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Nanostructured zirconium titanate fibers prepared by particulate sol-gel and cellulose templating techniques

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Abstract

In this paper, a method for cost-effective production of nanostructured zirconium titanate ($ZrTiO_4$) fibers is introduced. In this method, $ZrTiO_4$ fibers were synthesized by a sol-gel technique using cellulose fibers as the template. The resultant structures were studied by transmission electron microscopy, X-ray diffraction, scanning electron microscopy, and Brunauer–Emmett–Teller (BET) analyses. The photocatalytic activity of the fiber was compared to that of $ZrTiO_4$ powders prepared by the same sol-gel method, in dark and under UVA and UVC radiations. According to the results, after calcination accompanied by the template removal, the $ZrTiO_4$ fiber consists of uniformly-deposited, crystalline nanoparticles. This nanostructured fiber exhibited a higher surface area and a higher porosity compared with the $ZrTiO_4$ powders, resulting in considerably higher photocatalytic characteristics, as

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confirmed by the experiment. The large surface area and the enhanced photocatalytic activity of the ZrTiO₄ fibers also offer applications in sensors and bioactive films.

Keywords: Ceramics; Nanostructured materials; Sol-gel processes; Catalysis

1. Introduction

Zirconium titanate (ZrTiO₄) is used in a wide range of applications, including as high-dielectric materials [1-3], high-temperature pigments [4], humidity sensors [5], and bifunctional catalysts, albeit the latter in features of the TiO₂-ZrO₂ binary system [5-9]. It is well-known that in applications like catalysts, sensors, and bioactive films, having a high surface area, purity, and homogeneity is essential, while considering a low-cost and environmental friendly method is acknowledged.

ZrTiO₄ can be prepared by different methods like a time-consuming, solid-state reaction between ZrO₂ and TiO₂ at high temperatures [8-14]. Also, high-energy milling of ZrO₂ and TiO₂ is another method that can yield into amorphous powders in a lower temperature, but this method is still energetically costly, as well as has the disadvantage of introducing impurities of milling balls [9,10]. The sol-gel method is an outstanding method to produce homogeneous and amorphous ZrTiO₄ powders which can crystallize at low temperatures, compared to the other methods. Ceramics synthesized by sol-gel processes are also very pure and their microstructure is comparatively easy to tailor [15-18]. The sol-gel synthesis of ZrTiO₄ can be conducted by hydrolysis and condensation reactions of inorganic salts [3,9-11] or alkoxides [2,12-14].

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Photocatalytic materials have attracted a considerable interest and have emerged as an important destructive technology leading to the total mineralization of most organic pollutants, including organic dyes for wastewater treatments [19]. There are a few studies on the photocatalytic property of $ZrTiO_4$ which indicates a lower activity of $ZrTiO_4$ in comparison to TiO_2 and ZrO_2 [20]. To improve the photocatalytic characteristic of materials which is directly related to surface area, there are different approaches. Considerable efforts have been devoted to the design and synthesis of one-dimensional nanomaterials, such as nanorods, nanowires, nanotubes, and nanofibers, due to their unique properties in fabricating electronic and optoelectronic devices, biosensors, and high surface area electrodes in electrochemistry [20-26].

Fiber composites can be produced by interfacial polymerization and electro spinning [26-29]. Template synthesis has also been adopted to prepare one-dimensional materials, using different templates such as nano-channel glasses and polymeric membranes, and anodized aluminum substrates [30]. However, their synthesis usually consists of a complicated process. As an alternative, a conformal replication of the morphologies of natural fibrous materials has been used in this study, which offers a low-cost, simple, and environmentally safe method for the formation of sophisticated nanostructures [31-33]. There are reports that described the use of natural templates to grow nanostructures of ceramics and ceramic-based composites [34-36]. Cellulose is the most abundant natural polymer, and in the form of cotton consists of fibers of a few micrometer diameters, with a surface area of about $1 \text{ m}^2/\text{g}$. It is low cost and economically favored for practical applications [37,38].

