



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Short communication

Efficient encapsulation of LaCoO₃ perovskite in mesoporous silica induced by a chelating template



Kui Niu*, Liman Liang, Jingshi Li, Fan Zhang

Chemistry Department & Life Science and Technology Institute, Hebei Normal University of Science and Technology, Qinhuangdao 066004, China

ARTICLE INFO

Article history:

Received 7 February 2015

Received in revised form

2 September 2015

Accepted 3 September 2015

Available online 11 September 2015

Keywords:

LaCoO₃ perovskite

Metal oxide

Rhombohedral phase

Mesoporous silica

Chelating template

ABSTRACT

A novel and facile chelating–template route for encapsulation of nanosized LaCoO₃ into mesoporous silica has been investigated. An amphipathic triprotic acid, which has capability to prepare perovskite LaCoO₃ powder through Pechini-type method, directs the construction of silica host and thereby fabricates LaCoO₃/mesoporous silica composites. Powder X-ray diffraction and X-ray photoelectron spectroscopy analyses were undertaken to determine the formation of the perovskite crystalline phase. Electron microscope and nitrogen adsorption–desorption analyses were carried out to elucidate the structural features of the host–guest composites. It was demonstrated that ultrafine guest LaCoO₃ nanoparticles with perovskite rhombohedral phase were formed after calcination, and the host silica skeleton remained short-range ordered mesoporous feature after implantation. This study therefore presents a potential simple approach to encapsulating well-dispersed composite metal oxide in mesoporous silica.

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1. Introduction

ABO₃ type perovskite metal oxides, in which A is a rare earth or an alkali earth element and B is typically a transition metal, have envisioned uses in magnetics, catalysis and electronics owing to their outstanding properties and functionalities, together with the benefit in terms of low-cost and high thermal stability [1–3]. Among them, LaCoO₃ based ceramics exhibit unique mechanical behavior, interesting electrical properties and excellent catalytic performance which have attracted growing attention for potential application [4–6]. The physical–chemistry properties of these materials strongly rely on their surface areas, while uncontrollable aggregation of the generated nanocrystals frequently occurs in conventional synthetic procedures. To alleviate this problem, a revolutionary strategy to reducing the particle size and lowering the calcination temperature has been developed by using complexing agent such as poly(acrylic acid), maleic acid, or citric acid via a sol–gel process [7–9]. On this basis, polyhydroxyalcohol is always chosen to treat with the formed chelates to generate a stable polymeric network for inhibiting segregation of particles. Compared with other routes, the introduction of complexing agent allows more homogenous mixing of the components on an atomic

scale and achieves an increase in the specific surface area due to the low decomposition temperature of the mixed-metal complex precursors, and the organic network conduces to the formation of single-phased and more homogeneous powders.

Besides improving the synthetic methods, another effective approach for achieving nanoscaled perovskite oxides is loading them on porous supports so as to mitigate nanoparticle growth and hinder interparticle aggregation. Intensive efforts have been undertaken to employ silica-based mesoporous materials as hosts for embedding LaCoO₃ into their well-ordered pores to fabricate host–guest composites with high surface area and good hydrothermal stability. The in situ synthetic route, which is commonly applied to prepare LaCoO₃/mesoporous silica composite, has been developed to introduce the precursors in the form of metal–citric acid chelates during the construction of porous skeleton or thereafter [10–12]. Likewise, the guest precursors with uniform distribution in mesopores could convert to LaCoO₃ nanocrystals at relatively low temperature with the aid of citric acid, and furthermore, excessive aggregation of the generated perovskite oxides could be inhibited during the subsequent sinter process owing to the confinement effect of the host silica framework.

In our previous work, we have presented a simple route for encapsulation of nanoscaled transition-metal oxides, such as ZnO or Co₃O₄, in silica mesopores with the guidance of a chelating surfactant N-hexadecyl ethylenediamine triacetic acid (HED3A) [13,14]. Besides binding the guest metal cation, the amphiphilic

* Corresponding author. Tel./fax: +86 335 8387040.

E-mail address: kui-niu@outlook.com (K. Niu).

molecule also plays the role of structure-directing agent for fabricating the host mesoporous silica. The present paper describes our efforts to prepare lanthanum cobalt oxide powder via a modified Pechini method by using HED3A instead of citric acid as complexing agent. As an improvement and comparison, attempts have also been made to construct silica matrix based on the self-assembly of the hybrid metal–HED3A complex, aiming for incorporating lanthanum cobalt oxide nanoparticles within mesopores based on the confinement effect of the host framework in subsequent calcination process. The eventual presence of the precursors, accompanied with the structural characteristics of the obtained materials is investigated.

2. Experimental procedure

2.1. Materials

The chelating surfactant HED3A was synthesized according to the route described in the literature [15], and the molecular structure was confirmed by Fourier transform infrared (FTIR) spectroscopy, mass spectrometry (MS) and proton nuclear magnetic resonance (^1H NMR) spectroscopy, respectively. All other reagents purchased from SCRC are analytical grade and used without further purification.

