Nano cellulose-assisted synthesis of zirconia nanorods from local zircon-based Zr(OH)₄ precursors

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Zirconia nanorods have been successfully synthesized from local zircon-based Zr(OH)₄ precursors through a facile precursor-templating method assisted by sugarcane bagasse based-nano cellulose as the one-dimensional (1D) structure directing template. However, the 1D structure arrangement of the zirconia precursors by the cellulose template during synthesis undergoes at selective precursor pHs. The final products of zirconia consist of the t-metastable and the m-phases, exhibit microstructures of nanorods and elongated agglomerates, and reveal large specific surface areas.

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One-dimensional (1D) ZrO₂ nanomaterial has excellent characteristics such as a high aspect ratio, a large specific surface area, huge porosity, excellent mechanical strength and fracture toughness.¹-⁵ Many methods have been introduced in fabrication of 1D ZrO₂ nanomaterial. Nevertheless, the present methods show some drawbacks that limit in their small-scale production.⁶ Thus, a less expensive-simple method is needed to fabricate 1D ZrO₂ nanomaterial in large-scale production.

Zirconium silicate (ZrSiO₄) is a precious material as the ZrO₂ precursor because of its abundance in the large deposits. The ZrO₂ content of ZrSiO₄ reaches 62–65 wt.% that show a good economic value.⁷-¹⁰ Some methods have been explored to extract ZrO₂ from ZrSiO₄ such as alkaline fusion,¹¹ a chlorination method, carbothermal reduction process, and a sodium carbonate sintering Technology.¹² Hence, this study aims to use local ZrSiO₄ as the ZrO₂ precursor in the fabrication of 1D ZrO₂ nanomaterials. Some studies reported the use of ZrSiO₄ as the ZrO₂ precursor in the preparation of 3D and 1D ZrO₂ nanomaterials.⁶-¹¹ Our previous work reported the synthesis of 1D ZrO₂ nanomaterials from local zircon-based Zr(OH)₄ precursors assisted by organic compounds as the 1D directing structure templates.⁶,¹¹ Cellulose and its derivatives are promising inexpensive organic templates for fabrication of metal oxides in nanostructures, which can be extracted from natural resources. Previous studies reported the use of nanocrystalline cellulose template for fabricating NiO₂ and TiO₂ nanoparticles¹²,¹³ and hematite nanorods.¹⁴ In this study, nano cellulose is used as the 1D directing template in fabricating ZrO₂ nanorods from local zircon-based Zr(OH)₄ precursors. Besides, we want to explore the capability of nano cellulose as a 1D directing template in the synthesis of 1D ZrO₂ nanomaterial. Nano cellulose comprises hydroxyl groups in its linear chain of ringed glucose molecules,¹⁵ allowing this compound to interact with Zr(OH)₄ through the hydrogen bonding. This leads to a 1D structure direction of the ZrO₂ precursor.

In this study, the Zr(OH)₄·xH₂O precursor (pH 9) was synthesized from ZrSiO₄ via a modified sodium carbonate sintering method, containing 83.37 wt.% ZrO₂, 5.14 wt.% SiO₂, 0.7075 wt.% Na₂O, 0.9511 wt.% SO₃, and 4.61 wt.% LOI (at 800°C).¹⁰ Meanwhile, nano cellulose as a 1D template was extracted from sugarcane bagasse through sulfuric acid hydrolysis. The other materials used were a 96%
H₂SO₄ solution and Na₂CO₃ (99.9% purity) from Merck Inc. All materials were used without further purification. The procedure in the synthesis of zirconia nanorods from local zircon-based Zr(OH)₄ precursors assisted by nano cellulose applied the optimum synthesis condition in our previous study. The precursor pH was initially adjusted to pH 3 (ZNS-pH 3) and 5 (ZNS-pH 5). The procedure of pH decreasing referred to the previous study. Then, 10 ml of a 10% (w/v) nano cellulose solution was added to 25 ml precursor solution under stirring and heating at 100°C. The heating temperature was then turned down to 65°C. Aging process was carried out at 65°C for 3 h. The solid formed was collected, separated, and dried in an oven at 70°C. The as-synthesized products of ZNS-pH 3 and ZNS-pH 5 were then calcined at 600 and 800°C for about 2 h. The phases of zirconia were investigated using a Bruker D8 Advance X-ray diffractometer at 40 kV with a Cu/Kα (λ=1.54060 Å) (1 Å = 0.1 nm) radiation source. Fourier transform infrared spectroscopy (FT-IR) spectra of all samples including nano cellulose, the as-synthesized and the calcined zirconias were analyzed using a Prestige 21 Shimadzu FT-IR Spectrophotometer. A transmission electron microscope (TEM, LR HT-7700) were used to observe the microstructure of the calcined zirconias. The BET specific surface areas of the calcined zirconia samples were measured using a Quantachrome Nova Win instrument.