In this work, a facile approach to the deposition of $ZrTiO_4$ nanoparticles onto cellulose fibers is originally considered. Self-standing nanostructured $ZrTiO_4$ was fabricated by the

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heat removal of the cellulose template, followed by sintering. The morphology of the fibers consists of chains of $ZrTiO_4$ connected to each other, which makes $ZrTiO_4$ hybrid, and could be practical to increase surface area and adsorption compared to $ZrTiO_4$ powders when used as a photocatalytic surface. During this investigation, cellulose fibers were used as templates to make porous fibers of $ZrTiO_4$. The photocatalytic behavior of $ZrTiO_4$ fibers was studied and compared to $ZrTiO_4$ powders by analyzing the photodegradation of methylene blue under exposure to UV A and UV C. Methylene blue (MB) is a heterocyclic aromatic dye which is one of the most prominent dyes used as a probe molecule to investigate the heterogeneous photocatalytic behavior [38-40].

2. Materials and Method

18.2 mmol of $ZrCl_4$ (Alfa Aesar, 99.5%) was added to 400 ml deionized water and stirred for 30 min. 18.2 mmol of $TiCl_4$ (Alfa Aesar, 99.99%) was then added to the solution dropwise while stirring. 1 g of natural cellulose fibers was put in the prepared solution having a pH value of 1. The pH value of the solution was increased by adding NaOH (2M) dropwise while stirring to reach pH = 4 at room temperature. The fibers were then removed from the solution and were rinsed with deionized water to remove remaining species. The obtained fibers were dried at room temperature and were calcined in air at 600 °C for 1 h, which removes the cellulose template and produces the final $ZrTiO_4$ fibers. Fig. 1 shows a schematic of the synthesis method, where particles have a negative charge and absorb to the cellulose having a positive charge. Some $ZrTiO_4$ powders were produced by the same sol-gel and calcination procedures for microstructural characterization.

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A transmission electron microscope (TEM, JEOL JEM-2100) operating at an acceleration voltage of 200 kV was used to evaluate the powder particle size and morphology. To do so, a small amount of the powder was dispersed in ethanol, ultrasonicated for 15 min, and then dropped on a carbon grid. The X-ray diffraction (XRD) pattern of the calcined powders was recorded by a Bruker. AXS Inco. diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The surface morphology of the ZrTiO₄ fibers was investigated using a scanning electron microscope (SEM, Hitachi S-4800). Also, the specific surface area of the fibers and powders was measured by the Brunauer–Emmett–Teller (BET) analysis from the N₂ isotherms collected with a Belsorp mini II BEL system on the degassed samples.

To measure the photocatalytic efficiency, methylene blue degradation tests under ultraviolet (UV) light were performed. To do so, 1 mg of the photocatalyst powder was dispersed in 10 ml MB solution of 5 μM concentration. The suspension was placed in a dark chamber under stirring for 1 h for the adsorption of dye molecules on the powders, and then irradiated using a UV lamp (4 W, UVA, UVC low pressure Hg lamp). The decrease of the MB absorption peak upon irradiation time was measured using a UV-Vis spectrophotometer, NanoDrop 2000, Thermo Science. The same procedure was also run for the ZrTiO₄ fibers.

3. Results and discussion

Fig. 2a presents the TEM micrograph of the powder calcined at 600 °C. As can be seen, the powder particles have an average size of 50 nm with a relatively wide size range of 20 nm to 100 nm. Furthermore, the crystallinity of this powder led to Debye-Scherrer diffraction spots in the selected area diffraction (SAD) pattern, as represented in the insert of Fig. 2a.