2.2. Preparation of lanthanum cobalt oxide powder (LCP)

The synthetic procedures of LCP were referred to the Pechini method. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HED3A were mixed and dissolved in a small amount of distilled water. After that, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the mixture under a continuous stirring. The solution was slowly heated to 363 K followed by addition of ethylene glycol (EG) and then maintained at 363 K for 3 h to accelerate the polyesterification and remove excess solvent. The resulting resin was dried at 383 K for 3 h, and then successively calcined at 473 K in N_2 flowing for 1 h and at 873 K in air for 6 h. The reactant molar ratio of cobalt nitrate/lanthanum nitrate/EG/HED3A is designated as 1:1:2:3.

2.3. Fabrication of lanthanum cobalt oxide/mesoporous silica composites (LCSs)

HED3A was dissolved in distilled water and titrated to neutrality using 0.5 M sodium hydroxide at 315 K. A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ aqueous solution was then added to the system under vigorous stirring, and the final pH value of the medium was adjusted to 8.0. 3-Aminopropyltrimethoxysilane (APS) was subsequently injected into the above mixture with an additional stirring for 30 s to form a suspension. Afterward, tetraethylorthosilicate (TEOS) was mixed into the suspension with a continuous stirring for 3 min, and the mixture was aged at 315 K for 48 h. The resultant precipitates were filtered and dried at room temperature, and the calcination procedures were the same as those used for the powder listed above. The reactant molar ratio of HED3A:cobalt nitrate:lanthanum nitrate:APS:TEOS: H_2O is 1:($x/10$):($x/10$):3:4:1750. The variable x was determined as 1, 3 or 5, and each sample was denominated x -LCS.

2.4. Sample characterization

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffraction using $\text{CuK}\alpha$ radiation operating at 40 kV/40 mA with a 0.020° step size and a 1 s step. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo ESCALAB 250 spectrometer using $\text{AlK}\alpha$ ($h\nu = 1486.6$ eV) as

the radiation, and all binding energies were referenced to C 1s at 284.5 eV. Scanning electron microscope (SEM) images were taken using an FEI Quanta 200 scanning electron microscope. High-resolution transmission electron microscopy (HRTEM) images were observed on a JEOL JEM-2100 instrument equipped with an energy-dispersive spectrometer (EDS) and used at an accelerating voltage of 200 kV. The nitrogen adsorption–desorption isotherms were measured at 77 K with a Micromeritics ASAP-2020 surface area and porosity analyzer.

3. Results and discussion

Our earlier research has demonstrated that HED3A could be completely decomposed by calcination at 873 K in air flow. On this basis, the small-angle XRD (SAXRD) and wide-angle XRD (WAXRD) patterns of the as-synthesized powder and composites are displayed in Fig. 1. The WAXRD pattern of LCP reflects a perovskite rhombohedral phase of LaCoO_3 (JCPDS 48-0123) was obtained through the Pechini-type reaction route [16]. In addition to the broad band peak belonging to amorphous silica matrix around $2\theta = 25^\circ$, the WAXRD patterns of LCSs also exhibit typical reflections of perovskite LaCoO_3 , especially for the composite with high doping amount. Compared to the SAXRD pattern of LCP, obvious reflections appear in the range of $2\theta = 1\text{--}5^\circ$ in that of LCSs, verifying the mesoporous characteristics of these samples. In addition, the SAXRD peaks of LCSs present a shift to higher angles, together with an attenuation of the peak intensities as the doping level is increased, which can be attributed to the change of the X-ray scattering caused by the incorporation of LaCoO_3 [17]. The XRD results confirm the effectiveness of shaping perovskite LaCoO_3 and the functionality of constructing mesoporous silica wall under the guidance of HED3A, even if both stages are accomplished synchronously.

Fig. 2A shows the position of La $3d_{5/2}$ at the binding energy of 834.5 eV and 834.7 eV for LCP and 5-LCS, respectively. Satellite peaks separated from the La $3d_{5/2}$ peak by 4–5 eV can be assigned to a transition from the anion valence band to a free lanthanum 4f band [18]. For LCP, peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ centered at 780.3 eV and 795.3 eV can be identified in Fig. 2B. Lack of shake-up satellite peaks in the Co 2p spectra confirms the absence of valence state of cobalt, and the energy splitting of 15 eV matches well with previously reported perovskite LaCoO_3 [19]. The binding energies

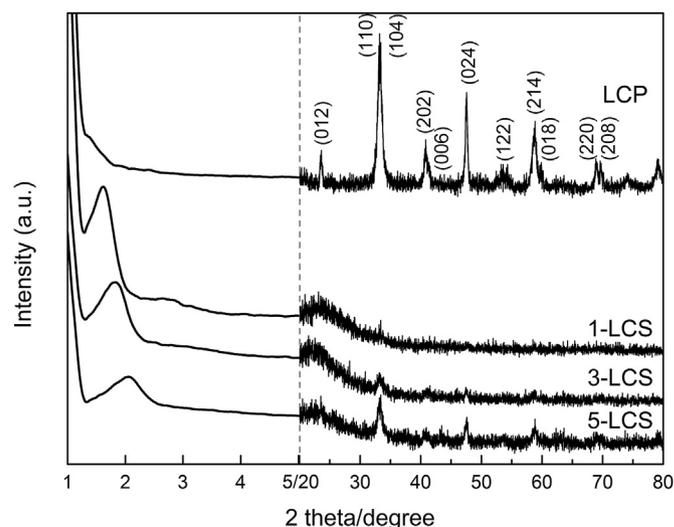


Fig. 1. XRD patterns of LCP and LCSs.

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