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Synthesizing and Characterization of Monoclinic and Tetragonal Phases of Zirconium Oxide (Zro_2) Nanofibers with the Aid of Electrospinning Technique

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Abstract: Zirconium oxide has found extensive applications in various industries because of its excellent properties such as high strength; high-temperature resistance; extraordinary wearing resistance; ionic conductivity; and corrosion resistance. Also, some Properties like high melting point, high mechanical and thermal strength, high dielectric constant and low conductivity have introduced this material as a prominent candidate for engineering applications. In this study, zirconium oxide (ZrO_2) Nano fibers was synthesized by calcination of propoxide zirconium oxide/polyvinyl alcohol using sol-gel and electrospinning methods. The morphology of the Nano fibers was verified by scanning electron microscopy (SEM) and its crystalline phase was investigated by x-ray diffraction and energy-dispersive x-ray spectroscopy (EDS). The mean diameter of the Nano fibers varied in the range of 70-200 nm. XRD patterns also indicated the presence of monoclinic and tetragonal phases in the Nano fibers calcined at 700 ℃. Results also revealed that this new precursor can be used in the electrospinning technique to obtain ZrO_2 Nano fibers with relatively high purity.

Keywords: Zirconium Oxide Nano Fiber, Electrospinning, Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Energy-Dispersive X-Ray Spectroscopy (EDS)

1. INTRODUCTION

Nano fibers are nanostructures with a nonmetric diameter, which have received much attention due to their unique properties in comparison with microfibers such

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as high volume to mass ratio and high specific surface area [1]. Among ceramic Nano fibers, zirconium oxide (ZrO_2) Nano fibers are widely used in different industries due to high mechanical strength, resistance at high temperatures, exceptional abrasion strength, ionic conductivity and high corrosion resistance [1,2]. Properties such as high melting point, high mechanical and thermal strength, high dielectric constant and low electrical conductivity have made this compound a suitable candidate for engineering applications [3]. Mechanical properties of composites [4] and performance of solid oxide fuels [5] are improved in the presence of ZrO_2 Nano fibers.

Zirconium oxide is found in tree crystal structures; cubic, tetragonal and monoclinic. Monoclinic, tetragonal and cubic phases are respectively observed at 25-1150 C, 1150-2370 C and above 2370 C [3,6]. Various methods, including hydrothermal methods [7, 8], sol-gel [9,10], chemical vapor deposition [11], chemical decomposition [12] and electrospinning [6, 13-15], spray pyrolysis [16] and precipitation [17] have been used for the synthesis of ZrO_2 nanostructures.

Electrospinning is an effective method which widely used for fabrication of Nano fibers. The method has the benefits of simplicity and cost-effectiveness [13].

Various precursors such as zirconium propoxide/polyvinyl acetate [18], zirconium N-propoxide/PVP [8], zirconium acetate/PVA [19] and zirconium acetyl acetone/PVP [13] have been used for the synthesis of ZrO_2 Nano fibers.

In this research, zirconium oxide Nano fibers were synthesized by electrospinning of zirconium propoxide/PVA followed by calcination at 700 C.

2. MATERIALS

Zirconium propoxide (P. No. 333972, Sigma-Aldrich), ethanol 99.9% (Ca. No. 100983), Nitric acid (P. No. 1004560510, Merck), hydrochloric acid (P. No. 1003170510, Merck) and polyvinyl alcohol (Ca. No. 814894, Merck) were used for the synthesis of ZrO_2 Nano fibers.

3. Preparation of zirconium oxide nanofibers

Typically, 3.6 cc zirconium propoxide was dissolved in 12.6 cc pure ethanol, 54 µL nitric acid and 88 µL hydrochloric acid were added and then stirred for 6h at ambient temperature. Then, a solution of 10 wt. % PVA in water/ethanol (1:1 Vol/) was prepared. To prepare a homogenous PVA solution, it was stirred 4h at 70 C.

In order to prepare the electrospinning solution, zirconium propoxide gel and PVA solution were mixed with aspect ratio of 1:2 and stirred for 10h at ambient

temperature. The solution was then used for electrospinning. The positive terminal of a high-voltage power supply was connected to the needle and the negative terminal to the collector. The distance between electrospinning needle and collector set 16 cm and then electrospinning of the solution was accomplished under 20 KV. After that the obtained fiber calcined at 700 C for 4^{hs}.

4. Characterization of nanofibers

Scanning electron microscope (SEM) images and EDX of samples were taken by TESCAN-Vega 3 SEM. X-ray diffraction (XRD) pattern of samples were taken by an X-ray device (Bruker - D8-Advance), in the range of 20-80°.

