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OPTIMIZATION OF TEMPERATURE ON SYNTHESIS OF ZIRCONIA (ZrO_2) NANO PARTICLES

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Abstract —*In this attempt, Zirconia (ZrO_2) was successfully synthesized using the optimized content of Zirconium nitrate as a source material and the appropriate amount of Potassium hydroxide (KOH) as precipitation agent using co-precipitation method in the absence of surfactant in view to observe, the effect of temperature such as 600, 700, 800and 900° C on synthesis of ZrO_2nano particles. The prepared samples were examined by XRD, FTIR, SEM and Photoluminescence studies. The monoclinic structure was confirmed using XRD analysis (JCPDS card no.89-9066). The crystallite size was calculated as 20-58nm using Debye-Scherer formula. Zr-O stretching vibration and Zr-O_2-Zr asymmetric vibrations were confirmed through FT-IR analysis. The different morphology was obtained through SEM analysis. The optimized sample was analyzed through TEM analysis. The as prepared ZrO_2 could be used as filler in the lithium polymer battery electrolyte application.*

Keywords*-ZrO_2, modified co-precipitation method, monoclinic structure.*

I. INTRODUCTION

Zirconium oxide has been renowned as a high -eminence reproduction due to its thermal, chemical stability and outstanding mechanical properties such as high strength and crack robustness, high melting point, low thermal conductivity, high coefficient of thermal expansion, high resistance to rust and high fracture toughness. ZrO_2 is always a very significant ceramic material due to its extensive range of application as structural materials, solid-state electrolytes, thermal barrier coatings, electro-optical materials, gas-sensing, corrosion-resistant, automobile parts, metal components and catalysts etc., [1]. Stabilized Zirconia is used in oxygen sensors and fuel cell membranes because it had the competence to allow oxygen ions to move freely through the crystal structure at high temperature. The amorphous nature of the polymer electrolyte was enhanced when the addition of ZrO_2, owing to its high dielectric constant [2].

The nano crystalline particles revealed size-dependent properties such as optical, electronic, magnetic, mechanical properties that cannot be attained using their mass counterparts. There are three polymorphic modifications of Zirconia: monoclinic (m), tetragonal (t) and cubic (f) [3, 4]. Among the various synthesis methods of nano-sized ZrO_2 namely sol-gel [5], combustion [6], Microwave assisted [7], hydrothermal [8], co-precipitation method [9] etc., co-precipitation method has been a widely practiced for production of homogenous, high-purity and crystalline oxide powders at low cost and also the simplicity of the method allows for mass production [10]. Furthermore, the ceramic particles with preferred shape and size can be produced if solvent pH, solute concentration, reaction temperature, reaction time, seed material and the type of solvent conditions are monitored [11].

The precipitation reaction is a fundamentally double displacement response which involved the development of solid deposit called precipitation. The precipitation agent leads to the formation of Zr-O coordination number, influences the size and also stabilizes the pH of the solution. The reactants are mixed together manually and subsequent reaction rate depends to a large degree on the particle size of the reactants. The degree of homogenization can be achieved by mixing together and by the intimacy of contact between the grains, as well as by the obvious effect of temperature. The role of temperature in the formation of phase, morphology, size was examined through the various temperatures such as 600, 700,800 and 900°C named as ZP1, ZP2, ZP3 and ZP4 respectively.

Dang Fang et.al.,[12] reported ZrO_2 membrane have both monoclinic and tetragonal phases in the annealing temperature range between 400°C and 900° C. Hitherto reported that ZrO_2 nano particles prepared from aqueous solution with pure monoclinic structure is scarce in the literature. Hence, in the present work, we synthesize and characterize pure monoclinic ZrO2 nanoparticles with control morphology and crystalline nature in the absence of capping agent using co-precipitation method by varying temperature.