The X-ray diffraction (XRD) identification results in Fig. 1 show that all ZrO₂ samples consisting of the t-metastable and the m-phases. The t-metastable is indicated by a peak at a diffraction angle, 2θ, of 30.3°, corresponding to the (101) crystal plane of the t-ZrO₂ structure. Meanwhile, peaks at diffraction angles, 2θ, of 28.2 and 31.5° are the reflection of the (111) and (111) crystal planes of the m-ZrO₂ structure. An increase in calcination temperature from 600 to 800°C has altered the t-metastable to the m-phases. However, the higher precursor pH led to the formation of the preferred t-structure, as shown by ZNS-pH 5-T600°C (Fig. 1). The FT-IR analysis results in Fig. 2 show transmission bands at 3152-3154 cm⁻¹ in the as-synthesized samples of ZNS-pH 3 and ZNS-pH 5.
that are attributed to the intermolecular hydrogen bonding. Those bands are not found in the nano cellulose FT-IR spectrum. Therefore, the intermolecular hydrogen bonding in the as-synthesized samples explicitly reveals the interaction between the ZrO₂ precursor and nano cellulose template during synthesis.

The calcined ZNS-pH 3 and ZNS-pH 5 samples at 600°C show nanorod particles in their microstructures, as shown by the TEM results in Fig. 3(A). At 800°C, ZNS-pH 3 exhibits nanorod particles and ZNS-pH 5 reveals elongated agglomerates in their microstructures [Fig. 3(B)]. Meanwhile, the nano cellulose template used in this study show a microfiber structure (microfibrillated cellulose, MFC), exhibiting a high aspect ratio of \( \geq 100 \text{ nm} \) wide and \(<10 \mu\text{m} \) in length [Fig. 4(A)].\(^{15,17}\) In general, sugarcane bagasse based-nano cellulose used in this study.

![Fig. 3. The TEM micrographs of all samples calcined at 600°C (A) and 800°C (B).](image-url)
has a high aspect ratio (10–100 nm wide, 2000–3000 nm in length) and has branched structures, as shown in Fig. 4(A). Based on the TEM results in Fig. 3, the produced ZrO2 nanorods exhibit a lower aspect ratio (20–50 nm wide, 200–500 nm in length). This phenomenon might be caused by the condition of the precursor pH during synthesis. The Zr(OH)4·xH2O precursor show the origin pH 9 and contain hydrates which restrict the interaction between the ZrO2 precursor and nano cellulose. To overcome the hydrate inhibition, the precursor pH was adjusted to the selective pHs 3 and pH 5, resulting in ZrO(OH)2 and a mixture of ZrO(OH)2 and ZrO(OH)2·xH2O species, respectively. At pH 3, the precursor is in the form of ZrO(OH)2 without hydrates, allowing the template connect to the precursor through the hydrogen bond interaction between their hydroxyl groups. However, the hydrogen bonding between nanocellulose chains will be disturbed in the presence of acid, resulting in more dispersed nanocellulose. In this case, instead of branched structure of ZrO2, the fiber or rod structure is preferable. Under acidic condition, the amorphous region of sugarcane bagasse based-nano cellulose is highly susceptible to hydrolysis process.3) The nanocellulose will be hydrolyzed via glycosidic cleavage to result in shorter length of nanocellulose chains compared to untreated nanocellulose. This phenomenon could lead to the formation of shorter ZrO2 nanorods. Thus, a higher precursor pH 5 was applied with the consequence that more water molecules absorbed in the surface of the ZrO2 precursor. This phenomenon is corroborated by the FT-IR spectrum of the as-synthesized ZNS-pH 5, showing the sharp band at a region 1400 cm⁻¹ that is assigned to the stretching vibration of OH bonds from the bonds of the absorbed water (Fig. 2). The band in the FT-IR spectrum of the as-synthesized ZNS-pH 5 has a higher intensity than the band in the FT-IR spectrum of the as-synthesized ZNS-pH 3 (Fig. 2). After all, based on the FT-IR spectra of ZNS-pH 3 and ZNS-pH 5, the plausible reaction between the precursor of ZrO(OH)2 and the nano cellulose during synthesis is as shown in Fig. 4(B). During heating in calcination process at higher temperatures, the organic structure of nano cellulose in the as-synthesized samples are burnt out as gaseous species, leaving residual ZrO2 in the 1D structures. The formation of elongated agglomerates in the calcined ZNS-pH 5 [Fig. 3(B)] was probably caused by a higher initial heating temperature at 100°C than an aging temperature at 65°C, which led to the rapid nucleation of a number of ZrO2 crystals and they directly joined each other forming elongated agglomerates.

In addition, the calcined ZNS-pH 5 exhibits a greater BET surface area of about 21.45 m²/g than the ZNS-pH 3 one of about 12.71 m²/g at 800°C. The result is in agreement with the TEM results in Fig. 3(B). The calcined ZNS-pH 3 exhibits particle sizes larger than the calcined ZNS-pH 5, indicating a lower specific surface area.

In summary, the present study explores the use of a promising natural bio-template of sugarcane bagasse based-nano cellulose as the 1D structure directing agent in the synthesis of zirconia nanorods from local zircon-based Zr(OH)4 precursors. The experimental results show that the nano cellulose template has assisted the formation of ZrO2 nanorods at selective precursor pHs during synthesis.

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Fig. 4. The TEM micrograph of nano cellulose extracted from sugarcane bagasse (A) and the proposed interaction between the ZrO2 precursor and nano cellulose at the precursor pHs 3 and 5 (B).
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