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Short communication

Synthesis and characterization of hollow metal oxide micro-tubes using a biomaterial template

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ABSTRACT

Various hollow metal oxide micro-tubes (SnO_2, ZrO_2, ZnO, and NiO) were prepared by a simple impregnation method using *Ceiba pentandra* (L.) Gaertn. (kapok) as a biomaterial template. Calcination heat treatment was successfully used for the removal of the kapok template. Field emission scanning electron microscopy (FE-SEM) was used to study the uniform morphology of the hollow metal oxide micro-tubes, which had an average diameter of 15–20 μm. The hollow metal oxide micro-tubes were further characterized by thermal gravity analysis (TGA), X-ray diffraction (XRD), and X-ray photo-electron spectroscopy (XPS). This synthesis method provides a new facile route for the fabrication of hollow metal oxide micro-tubes.

1. Introduction

Metal oxides (SnO_2, ZrO_2, ZnO, and NiO) have many applications in energy and environmental research [1,2]. SnO_2 is an important *n*-type wide band gap (3.64 eV) semiconductor that has a wide range of applications in solid-state gas sensors, transparent conducting electrodes, rechargeable Li batteries, and optical electronic devices [3–6]. Over the past decade, SnO_2 nanostructures have emerged as one of the most important oxide nanostructures owing to their advantageous properties and potential applications [7,8]. ZrO_2 has been reported to have a band gap in the range of 5.1–6.0 eV, and has therefore been used in the membranes of secondary batteries and in extra-high temperature insulation materials [9]. ZnO is of wide research interest because it exhibits a wide band gap (3.37 eV) and large binding energy (60 meV) and has a wide range of applications in photo-detectors, sensors, solar cells, medical antibacterial, and cosmetics [10–15]. NiO, a *p*-type semiconductor with a wide band gap (3.6–4.0 eV) [16], is an

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important material extensively used in catalysis, battery cathodes, gas sensors, electrochromic films, magnetic materials, and photovoltaic devices [17,18]. The performances of metal oxides depend on their chemical composition and surface properties as well as on their textural properties including morphology, surface area, pore volume, and pore dimensions. Recently, many researchers have studied the different metal oxide morphologies such as spherical and ordered porous particles, rods, fibers, and hollow structures [19,20]. In particular, hollow metal oxide structures have been extensively investigated because they offer advantages over other shapes, including a high surface area, narrow pore size distribution, effective light scattering, light weight, and hollow structure that facilitates mass diffusion [21]. The currently used techniques for preparing hollow metal oxide structures include a template approach, dry or wet spinning, electrospinning, and centrifugal spinning [22]. The template approach is very simple and cost-effective compared to the other synthesis methods [23]. Further, if natural biomass materials are used as templates, a hollow metal oxide structure can be easily obtained after removal of the template material through heat treatment [24].

In this work, various hollow metal oxide micro-tubes (SnO_2, ZrO_2, ZnO, and NiO) have been successfully prepared by an impregnation method using a precursor material and a natural biomass template, namely, *Ceiba pentandra* (L.) Gaertn. (kapok). Kapok fibers, derived from the seed wool of kapok trees, are fine and have a homogeneous hollow tube shape with a wall thickness of about 15 μm [25,26]. The kapok fiber has a large quantity 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 into metal oxide hollow structures upon removal of the kapok template [27]. This synthesis method provides a new facile route for the fabrication of hollow metal oxide micro-tubes. These hollow metal oxide micro-tubes have a wide range of potential applications in many fields of research.

