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Direct synthesis of hollow polyhedral ceria nano powders via a template-free mixed solvothermal route

LIU Junliang (刘俊亮)[1,2,*], YAN Leiming (颜雷鸣)[1], CHEN Xiulei (陈秀雷)[1], WANG Shengyun (王绳芸)[1], ZHANG Ming (张 明)[1,2,3], TIAN Chang'an (田长安)[4]

(1. School of Chemistry and Chemical Engineering, Yangzhou University; 2. Key Laboratory of Environmental Materials and Engineering of Jiangsu Province; 3. Testing Center, Yangzhou University, Yangzhou 225002, China; 4. Department of Chemistry and Materials Engineering, Hefei University, Hefei 230601, China)

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Abstract: Novel mono-dispersed hollow polyhedral ceria nano powders with the average particle size of 250 nm were directly synthesized via a simple template-free mixed solvothermal method by using water-ethanol as the solvent. The formation of such hollow structure with the regular polyhedral particle shape was based on a solvent-controlled Ostwald ripening coupled self-templating process. The mixed solvent promoted the formation of the regular solid particles at the beginning of solvothermal reaction and drove the Ostwald ripening as the reaction went on. Owing to the Ostwald ripening and self-assembly of nano crystallites, ceria nano particles converted into the hollow structures with regular polyhedral shape during the solvothermal process just by increasing solvothermal reaction time. The as-synthesized hollow ceria nano powders exhibited strong absorptions in the UV-vis spectrum and the evaluated energy band gaps increased according to the shape evolution and size decrease of the nano particles, which demonstrated obvious blue shift effects.

Keywords: ceria; hollow structures; nano powders; solvothermal reaction; rare earths

As one of the most widely used rare earth metal oxides, ceria with a cubic fluorite structure has attracted continuous attention due to its excellent properties, which has extended into a very broad range of application fields including optical additives, oxygen sensors, solid electrolytes for fuel cells and catalysts for automotive exhaust treatment as well as anti-wearable coatings owing to its oxygen storage capacities, good ion conductivities, fine optical properties and excellent catalytic properties as well as low cost[1–3]. As well-known, the final performances of ceria are greatly dependent on its particle size, morphology and micro-structure[1,4]. Over the past several decades, ceria nano-materials with various morphologies and micro-structures including nano-powders[5,6], nano-wires[7], nano-tubes[8], nano-rods[4,9,10] and hollow-structured nano powders[11–17] have been fabricated to satisfy the requirements for the actual applications. Among the various kinds of ceria nano-materials, ceria nano powders with hollow structures arouse great interest in a number of potential applications such as pigments, drug-delivery carriers, catalysts and catalyst supports as well as chemical sensors[11–18]. To fabricate hollow ceria nano powders, there are mainly two distinct types of synthetic methods: one is the templating method; the other is the template-free route. The templating method has been proved to be very effective and versatile for constructing a hollow structure for its inherent advantages of defining the size and shape of the desired hollow materials[15]. Kartsonakis et al.[12] fabricated hollow ceria nano spheres by using polystyrene microspheres as the templates. Wang et al.[13] synthesized porous ceria hollow spheres with large surface area and pore volume via a carbon sphere template method. However, the difficulties in preparing high quality templates as well as the complexities of multi-step synthetic procedures drove scientists explore template-free methods for preparing hollow structures[15]. Therefore, it is very desirable to explore a facile and template free route to obtain ceria hollow nano materials based on self-assemble or controllable crystal growth[14,17,18]. Jiao et al.[14] presented a simple one-step solvothermal reaction without using any template and successfully prepared porous ceria hollow nano spheres composed of small nano particles, which was a good example. Chen et al.[17] developed a solvothermal method free from templates to synthesize ceria hollow nano-crystals, in which $CeCl_3$ was proposed to hydrolyze with the assistance of poly(vinylpyrrolidone) (PVP) in the water-ethanol mixed solvent. The formation of ceria hollow nano-crystals was believed to be ascribed to a dissolution-recrystallization

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* **Corresponding author:** LIU Junliang (**E-mail:** liujunliang@yzu.edu.cn; **Tel.:** +86-514-87975590-9119)

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mechanism. That is another good example for preparing ceria hollow nano-crystals. However, to our knowledge, a few of the other reports focused on fabricating ceria hollow nano-spheres, but there are still few works on synthesizing ceria hollow nano materials with specific regular particle shapes, which could alter their functional properties especially on catalyzing properties[10]. It appears to be more difficult to well control the particle shapes just by self-assemble based on the crystal growth. Herein, in order to fabricate hollow ceria nano powders with a regular shape, a simple one-pot mixed solvothermal route was presented and the possible formation mechanism was discussed in this paper.

