prepared according to our previously reported procedures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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