

Nanocrystalline Ytria-Stabilized Zirconia Fibers from Plant Fibers and their Polymer Composites

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Nanocrystalline zirconia–8-mol% yttria (yttria-stabilized zirconia (YSZ): ZrO₂–8-mol% Y₂O₃) fibers have been prepared from aqueous poly vinyl alcohol (PVA)–zirconium oxy nitrate solution and jute (plant fiber). Soluble Zr and Y ions in PVA solution formed a uniform coating on the surface of jute once it dried completely. Slow hydrolysis of zirconium ion with ammonium hydroxide deposited zirconium hydroxide on the jute surface. Decomposition of the dried zirconium hydroxide-coated jute at high temperature (1200°C/2 h) resulted in the formation of single-phase, nanocrystalline cubic-YSZ with the corresponding average X-ray crystallite size 30–35 nm. Heat-treated fibers have been characterized by X-ray diffraction and scanning electron microscopy. We also prepared polymer composites by incorporating chopped, ground YSZ fibers into epoxy matrix and investigated polymer/fiber interface by transmission electron microscopy analysis.

I. Introduction

RECENTLY, significant progress has been achieved in the development of nanocrystalline zirconia to meet the growing demand for high-performance engineering materials.^{1–4} Zirconia exists in three polymorphs⁵; these are monoclinic (*m*) tetragonal (*t*), and cubic (*c*). Among them tetragonal and cubic phases are metastable forms but monoclinic is the stable form at room temperature. Various dopants such as calcium oxide,⁶ silica,⁷ cerium oxide,⁸ yttrium oxide,^{9,10} chromium oxide,¹¹ niobium oxide,¹² tantalum oxide,¹³ tin oxide,¹⁴ etc., have been used to stabilize metastable zirconia phases. Addition of Y₂O₃ (yttria-stabilized zirconia (YSZ)) results in the stabilization of the cubic fluorite structure of ZrO₂. The high oxygen conductivity (0.1 (Ω·cm)⁻¹) of YSZ (ZrO₂:Y₂O₃) at high temperatures (1000°C) has made this material one of the most extensively studied fast anionic conductors for its applications in solid oxide fuel cells (SOFCs) and oxygen sensing devices. Yttrium (Y³⁺) cations replace some of the Zr⁴⁺ ions that create oxygen vacancies responsible for the ionic conduction. As far as the synthesis of ceramics is concerned, there is an ever-growing need to develop simple synthetic procedure from easily available raw materials. Consequently, researchers in the field of material processing have been looking at biological systems for inspiration. The above factors, combined with academic curiosity, have led to the development of bio-mimicking approaches for the growth of advanced materials.

In this work, the authors report a novel chemical route for the preparation of fiber like YSZ using aqueous PVA (10 wt%), zirconium nitrate, yttrium nitrate, and jute (plant fiber).

The process involves *in-situ* precipitation of yttrium–zirconium hydroxides into the porous fibrous structure of jute. Heat treatment of the plant fibrous mass in furnace air environment results in YSZ fibers. YSZ chopped and ground fibers were also mixed with epoxy matrix to fabricate polymer composites and investigated through transmission electron microscopy (TEM) studies. Polymer composites are key to the development of low cost, high-performance materials for applications ranging from automotive to food packaging to tissue engineering. A major challenge for further development of polymer composites is the lack of even simple structure–property models. The present objective is to develop YSZ–epoxy composites, which can further be extended to fabricate proton exchange membrane (PEM) fuel cells where YSZ will be dispersed in the Nafion resin.^{15,16}

Jute is a plant fiber obtained from the bark of the plants. Traditionally, jute is used as an industrial raw material for making packaging materials. In this process, we have used jute as a network for growing YSZ fibers. As far as we know, this is the first time any plant fiber (jute) has been used to fabricate ceramic fibers.

II. Experimental Procedure

All the chemical reagents used in these experiments were analytical grade. The raw materials that were used for the preparation of YSZ (ZrO₂: 8 mol% Y₂O₃) were zirconium oxychloride (Aldrich Chemicals, Milwaukee, WI), yttrium oxide, poly vinyl alcohol (PVA), jute, nitric acid, and ammonium hydroxide.

