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Preparation and characterization of hollow CeO_2 structures using kapok fibers as biomass template

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ABSTRACT

Hollow cerium dioxide structures (HCSs) were prepared by a simple manufacturing method using *Ceiba pentandra* (L.) Gaertn. (kapok) fibers as a natural biomass template. The heat decomposition of the kapok template and the subsequent formation of a nanocrystalline phase of CeO_2 in HCSs were studied by thermal gravimetric analysis and X-ray diffraction. The uniform morphology of the obtained HCSs with a diameter of 10–15 μm was investigated by field-emission scanning electron microscopy. Despite the micrometer size of the HCSs, the walls had a high specific surface area and mesopores that were well developed, as determined by N_2 gas adsorption–desorption analysis. Further, X-ray diffraction analysis revealed that the formation of HCSs was largely influenced by the calcination temperature.

1. Introduction

Recently, rare-earth oxides have received much attention in scientific and industrial fields [1]. Among these, cerium dioxide (CeO_2) is one of the most useful ceramic materials for several applications such as cosmetics, gas sensors, fuel cells, catalysts, and catalyst supports [2]. In general, CeO_2 is synthesized by the sol–gel, hydrothermal, and sonochemical methods or by heat decomposition using a precursor [3]. The various morphologies of CeO_2 such as cubic, spherical, rod-like, and mesoporous have been studied by many researchers in the past few decades [4]; the properties of such particles are significantly different from those of the bulk state of CeO_2 [5]. Of all the stated morphologies, hollow structures have been extensively investigated because of the attractive advantages they offer over the other shapes, including a higher surface area, more effective light scattering, and lighter weight [6]. Various technologies have been employed to prepare hollow ceramic structures, such as the polymer-template, dry/wet, electro-spinning, and emulsion methods [7]. The template approach is a simple route that involves lower production costs than the other fabrication methods [8]. Additionally, when bio-resources are used as templates to ensure an eco-friendly process, hollow CeO_2 structures (HCSs) are easily obtained upon heat decomposition of the templates.

In this study, HCSs were successfully fabricated through an impregnation method, with cerium(III) chloride heptahydrate ($CeCl_2 \bullet 6H_2O$) as the precursor material and *Ceiba pentandra* (L.) Gaertn. (kapok) as the biomass template. Kapok fibers derived from the seed wool of kapok trees have a fine and homogeneously hollow structure [9]. The decomposition of the kapok template and the subsequent formation of CeO_2 with a hollow structure were investigated by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, X-ray photoelectron spectroscopy (XPS), and field-emission scanning electron microscopy (FE-SEM). We also investigated the microstructural changes in HCSs fabricated at different calcination temperatures.

2. Experimental

The kapok fibers were obtained from the island of Java, Indonesia. The kapok fibers were air-dried and subsequently oven-dried at 120 °C for 24 h to rid them of moisture. The CeO_2 precursor, 0.1 M $CeCl_2 \bullet 6H_2O$ (Aldrich Co.), was diluted with distilled water at 25 °C. The kapok fibers were added to the reactor filled with the CeO_2 precursor solution, and the impregnation reaction was performed at 25 °C for 6 h under an inert atmosphere. After the reaction, the CeO_2/kapok template was washed

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with anhydrous ethanol and dried under vacuum at 80 °C for 24 h. These samples were then heat-treated to remove the kapok fiber templates. The HCSs were calcined at 500, 600, and 700 °C for 4 h, and the samples are denoted as HCS-500, HCS-600, and HCS-700, respectively.

TGA (STARSW, Mettler) was conducted up to 1000 °C with a heating rate of 2 °C/min under air atmosphere to evaluate the thermal behavior of the HCSs. In addition, the chemical structure of the HCSs was examined by X-ray photoelectron spectroscopy (XPS; Multilab 200 system, SSK). Surfaces and cross sections of the HCSs were investigated by FE-SEM (S-4700, Hitachi). Surface area and pore volume of the HCSs were determined by Brunauer–Emmett–Teller analysis (BET; ASAP2020, Micromeritics). Pore-size distribution was obtained by employing the Barrett–Joyner–Halenda (BJH) method to N_2 adsorption–desorption isotherms using the software ASAP2020. XRD patterns were obtained on a D/MAX-2500 unit using Cu Kα radiation ($\lambda = 1.540$ Å).

3. Results and discussion

A Kapok fiber has a large number of surface functional groups such as –OH and C=O, which offer an important chemical environment for the adsorption of metal cations and the subsequent conversion to HCSs upon removal by decomposition of the kapok template [10]. Fig. 1 (a and b) shows the FE-SEM images of the raw kapok fiber template and the CeO_2/kapok fibers prepared by heat treatment at 500 °C. The low-magnification FE-SEM images show that the morphology of the prepared samples is very similar to that of the original kapok fibers. HCS-500 exhibited a regular hollow structure with outer and inner diameters of 10–15 μm and 8–12 μm, respectively. No destruction of the hollow structures was observed, as can be seen in Fig. 1 (a and b; inset). This HCS-500 sample is expected to show superior photocatalytic performance because its hollow structure offers a large and effective surface area for adsorption and catalytic reactions [7].