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The XRD pattern of the xerogel (before calcination) and the powder calcined at 600 °C is indicated in Fig. 2b. The broad halo pattern of the xerogel suggests a typical amorphous structure. Nonetheless, the presence of ZrTiO₄ reflections for the calcined powder is indicative of the occurrence of structural ordering and crystallization, as confirmed in the TEM studies (Fig. 2a). The XRD reflections were also confirmed by the ICSD reference code of 00-034-0415 for zirconium titanate with the orthorhombic α -PbO₂ type structure. The direct crystallization of ZrTiO₄, rather than TiO₂ and ZrO₂, at the low temperature is due to the high level of homogeneity of the xerogel [41].

Fig. 3a depicts the SEM micrograph of the coated cellulose fibers (before calcination), showing a uniform deposition of nanoparticles on the surface. It was found that the uniformity of the coatings depends on growth conditions, especially pH. Note that the conditions detailed in the experimental section are optimized ones for achieving a uniform coating. Also, the thickness of the ZrTiO₄ film can be controlled by changing the deposition time. After calcination, the organic parts are removed and pure ZrTiO₄ fibers remain. So, a relatively thick wall of ZrTiO₄ is required to prevent the collapse of the hollow structure due to shrinkage of the tube during calcination. As shown in Fig. 3b, a sound ZrTiO₄ fiber was prepared by the template, sol-gel, and calcination procedures used. The appearance of particles on the fiber surface after calcination is due to particle coarsening, as reported already [41-43]. Indeed, as a result of sintering, the nanoparticles grow and start appearing on the surface due to a mass transfer caused by transformation from a glass state to a crystalline one. In other words, initially a strained continuous layer is formed on the fiber and then the strain is released by the formation of three-dimensional islands on that layer (Stranski-Krastanov growth model) [42-43].

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The BET surface area of the ZrTiO₄ powders was measured to be 29.71 m²/g with a total pore volume of 0.0084 cm³/g, while that of the ZrTiO₄ fibers was 72.43 m²/g with a total pore volume of 0.257 cm³/g. Such a result indicates that the surface area of the ZrTiO₄ fibers increases about 2.5 times in the hybrid structure. Both the ZrTiO₄ powder and fibers have solid mesoporous structures, but the total pore volume of the ZrTiO₄ fibers was almost 30 times greater than that of the ZrTiO₄ powders, which yields into a material with a higher porosity level. It is anticipated that the higher surface area and higher porosity level of the ZrTiO₄ fibers make them more active than the ZrTiO₄ powders.

The photocatalytic activity of the ZrTiO₄ fibers was studied by the degradation of the MB dye as a model pollutant. Fig. 4a presents the results of MB removal using the ZrTiO₄ fibers and powders. Prior to UV irradiation, the samples were placed in dark for 60 minutes to evaluate the MB adsorption power of the ZrTiO₄ fibers and powders. As shown in Fig. 4a, about 7 % MB was adsorbed on the ZrTiO₄ powders, while this amount is up to 30 % on the ZrTiO₄ fibers under the dark condition. This shows that the ZrTiO₄ fibers improve the adsorption of the MB molecules. As shown above, the surface area of the ZrTiO₄ fibers is higher than that of the pure ZrTiO₄ powders, which facilitates the additional adsorption of dye molecules. Since absorptivity increased about 23 % for the ZrTiO₄ fibers, one can conclude that the fibers provide more adsorption sites compared to the ZrTiO₄ powders. Also, Fig. 4b shows the photocatalytic degradation of MB under UVA illumination for the ZrTiO₄ fibers and powders. The effect of initial dark adsorption has been eliminated. It can be observed that the photocatalytic decomposition of MB over the ZrTiO₄ fibers is more than that of the powders.

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Fig. 4c indicates the results of photodegradation of MB by the ZrTiO₄ powders and fibers under UVA irradiation. As can be seen, the ZrTiO₄ fibers are able to remove almost 95% MB after 130 minute, while the ZrTiO₄ powders remove 35% MB after the same duration. The MB concentration does not change after 80 minutes of UVA irradiation for the ZrTiO₄ powders, which might be related to the powders covered by MB molecules and the low energy of UVA to irritate. To investigate the effect of UVC irradiation on MB decomposition, the same test was run with UVC lamp. For the fiber sample, about 95% MB is decomposed after 50 minutes of irradiation of UVC, while this duration is 280 minutes for the ZrTiO₄ powders. It is noticeable that the UVC irradiation is powerful enough to active the photocatalytic effect of the ZrTiO₄ powders in comparison to the UVA irradiation.