Zirconium oxychloride (Aldrich Chemicals) was dissolved in a minimum quantity of distilled water. Zirconium hydroxide (or hydrated zirconium oxide) was precipitated from zirconium oxychloride solution by the addition of ammonium hydroxide. The precipitate was filtered and washed several times. Zirconium hydroxide was then dissolved in nitric acid solution. Similarly, yttrium (99.9% Aldrich Chemicals) oxide was dissolved in nitric acid to form yttrium nitrate solution. Appropriate amounts of yttrium nitrate and zirconium nitrate were mixed with each other to produce precursor solution. About 1–10-cm well-separated jute fiber was then soaked into the precursor solution with 10% PVA solution for 24 h. After 1 day, the soaked fibers were dried for 12–24 h to remove excess PVA and metal nitrate solution. The dried fibers containing metal nitrate and PVA were again soaked for 24 h into ammonium hydroxide solution. In the presence of ammonium hydroxide, metal nitrates were hydrolyzed to yttrium–zirconium hydroxide, which was deposited slowly on jute fiber. Heat treatment of the dried yttrium–zirconium hydroxide containing jute fibers at 1200°C for 2 h in a muffle furnace resulted in the YSZ fibers. Figure 1 shows scanning electron micrograph (SEM) photographs of the as-formed mass of YSZ fibers. Fiber mass was chopped and ground to powder, which was used for X-ray diffraction studies. X-ray diffraction studies of fibers were performed using fully automated system (Philips, Eindhoven, the Netherlands). A setting of 40 kV and 30 mA was applied to the CuK α target, with a step size of 0.02° (2 θ) and a count time of 0.5 s per step.

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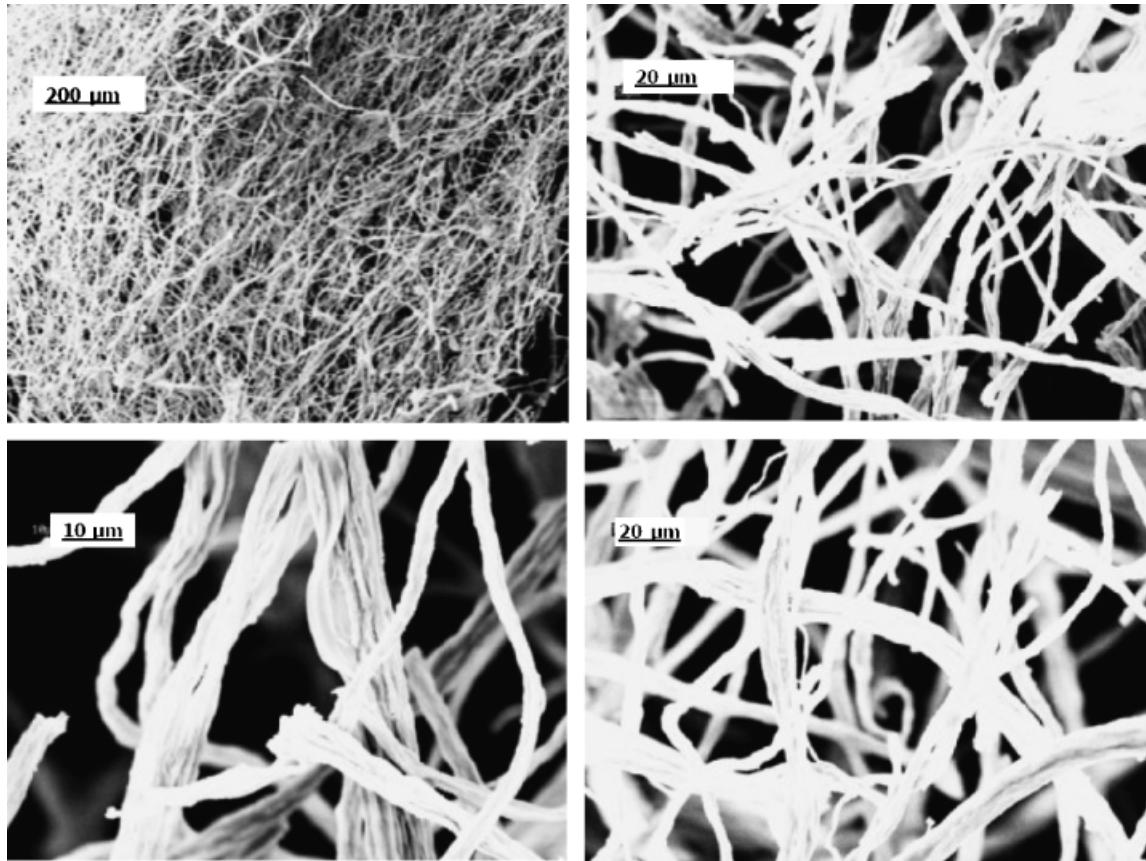


Fig. 1. Scanning electron micrograph of yttria stabilized zirconia (YSZ) fibers (close up and wider view).