5. XRD pattern of nanofibers

Crystalline phases of the synthesized Nano fibers were evaluated by X-ray diffraction (XRD). Figure 1 shows the XRD pattern of Nano fibers after calcination. According to the XRD pattern, crystalline Nano fibers are obtained after calcination at 700℃. In fact, the peaks indicate crystalline phases of the synthesized Nano fibers. The most important peaks appeared at $2\theta = 28.08^{\circ}$, 31.41°, 34.23° and 50.08° are assigned to the monoclinic phase of ZrO_2 which respectively belong to (111), ($\bar{1}11$), (020) and (220) planes. The peak at 50.066° is related to the (200) plane of tetragonal phase of ZrO_2. The XRD peaks of monoclinic and tetragonal phases of ZrO_2 are respectively consistent with ICDD File No. 37-1484 and ICDD File No. 42-1164 in ICDD database and also data in X'Pert. Ghelich et al. [20] calcined Nano fibers at 650 ℃ and found only tetragonal phases at this temperature. In contrast, a combination of monoclinic and tetragonal phases was observed in the XRD pattern of Nano fibers synthesized at 850 ℃. Rodaev et al. [13] reported similar results at calcination temperatures of 500 and 800℃. According to their results, only monoclinic phase was observed at 1300℃ with characteristic peaks at 28.2° and 31.5°. The angles related to the monoclinic phase of Nano ZrO_2 were reported by Mangla et al. [3].

According to Keiteb et al. [12], both monoclinic and tetragonal phases were formed in the nanostructure by calcination of nanoparticles at 700-900℃.

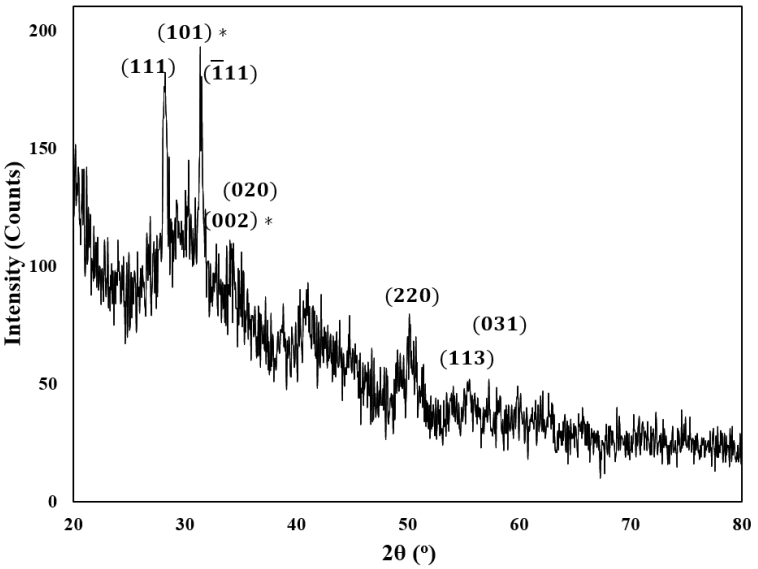

Fig. 1: XRD pattern of the synthesized nanofibers after calcination at 700℃. Stared indexes belong to a tetragonal phase of ZrO_2.

The crystallite sizes of the synthesized Nano fibers can be calculated by the Debye-Scherrer equation (Eq. 1) With the help of XRD data.

$$D = 0 \cdot 9\lambda/\beta Cos\square \quad (1)$$

Where D represents mean diameter crystallite sizes of fabricated nanofibers (nm), λ X-ray wavelength in nm, β full width of half-maximum intensity (FWHM) in terms of radians and θ is diffraction angle [21].

The results obtained from the Debye-Scherrer equation showed that crystalline sizes of the synthesized nanofibers have a mean diameter of about 27.5 nm.

6. Morphology of nanofibers

The morphology of Nano fibers was studied by scanning electron microscope (SEM). Figure 2 shows the SEM images of Nano fibers before and after calcination. As seen in Fig.2a, ZrO_2/PVA Nano fibers have been formed with an approximate diameter of 400-500 nm. After calcination of Nano fibers at 700 ˚C and removal of PVA molecules, Nano fibers with a diameter of 70 to 200 nm were obtained (Fig.2b). This diameter reduction is due to the removal of PVA used in preparation of the initial solution.

