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Rapid hydrothermal synthesis of CeO_2 nanoparticles with (2 2 0)-dominated surface and its CO catalytic performance

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ABSTRACT

Uniform CeO_2 nanoparticles with diameter in the range of 13–17 nm were synthesized through a one-step rapid hydrothermal strategy. The characterization indicated that (2 2 0) surface is the majority of the exposed CeO_2 surfaces. The reaction conditions including reactant amounts, reaction time were studied and optimized. The addition of hexamethylenetetramine is the key to the formation of (2 2 0)-dominated surface structure. The product shows better catalytic performance on CO conversion corresponding to the result of temperature-programmed reduction under a H_2 environment.

1. Introduction

Ceria has attracted a great deal of attention due to its wide applications in fields such as catalysis, electrochemistry, and optics [1–6]. Many endeavors have been devoted to the synthesis of CeO_2 nanomaterials with various morphologies and properties [7–13].

Recently, the influences of exposed surface structure on catalytic property of CeO_2 nanomaterials have been explored. Sayle et al. predicted in theory that the (1 1 0) surface is more reactive in CO conversion than (1 1 1) [14]. Conesa reported it is easier to form an anion vacancy on surfaces (1 1 0) or (1 0 0) [15]. Consequently synthesis of nanostructured CeO_2 with the more exposure of (1 1 0) and (1 0 0) surfaces is conducive to enhance ceria's properties. Yan and co-workers obtained high reactive CeO_2 nanorods, nanopolyhedra and nanocubes exposed different crystal planes through a hydrothermal route [16]. Well-dispersed CeO_2 nanocubes with (1 0 0) terminated surface were successfully synthesized using a supercritical hydrothermal method at 400 °C for 10 min [17]. Liu et al. reported the hydrothermal synthesis of CeO_2 nanosheets with (1 1 0)-dominated surface at 220 °C for 24 h [18]. However, to obtain the specific surface structure, high temperature or long reaction time are needed, and alkali should exist before the synthesis process. A mild and rapid synthetic strategy for producing CeO_2 nanocrystals with reactive surface exposure appears to be a challenging goal.

Herein, CeO_2 nanoparticles (NPs) with (2 2 0)-dominated surface have been prepared through a one-step rapid hydrothermal strategy at 180 °C for only 100 min, using $Ce(NO_3)_3$ as the cerium source, hexamethylenetetramine (HMT) as the precipitant, polyvinylpyrrolidone (PVP) as the surfactant. HMT plays a vital role in the formation of the (2 2 0)-dominated surface. Furthermore, the catalytic performance and properties of CeO_2 NPs are studied through CO catalysis, the Brunauer–Emmett–Teller (BET) method, and the temperature-programmed reduction under a H_2 environment (H_2-TPR).

2. Experimental

In a typical synthesis, 0.374 g $Ce(NO_3)_3{\cdot}6H_2O$, 0.09 g HMT and 0.4 g PVP were dissolved in 16 mL distilled water. Then the mixture was loaded into the 20-mL Teflon-lined autoclave. The autoclave was sealed and placed into an oven. It was maintained at 180 °C for 100 min and then cooled to room temperature. The precipitates were separated by centrifuging, washed with distilled water several times.

The phase identity, composition were recorded by using a D8 Advance X-ray diffractometer (XRD) with a graphite monochromater and Cu-K radiation ($\lambda = 0.15418$ nm). The structure, size, and shape of the products were characterized by a transmission electron microscope (TEM, JEM100-CXII) with an accelerating voltage of 80 kV, a field-emission scanning electron microscope

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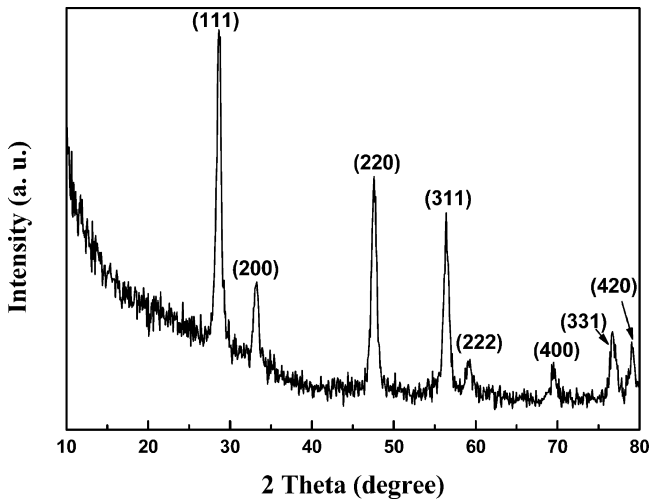

Fig. 1. XRD pattern of CeO_2 NPs prepared by the hydrothermal process at 180 °C for 100 min.

(FE-SEM, Hitachi, S4800), and a high-resolution transmission electron microscope (HRTEM, JEM-2100) with an accelerating voltage of 200 kV. The pH value was evaluated by the pH meter (Leici, PHSJ-3F).