Suspensions of the YSZ fibers in an epoxy resin were formulated by mixing appropriate amounts of YSZ fibers, bisphenol-epoxy resin (EPON[®] 828, $M_n \sim 377$), dicyan diamide, and 2-methylimidazole in *N*-methyl pyrrolidone (NMP). The mixtures were ultrasonicated for 25 min to yield homogeneous suspensions. The suspensions were slowly evaporated for 12–24 h. Partially evaporated mixtures were speed mixed at 3000 rpm for 3 min and were poured in teflon molds and the residual solvent was evaporated in a vacuum oven at a temperature of 75°C for 72 h to ensure complete drying. The dried composites were cured under vacuum at a temperature of 175°C typically for 15 h.

III. Results and Discussion

Figure 1 shows the SEM microstructures of YSZ fibers heat-treated at 1200°C for 2 h. Fiber samples were strong, stiff, and handleable, which are 1–10-cm long and 5-μm wide. SEM shows some fiber agglomeration. Proper jute fiber processing before soaking into the precursor solution possibly reduces fiber agglomeration.

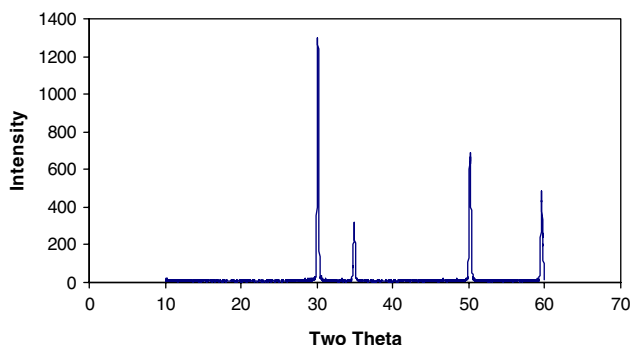


Fig. 2. X-ray diffraction pattern of the precursor powder heat-treated at 1200°C/2 h using CuK α .

Heat treatment of the fibrous mass at 1200°C for 2 h resulted in the formation of single-phase YSZ ($ZrO_2:Y_2O_3$) as determined by X-ray diffraction (XRD). However, the XRD lines of these powders were broad indicating fine crystals. The size of the

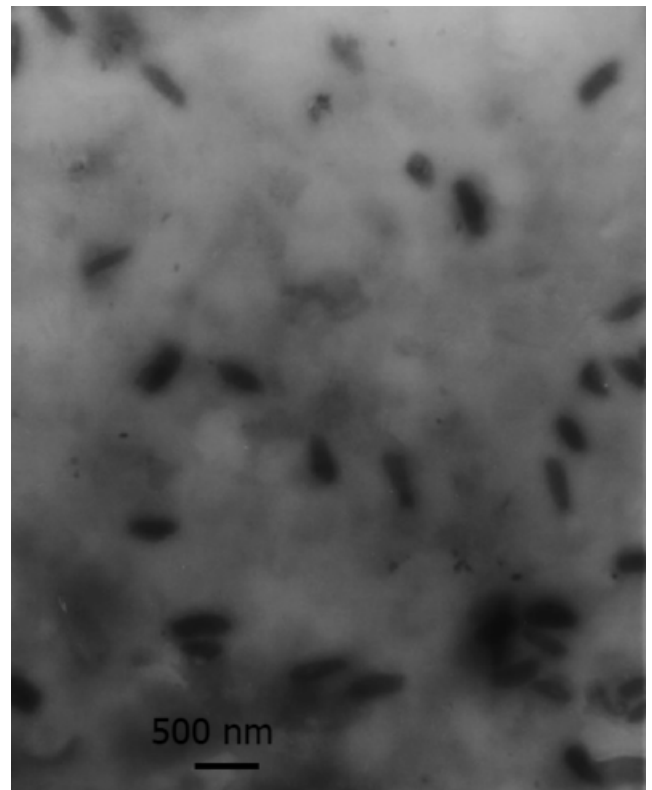


Fig. 3. Bright field electron micrograph of yttria-stabilized zirconia (YSZ)-epoxy composites.