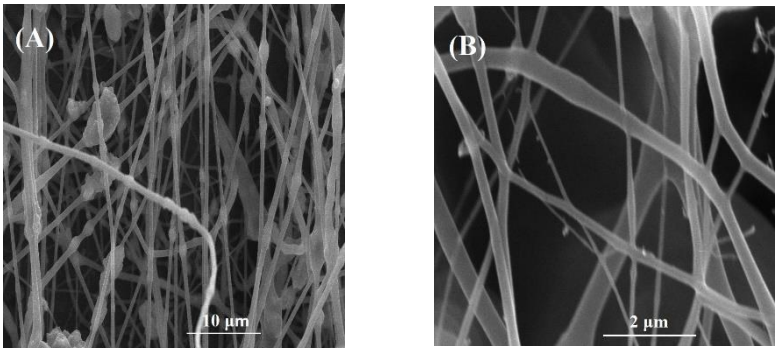

Fig. 2: SEM micrographs of (a) ZrO_2/PVA composite and (b) ZrO_2 nanofibers after calcination at 700℃

7. Energy-dispersive X-ray spectroscopy (EDS) of nanofibers

Figure 3 shows the EDS spectrum of the synthesized Nano fibers. The energy of each peak in this diagram is assigned to a specific atom. Sharper peaks indicate the higher concentration of elements. As shown in Fig. 3, zirconium and oxygen with a weight percentage of 63.75% and 35.98% are main elements and little amount of chlorine is also found due to the presence of chlorine in the precursor which remains in the nanofibers after calcination at 700℃. These results are in good agreement with those reported in the literature. Keiteb et al. analyzed Nano ZrO_2 calcined at 600℃ by EDS and found a weight percentage of 69 wt.% and 26 wt.% respectively for zirconium and oxygen. Zirconium showed maximum peaks at 0.27, 1.85 and 2.17 kV and oxygen at 0.5 kV. The Nano fibers synthesized in this study contained less than 5 wt.% carbon due to incomplete decomposition of PVP at 600℃ [12].

Ghelich et al. reported similar EDS results. According to their results, ZrO_2 Nano fibers calcined at 850℃ contained 75.22 wt.% Zirconium and 24.78 wt. % oxygen [20].

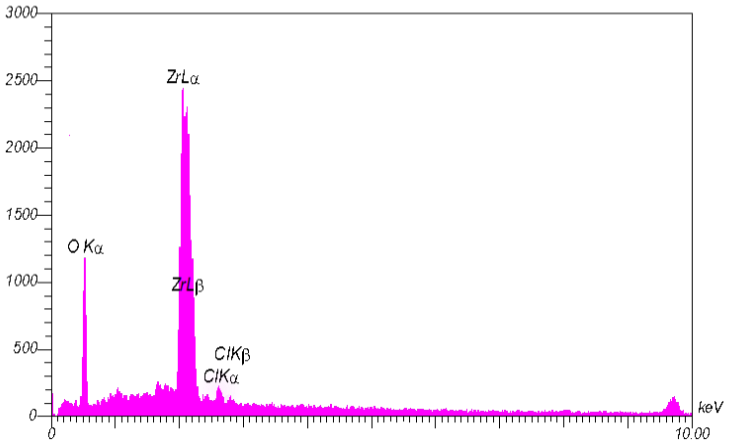

Fig 3: EDS pattern of ZrO_2 nanofibers calcined at 700℃

8. CONCLUSION

Zirconium oxide Nano fibers with a diameter of 70 to 200 nm were synthesized by electrospinning of a zirconium propoxide/polyvinyl alcohol precursor. The morphology of the synthesized Nano fiber was confirmed by scanning electron microscopy. The presence of monoclinic and tetragonal phases in the Nano fiber calcined at 700℃ was confirmed by X-ray diffraction pattern. The synthesis of highly pure ZrO_2 Nano fiber was confirmed by EDS analysis.

REFERENCES

[1] Y. Liu and C. Wang, *Advanced Nanofibrous Materials Manufacture Technology Based on Electrospinning*, Vols. CRC Press: Boca Raton, FL, USA, (2019), 370.

[2] L. Haodong, B. Jinxiao, Q. Siyu, J. Qiang and G. Wenrong, *Optical and mechanical properties of purplezirconia ceramics*, *Journal of Asian Ceramic Societies*, 7 (3), (2019), 306-311.

[3] O. Mangla and S. Roy, *Monoclinic Zirconium Oxide Nanostructures Having Tunable Band Gap Synthesized under Extremely Non-Equilibrium Plasma Conditions*, Proceedings, 3, 10, (2019), 1-7.

[4] E. Bódisa, K. Molnár, A. Mucsi, Z. Károly, J. Móczó, S. Klébert, A. M. Keszler, P. Fazekas and J. S. Szépvölgyi, *Silicon nitride-based composites reinforced with Zirconia nanofiber*, Ceram. Int., Vol. 43, (2017), 16811–16818.

[5] J. Koo, Y. Lim, Y. Kim, D. Byun, W. Lee, *Electrospun yttria-stabilized Zirconia nanofibers for low-temperature solid oxide fuel cells*, Int. J. Hydrogen Energy, Vol. 42, (2017), 15903–15907.

[6] V. V. Rodaev, S. S. Razlivalova, A. I. Tyurin, A. O. Zhigachev and Y. I. Golovin, Microstructure and Phase Composition of Yttria-Stabilized Zirconia Nanofibers Prepared by High-Temperature Calcination of Electrospun Zirconium Acetylacetonate/Yttrium Nitrate/Polyacrylonitrile Fibers, Fibers, 7 (82), (2019), 1-8.