In summary, the higher rate of the photocatalytic removal of MB by the ZrTiO₄ fibers as compared to the powders can be explained by the adsorption of intermediates on the large surface area. The decomposition rate considerably decreased in the case of the powder sample, due to the screening effect of the powders being denser than the fibers.

4. Conclusions

In this work, a ZrTiO₄ fiber was synthesized by a low cost, environmentally friendly method of sol-gel and by using cellulose fibers as the template. By removing the template during heat treatment, ZrTiO₄ particles were sintered to each other and made a hybrid structure with a high surface area of 72.43 m²/g. Such a hybrid structure showed an enhancement in the surface adsorbent and photocatalytic effect in comparison to the ZrTiO₄ powders. The increase in the photodegradation rate for the ZrTiO₄ fiber was attributed to its

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higher surface area which resulted in introducing more photocatalytic active sites to dye molecules.

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<https://doi.org/10.1016/j.jallcom.2013.03.142>

Figures

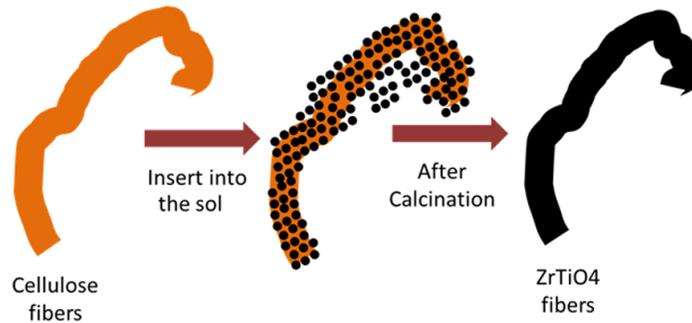


Fig. 1. Schematic illustration of the synthesis method of the fibers.

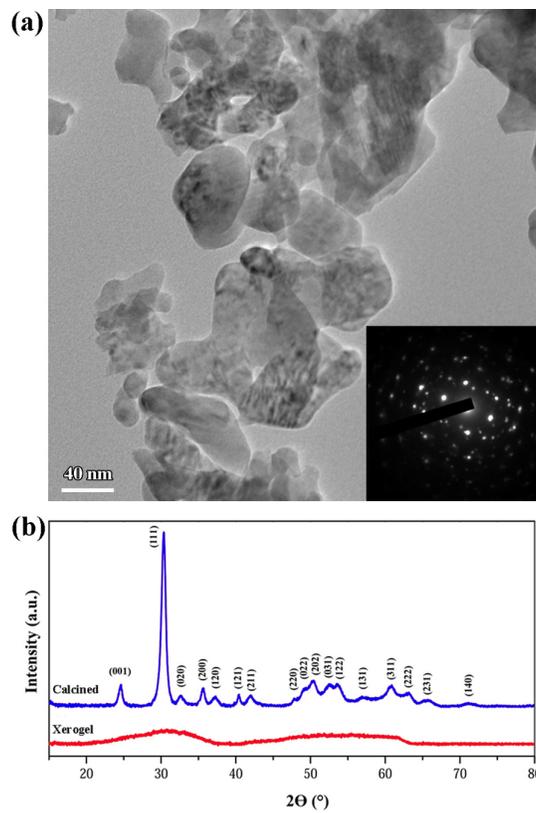


Fig. 2. (a) TEM micrograph and SAD pattern of the powder calcined at 600 °C and (b) XRD pattern of the xerogel and the powder calcined at 600 °C.