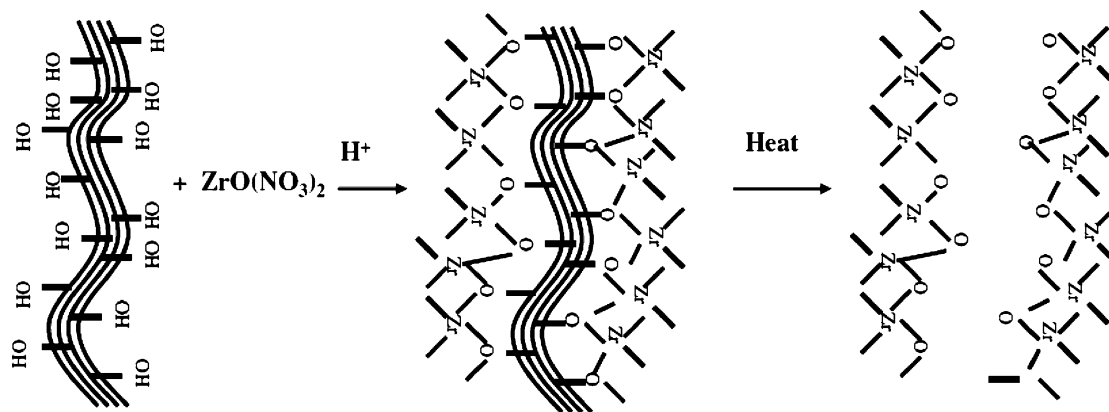


Fig. 4. Tentative mechanism.

crystals was determined from X-ray line broadening studies. Using Scherrer's formula and with $\lambda = 1.54 \text{ \AA}$, the crystallite size, t is estimated to be around 30–35 nm. Figure 2 shows a room temperature XRD plot of the heat-treated YSZ fibers.

The finer details of the fibers and their morphology into polymer matrix were investigated using a Philips TEM. The bright field electron micrograph of YSZ–epoxy composites is shown in Fig. 3. It consists of small submicrometer fibers about 300–500-nm long and around 100-nm wide uniformly distributed throughout the epoxy matrix.

Jute swells until the cell wall is saturated with water. Jute cell wall polymers contain hydroxyl and other oxygen-containing groups that attract water through hydrogen bonding.¹⁷ In our case, we have used aqueous metal nitrate, PVA solution that can easily interact with the jute cell wall either by hydrogen bonding (water and PVA) or by complex formation (zirconium, yttrium ion). Treatment of ammonia slowly hydrolyzes Y and Zr ions and precipitates yttrium zirconium hydroxide on the jute cells. PVA not only reduces hydrolysis process but also acts as a binder to stick zirconium hydroxide within the cell region. Heat treatment of jute grows nanocrystalline YSZ from individual cells and maintains the fiber's structure. Figure 4 shows a tentative mechanism for fiber formation.

IV. Conclusion

In conclusion, YSZ fibers have been prepared from the thermal decomposition of the dried PVA–metal hydroxide-coated jute mass. In this paper, we introduced plant fibers to produce ceramic fibers for the first time. This kind of YSZ fiber is expected to play a key role in the future development of low cost, high-performance electrolyte membranes for SOFCs.^{18,19} The current work also demonstrates the dispersion of YSZ fibers into epoxy matrix. TEM analysis of the composite shows uniform YSZ fiber dispersion into polymer matrix. The synthetic strategy presented here may be extended to other metal oxide systems of Ti, Nb, V, Si, Mn, W, Mo, etc.

References

¹M. Z.-C. Hu, R. D. Hunt, E. A. Payzant, and C. R. Hubbard, "Nanocrystallization and Phase Transformation in Monodispersed Ultrafine Zirconia Particles from Various Homogeneous Precipitation Methods," *J. Am. Ceram. Soc.*, **82** [9] 2313–20 (1999).

²B. Xia, L. Duan, and Y. Xie, "ZrO₂ Nanopowders Prepared by Low-Temperature Vapor-Phase Hydrolysis," *J. Am. Ceram. Soc.*, **83** [5] 1077–80 (2000).

³A. Benedetti, G. Fagherazzi, and P. Francesco, "Preparation and Structural Characterization of Ultrafine Zirconia Powders," *J. Am. Ceram. Soc.*, **72** [3] 467–9 (1989).