The TGA curves of the raw kapok fibers and CeO_2/kapok fibers are illustrated in Fig. 1c. It can be seen that the process of weight loss can be divided into two steps. Most of the organic components of the raw kapok fibers were decomposed by the heat process at 450 °C. In the case of CeO_2/kapok fibers, the first weight loss (20%), which occurred upon heating from 50 °C to 200 °C, was due to the release of incorporated water in the kapok fibers. The second weight loss (64%), which occurred from 200 °C to 450 °C, was caused by the elimination of tightly bound hydroxyl species, which accompanied CeO_2 crystallization on the kapok fibers template. Beyond 450 °C, the weight of the CeO_2/kapok fibers remained constant, indicating that the raw kapok fibers template had decomposed completely and that the formation of HCSs was complete. This was confirmed by the TG analysis, which indicated that the calcination temperature must be above 450 °C in order to obtain pure HCS.

Fig. 2a shows the XRD patterns of the HCS-500, HCS-600, and HCS-700 samples; as can be seen, all the HCS samples exhibit a cubic CeO_2 nanocrystalline phase. The main XRD peaks of all the samples are in excellent agreement with the powder data in JCPDS Card no. 34-0394 (cubic); accordingly, the samples have cell parameters of $a = 5.41134$ Å. With increasing calcination temperature from 500 °C to 700 °C, no new diffraction peaks appear, and the peaks corresponding to CeO_2 gradually become stronger and sharper, which indicates that the crystallinity of the HCSs increases with the increase in calcination temperature. It is thus obvious that the crystallite size of the HCSs increased with increasing calcination temperature. These results also are consistent with those obtained from the TG analysis.

Quantitative XPS analysis confirmed the chemical purity of the HCSs; its results are shown in Fig. 2 (b, c, and d). The XPS survey spectra of the HCS-500 sample show the Ce 3d and O 1s peaks of CeO_2 in Fig. 2b. The Ce $3d_{3/2}$ and Ce $3d_{5/2}$ spin-orbital splitting photoelectrons are located at binding energies of 900, 897, 887, and 882 eV as shown Fig. 2c. As can be seen in Fig. 2c, fitting of the O 1s peak of the HCS-500 sample reveals two binding energies at approximately 529 and 531 eV. The peak of 531 eV can be attributed to the presence of hydroxyl groups [10]. Constituent percentages of Ce and O in HCS-500 are 26.1% and 53.2%, respectively, corresponding closely to the Ce^{4+} state. In general, similar results have been observed for porous CeO_2 materials [2].

N_2 gas adsorption–desorption isotherms of HCS-500 at 77 K are shown in Fig. 3 (outside). According to the International Union of Pure and Applied Chemistry (IUPAC) classification, HCSs are characterized by type III adsorption isotherms, which indicate meso- and macroporous materials [11]. The pore-size distribution (inset) was determined by the BJH model, and shows that the hollow walls of HCS-500 were broad (3–100 nm), which is consistent with the meso- and macro-porous structures. The textural properties of the HCSs prepared at different calcination temperatures are summarized in Table 1. As the calcination temperature increased, the specific surface area and total pore volume decreased due to the growth of the crystalline phase [12]. The average pore size decreased with increasing calcination temperature. These findings enable us to conclude that the textural properties and crystallite size of HCSs are highly dependent on the calcination temperature. The synthesized HCSs can thus be employed as efficient photocatalysts for the removal of hazardous materials.

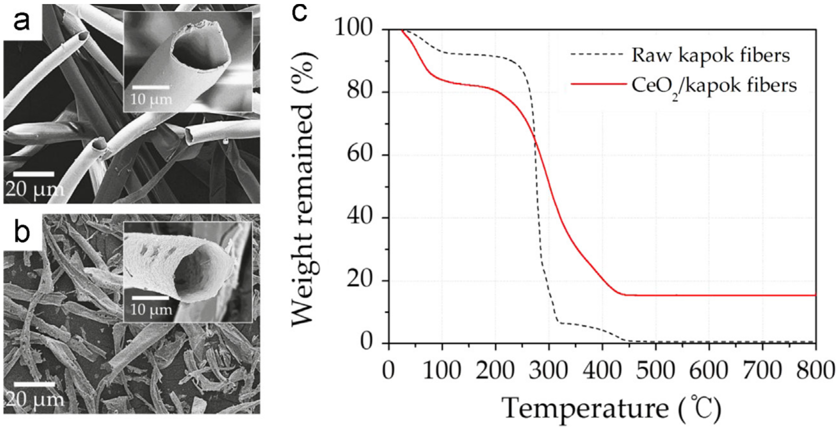

Fig. 1. FE-SEM photographs of (a) raw kapok template and (b) HCSs after heat treatment at 500 °C. (c) TGA curves of raw kapok fibers and CeO_2/kapok fibers under air atmosphere.