[7] T. Xue-Yu, . M. Jie, H. Rui-Lin, S. Xiang-Zhu, G. Lin, Z. Shi-Xiang, G. Li-Tong, L. Zhang-Sheng, F. He-Liang and Z. Ya-Bo, *Template-Free Synthesis of Star-Like ZrO_2 Nanostructures and Their Application in Photocatalysis*, Advances in Materials Science and Engineering, (2018), 1-10.

[8] N. Yazdani, J. Javadpour, Y. Eftekhari and M. Hamrang, *Hydrothermal Synthesis of Cobalt- Doped Hydroxyapatite Nanoparticles: Structure, Magnetic Behavior, Bioactivity and Antibacterial Activity*, Iranian Journal of Materials Science & Engineering, 16 (1), (2019), 39-48.

[9] M. C. U. López, M. A. A. Lemus, M. C. Hidalgo, R. López González, P. Q. Owen, S. O. Ruiz, S. A. U. López and J. Acosta, *Synthesis and Characterization of ZnO-ZrO_2 Nanocomposites for Photocatalytic Degradation and Mineralization of Phenol*, Journal of Nanomaterials, (2019), 1-9.

[10] A. P. Ayanwale, A. D. Cornejo, J. C. C. González, L. F. E. Cristóbal and S. Y. R. López, *REVIEW OF THE SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ZIRCONIA MIXED METAL OXIDE*

NANOPARTICLES, International Journal of Research GRANTHAALAYAH, vol. 6, no. 8, (2018), 136-145.

[11] M. Baek, S. Park and D. Choi, *Synthesis of Zirconia (ZrO_2) nanowires via chemical vapor deposition*, Journal of Crystal Growth, vol. 459, (2017), 198-202.

[12] A. S. Keiteb, E. Saion, A. Zakaria and N. Soltani, *Structural and Optical Properties of Zirconia Nanoparticles by Thermal Treatment Synthesis*, Journal of nanomaterials, (2016), 1-6.

[13] V. V. Rodaev, S. S. Razlivalova, A. O. Zhigachev, V. M. Vasyukov and Y. I. Golovin, *Preparation of Zirconia Nanofibers by Electrospinning and Calcination with Zirconium Acetylacetonate as Precursor*, Polymers, vol. 11, (2019), 1067.

[14] Y. Zhoua, W. Songa, L. Zhanga and S. Tao, *Preparation of Hollow Magnetic Porous Zirconia Fibers as Effective Catalyst Carriers for Fenton Reaction*, Journal of Materials Chemistry A, vol. 6, (2018), 12298-12307.

[15] G. -X. Sun, L. Fu-Tian, J. Qiang and C. -A. Wang, *Electrospun Zirconia nanofibers and corresponding formation mechanism study*, Journal of Alloys and Compounds, vol. 649, (2015), 788–792.

[16] P. Murugavel, M. Kalaiselvam, A. R. Raju and C. N. R. Rao, *Sub-micrometre spherical particles of TiO_2, ZrO_2 and PZT by nebulized spray pyrolysis of metal-organic precursors*, *Journal of Materials Chemistry*, Vol. 7, No. 8, (2015), 1433–1438.

[17] S. Hassan, M. Elkady and H. Hamad, *Synthesis and Characterization of Stabilized Tetragonal Nano Zirconia by Precipitation Method*, Journal of Nano Research, Vol. 56, (2019), 142-151.

[18] S. Y. Ahmed, M. Obaid, M. M. Ibrahim, Y. Ahmed and N. A. M. Barakat, *ZrO_2 nanofibers/activated carbon composite as a novel and effective*

electrode material for the enhancement of capacitive deionization performance, RSCAdvances, vol. 7, (2017), 4616-4626.

[19] O. Saligheh, R. Khajavi, M. E. Yazdanshenas and A. Rashidi, *Production and Characterization of Zirconia (ZrO_2) Ceramic Nanofibers by Using Electrospun Poly(Vinyl Alcohol)/Zirconium Acetate Nanofibers as a Precursor*, JOURNAL OF MACROMOLECULAR SCIENCE, Vol. 55, No. 6, (2016), 605–616.

[20] R. Ghelich, R. Mehdinavaz Aghdam, F. s. Torknik and M. R. Jahannama, *Synthesis and characterization of biocompatible Zirconia nanofibers based on electrospun PVP/$Zr(OPr)_4$*, Materials Today: Proceedings 5, (2018), 5733–15738.

[21] Saeed Parhoodeh, Mohammad Kowsari, *Synthesis, characterization and study of band gap variations of vanadium doped indium oxide nanoparticles*, Physica B: Condensed Matter, 498, (2016), 27-32.