The surface areas were calculated by the BET method. H_2-TPR was carried out on a PCA-1200 instrument. The catalytic properties of the products were evaluated through the CO oxidation experiment. In a typical experiment, 25 mg catalyst particles mixed with 300 mg silica sand were placed in the reactor. The reactant gases (1% CO, 10% O_2, and 89% N_2) passed through the reactor at a rate of 60 mL/min.

3. Results and discussion

The powder XRD patterns (Fig. 1) of CeO_2 NPs prepared through hydrothermal process exhibit well resolved X-ray diffraction lines, indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) planes. On the patterns (Fig. 1), all lines are well indexed to a pure phase of face-centered cubic ceria structures (JCPDS 34-0394).

The morphologies of the CeO_2 sample were investigated by SEM, TEM and HRTEM. Fig. 2a displays the SEM image of the sample which shows that the products are composed of small particles with diameter in the range of 13–17 nm (the size distribution shown in Fig. S1). Similar results were obtained by the corresponding TEM observation (Fig. 2b and c). The NPs possess distinct boundaries and somewhat clean-cut edges and corners. The HRTEM image, which was recorded from a single particle, exhibits good crystallinity, as shown in Fig. 2d. Fig. 2d shows the well-defined 2D lattice planes, with d-spacing of 0.315 and 0.314 nm respectively, corresponding to (1 1 1) planes. The angle between the two planes is about 71°. According to crystal geometry and previous work [18], the exposure of the CeO_2 (2 2 0) surface is the majority plane. The corresponding selected area electron diffraction (SAED) pattern (the inset in Fig. 2d) confirms that the CeO_2 NPs were polycrystalline structures.

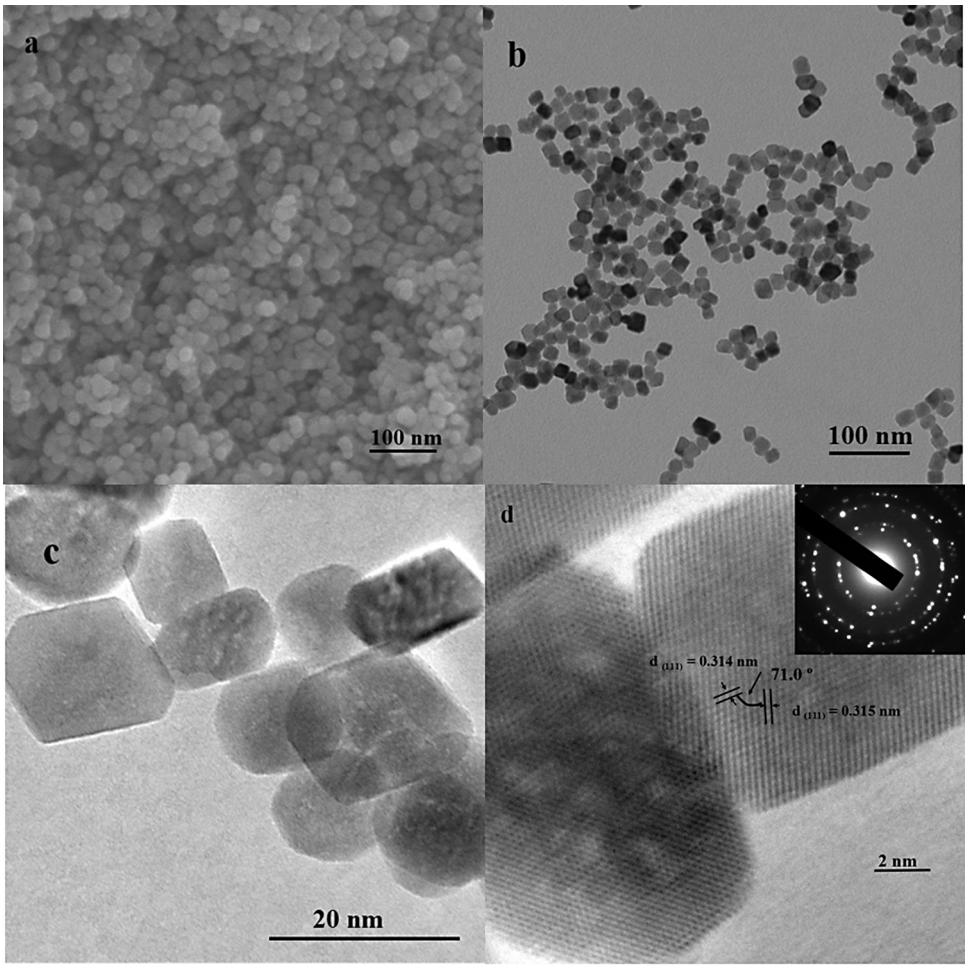

Fig. 2. (a) SEM image, (b, c) TEM images, and (d) HRTEM image of the typical CeO_2 NPs. The inset of (d) is the corresponding SAED.