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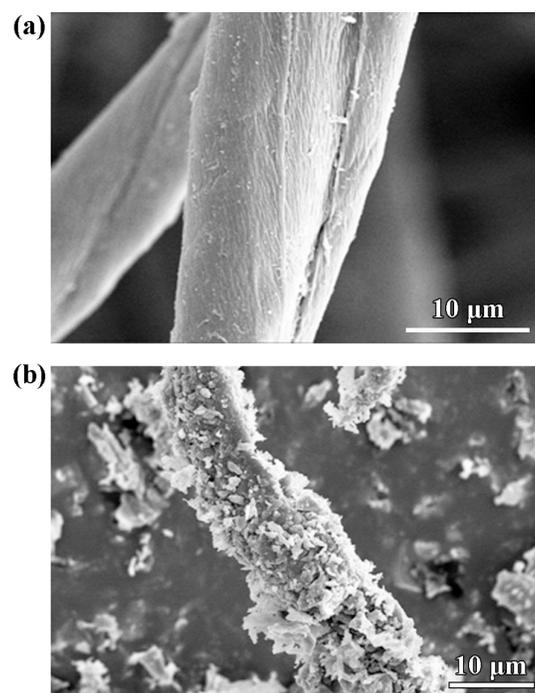


Fig. 3. SEM micrograph of the fiber (a) before calcination and (b) after calcination.

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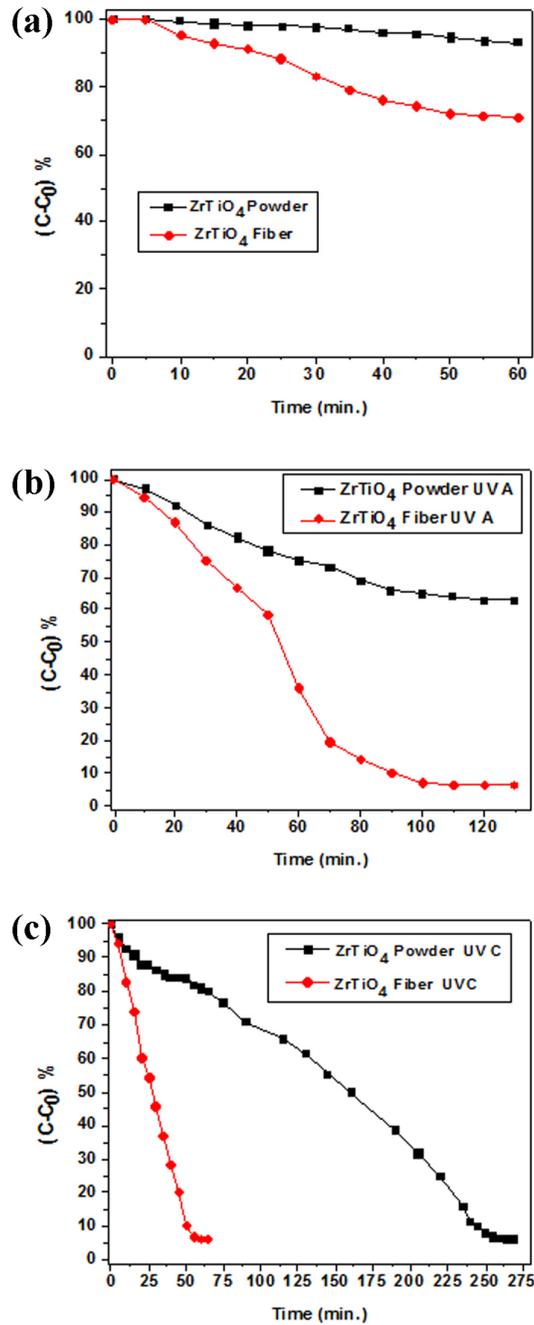


Fig. 4. (a) Adsorption graph in the dark condition, (b) photodegradation graph in the UVA condition, and (c) photodegradation graph in the UVC condition.