2. Experimental

Kapok [*C. pentandra* (L.) Gaertn.] fibers were obtained from Java island, Indonesia. The kapok fibers were air-dried and subsequently oven-dried at 120 °C for 24 h to remove the moisture content. Anhydrous ethanol (Sigma–Aldrich, USA), distilled water, tin (II) chloride dehydrate (for SnO_2), zirconyl chloride octahydrate (for ZrO_2), zinc acetate (for ZnO), and nickel (II) nitrate hexahydrate (for NiO), all purchased from Sigma–Aldrich (USA), were analytical grade (assay > 99%) and used without further purification. In a typical synthesis, 2.25 g tin (II) chloride dehydrate, 3.22 g zirconyl chloride octahydrate, 1.83 g zinc acetat and 2.91 g nickel (II) nitrate were added into a beaker and dissolved in a 0.1 L solvent (2-propanol or distilled water). The impregnation reaction was then performed at 25 °C for 6 h. After the reaction, the metal oxide/kapok template was washed with anhydrous ethanol and dried in vacuum at 80 °C for 4 h. The samples were then calcined at 600 °C for 4 h to remove the kapok templates and obtain hollow metal oxide micro-tubes. Thermogravimetric analysis (TGA; STARSW, Mettler-Toledo, USA) was conducted up to 1000 °C with a heating rate of 2 °C/min under air atmosphere to evaluate the thermal behavior of the hollow metal oxide micro-tubes. The surface and shape of the hollow metal oxide micro-tubes were investigated by field emission scanning electron microscopy (FE-SEM; S-4700, Hitachi, Japan). The surface area and pore volume were determined by Brunauer–Emmett–Teller (BET) analysis (ASAP2020, Micromeritics, USA). The pore size was obtained by N_2 gas adsorption isotherms using ASAP2020 software. The X-ray diffraction (XRD) patterns were obtained on a D/MAX-2500 (Rigaku, Japan) using Cu-Kα radiation ($\lambda = 1.540$ Å). The X-ray photoelectron spectra (XPS) were collected on a Surface Science SSX100 (Seal Laboratories, USA) using Mg-Kα X-rays as the excitation source.

3. Results and discussion

TGA curves of the raw kapok and metal oxide/kapok fibers are shown in Fig. 1. The weight loss occurs mainly through two processes. For most metal oxide/kapok fibers, the first loss (of approximately 10%), which occurs below 250 °C, is attributed to the release of water from the precursor, whereas the second sharp loss (of approximately 79%), which occurs between 250 and 500 °C, may be due to the elimination of tightly bound hydroxyl species accompanying metal oxide crystallization around the kapok template. Calcination is used for complete removal of the kapok template and preparation of the pure metal oxide. The obtained yield of raw kapok fibers at 800 °C was 0%. At this temperature, the obtained yields of most metal oxide/kapok fibers were about 15% (except for the ZrO_2/kapok fiber, which was about 7%). Therefore, pure metal oxide micro-tubes can be obtained by using kapok as a template. However, a sufficient calcination temperature above 600 °C is required to fully remove the kapok template. Because NiO has a relatively low crystalline temperature, its calcination proceeds at a lower temperature [28]. All metal oxide yields were as stated above, except that of the ZrO_2 structure, which was slightly lower.

Fig. 2 shows FE-SEM images of (a) the raw kapok template and (b, c, d, and e) the hollow metal oxide micro-tubes prepared by calcination at 600 °C. The low-magnification FE-SEM images show that the morphology of the prepared samples is very similar to that of the original kapok template. Hollow

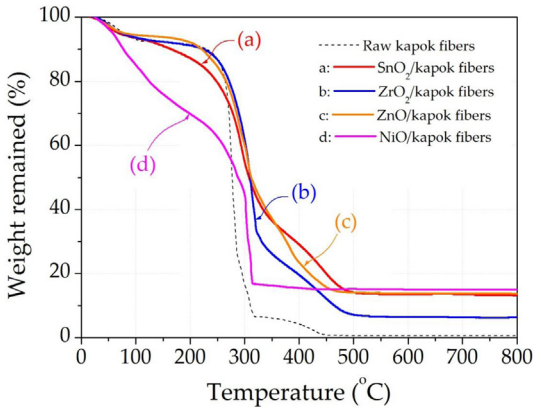

Fig. 1 – TGA curves of the raw kapok and metal oxide/kapok fibers under air atmosphere.