1 Experimental

As the starting material, cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) with A.R. grade was weighed and dissolved in the water-ethanol mixed solvent to form a clear solution. Polyvinylpyrrolidone (PVP-K30), as the surfactant, was added into the solution according to the molar ratio of PVP/Ce^{3+}=2:1. Subsequently, the resulting solution (75.0 mL) was transferred into a Teflon-lined autoclave with a total capacity of 100 mL, and solvothermally treated at 180 ºC for different time. After the solvothermal reaction finished, the obtained suspensions were cooled to room temperature and the precipitates were collected by the centrifugation and washed with the water-ethanol mixed solvent (1:1) to eliminate the surfactant. After vacuum-dried at 80 ºC for 12 h, the synthesized brown powders were obtained. The phase compositions of the as-synthesized powders were identified by X-ray diffraction (XRD) method with Cu Kα radiation (Bruker, D8 Advance) and their morphologies were observed by using a transmission electronic microscope (TEM, Philips Tecnai12). Also, their UV-visible absorption spectra were recorded by Varian Cary 5000 equipped with an integrated sphere.

2 Results and discussion

The typical XRD pattern of the nano powders synthesized at 180 ºC for 24 h is shown in Fig. 1. All the XRD diffraction peaks of the obtained nano powders are well ascribed to the reflections of fluorite-type CeO_2 rather than any others and the relative intensities agreed with JCPDS No. 34-0394, which evidently indicates that Ce^{3+} was oxidized into cerium oxide (Ce^{4+}) by NO_3^- with the aid of water under high pressure and single phase ceria powders had been successfully synthesized by the presented solvothermal route.

Fig. 2 gives the SEM and HR-TEM images of the obtained ceria nano powders synthesized at 180 ºC for 24 h. As shown in Fig. 2(a), it is obvious that the synthesized ceria nano powders are homogenous with nearly uniform

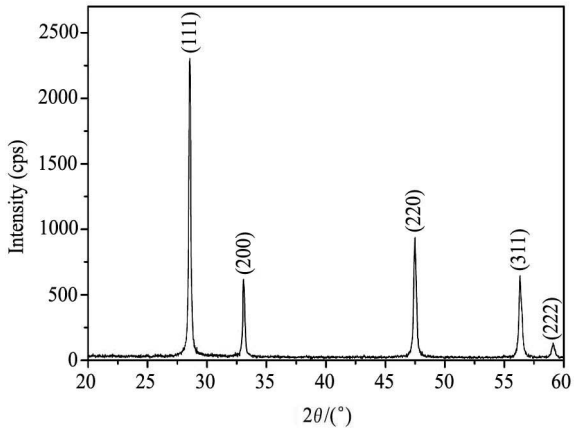

Fig. 1 Typical XRD pattern of the obtained hollow ceria synthesized at 180 ºC for 24 h

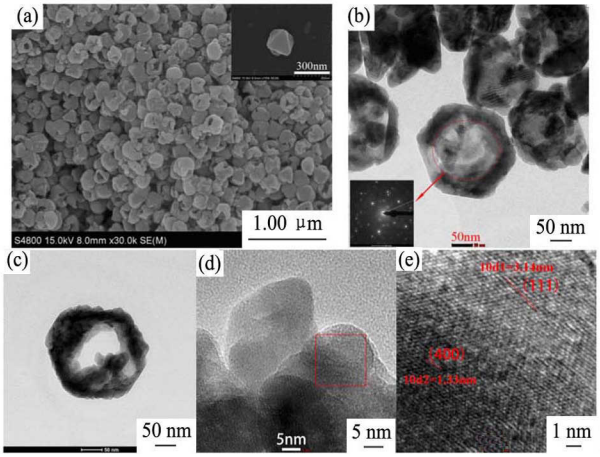

Fig. 2 SEM (a) and HR-TEM (b–e) images of the obtained hollow ceria synthesized at 180 ºC for 24 h

polyhedral particle shape. That is confirmed by the TEM image (Fig. 2(b)). The powders are characterized of mono-dispersed hollow polyhedral particles with the average particle size of 250 nm. The selected area electron diffraction (SAED) pattern demonstrates relative independent spots, indicating that the single hollow particle consisted of tiny crystallites with randon orientations. Taking a deep insight into a single hollow particle by HR-TEM (Fig. 2(c–e)), a direct support is presented that the single particle is piled up by tiny crystallites with the crystallite sizes about 25 to 30 nm. The spaces of the measured lattice fringes are 0.314 and 0.133 nm, which are indexed to the inter-planar spaces of (111) and (400) planes of ceria phase, respectively. It appears that the crystallites in the hollow particles are in the random orientation, which agrees with the results from the SAED pattern.

To understand the possible formation process of such hollow polyhedral ceria nano powders, ceria nano powders synthesized with various solvothermal reaction time ranging from 6 to 48 h have been collected and systematically investigated. From the XRD patterns shown in Fig. 3, all the obtained nano powders synthesized at various reaction time are characterized of single phase