⁴J. C. Ray, R. K. Pati, and P. Pramanik, "Chemical Synthesis of Nanocrystalline Zirconia by a Novel Polymer Matrix-Based Precursor Solution Method Using Triethanolamine," *Mater. Lett.*, **48** [2] 74–80 (2001).

⁵R. C. Garvie, R. H. Hannink, and R. T. Pascoe, "Ceramic Steel?," *Nature*, **258**, 703–4 (1975).

⁶S. K. Saha and P. Pramanik, "Innovative Chemical Method for Preparation Of Calcia Stabilized Zirconia Powders," *Br. Ceram. Trans.*, **94** [3] 123–7 (1995).

⁷F. del Monte, W. Larsen, and J. D. Mackenzie, "Stabilization of Tetragonal ZrO₂ in ZrO₂-SiO₂ Binary Oxides," *J. Am. Ceram. Soc.*, **83** [3] 628–34 (2000).

⁸J. D. Lin and J. G. Duh, "Crystallite Size and Microstrain of Thermally Aged Low-Ceria- and Low-Yttria-Doped Zirconia," *J. Am. Ceram. Soc.*, **81** [4] 853–60 (1998).

⁹Y.-H. Lee, C.-W. Kuo, and I.-M. Hung, "The Thermal Behavior of 8 mol% Yttria-Stabilized Zirconia Nanocrystallites Prepared by a Sol-Gel Process," *J. Non-Cryst. Solids*, **351** [49–51] 3709–15 (2005).

¹⁰J. C. Ray, R. K. Pati, and P. Pramanik, "Chemical Synthesis and Structural Characterization of Nanocrystalline Powders of Pure Zirconia and Yttria Stabilized Zirconia (YSZ)," *J. Eur. Ceram. Soc.*, **20** [9] 1289–95 (2000).

¹¹J. C. Ray, C. R. Saha, and P. Pramanik, "Stabilized Nanoparticles of Metastable ZrO₂ with Cr³⁺/Cr⁴⁺ Cations: Preparation from a Polymer Precursor and the Study of the Thermal and Structural Properties," *J. Eur. Ceram. Soc.*, **22** [6] 851–62 (2002).

¹²J. C. Ray, A. B. Panda, C. R. Saha, and P. Pramanik, "Synthesis of Niobium(V)-Stabilized Tetragonal Zirconia Nanocrystalline Powders," *J. Am. Ceram. Soc.*, **86** [3] 514–6 (2003).

¹³J. C. Ray, A. B. Panda, and P. Pramanik, "Chemical Synthesis of Nanocrystals of Tantalum Ion-Doped Tetragonal Zirconia," *Mater. Lett.*, **53** [3] 145–50 (2002).

¹⁴J. C. Ray, C. R. Saha, and P. Pramanik, "Chemical Synthesis of Nanocrystalline Tin-Doped Cubic ZrO₂ Powders," *Mater. Lett.*, **57** [13–14] 2140–4 (2003).

¹⁵M. Watanabe, H. Uchida, and M. Emori, "Analyses of Self-Humidification and Suppression of Gas Crossover in Pt-Dispersed Polymer Electrolyte Membranes for Fuel Cells," *J. Electrochem. Soc.*, **145** [4] 1137–41 (1998).

¹⁶M. Watanabe, H. Uchida, Y. Seki, and M. Emori, "Self-Humidifying Polymer Electrolyte Membranes for Fuel Cells," *J. Electrochem. Soc.*, **143** [12] 3847–52 (1996).

¹⁷S. Das, A. K. Saha, P. K. Choudhory, R. K. Basak, B. C. Mitra, T. Todd, S. Lang, and R. M. Rowell, "Effect of Steam Pretreatment of Jute Fiber on Dimensional Stability of Jute Composite," *J. Appl. Pol. Sci.*, **76**, 1652–61 (2000).

¹⁸T. Okubo, T. Takahashi, B. N. Nair, M. Sadakata, and H. Nagamoto, "Formation Mechanism of Crack-Free Porous YSZ Membrane," *J. Membr. Sci.*, **125** [2] 311–7 (1997).

¹⁹X. Xin, Z. Lü, Q. Zhu, X. Huang, and W. Su, "Fabrication of Dense YSZ Electrolyte Membranes by a Modified Dry-Pressing Using Nanocrystalline Powders," *J. Mater. Chem.*, **17** [16] 1627–30 (2007). □