II. MATERIALS AND METHODS

Zirconium nitrate hexahydrate [$Zr(NO_3)_2 \cdot 6H_2O$], Potasium hydroxide [KOH] and double distilled deionized water were obtained from Alfa Aesar with analytical grade. All the chemicals were used without further refinement. In a typical reaction, the appropriate amount of Zirconium nitrate was dissolved in four beakers using deionized water under stirring at 500 rpm at room temperature. Potassium hydroxide [KOH] with 0.5M was slowly added in the respective four beakers until pH > 10 were attained; the products were filtered and repeatedly washed with deionized water and acetone simultaneously. The Zirconia precursor was dried in vacuum oven for 4h followed by milling it for 30 minutes. Then the sample was calcined at 600, 700, 800 and 900°C for 4h in the muffle furnace. Finally ZrO_2 nano particles were obtained [13].

The samples ZT1, ZT2, ZT3 and ZT4 acquired by a co-precipitation method were analyzed by high resolution electron microscopy (HRTEM, FEI Techno F30 ST equipped with field emission gun at 300 KV). The morphology of the samples was evaluated by scanning electron microscopy (SEM, Hitachi S-4700 Type II) operated according voltage of 25 KV. The phase and crystalline size of the four samples were examined through X-ray Diffraction measurements (XPERT-PRO with Cukα radiation). FTIR study was made using Thermo Nicolet 380 Instrument Corporation.

III. RESULTS AND DISCUSSION

Fig.1 is the X-ray powder diffraction pattern of the ZrO_2 nano particles with varying temperature, such as 600, 700, 800 and 900° C. From the XRD patterns of ZT3 and ZT4 the broad diffraction peaks as seen at 2θ= 17.20, 23.71, 28.21, 30.10, 31.06, 34.60, 35.20, 38.51, 40.64, 44.66, 48.93, 50.10, 53.78, 55.68, 58.05, 6.36, 64.43, 65.74, 71.30 and 75.20 Å respectively are assigned to (100), (011), (110), (111), (111), (200), (002), (021), (211), (112), (202), (002), (220), (300), (310), 131), (213), (222), (322) and (041) reflections of monoclinic ZrO_2 which coincides with JCPDS-89-9066. The peak at (110) orientation has higher intensity than the other peaks, which is attributed to high crystalline nature of the particular orientation of the samples. In ZT1 and ZT2, the following peak signals at 2θ= 30.22, 35.08, 50.35 and 59.93 Å are observed and assigned to (111), (200), (220) and (311) reflections of cubic ZrO_2 which coincides with JCPDS-89-9069. The peak at (111) orientation has higher intensity than the other peaks, which is attributed to high crystalline nature of the particular orientation of the samples. No obvious XRD peaks arising from impurities or other phases are found, which undisputedly indicates the high purity of the as-prepared crystalline ZrO_2. The particle diameter is estimated from the broadening of the diffraction peaks by using the Scherrer formula, the estimated diameters are 9.38, 11.02, 14.54 and 30.6 nm corresponding to ZT1, ZT2, ZT3 and ZT4 respectively.

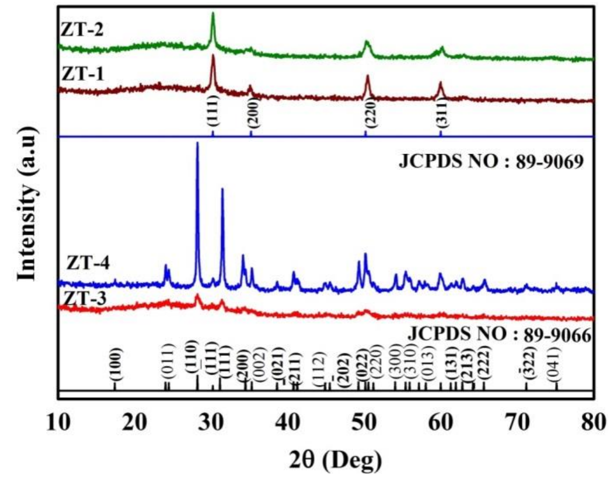

Figure 1. XRD pattern of ZrO_2 nano particle when ZT1) 600° C ZT2) 700° C ZT3) 800° C ZT4) 900° C as reaction temperature

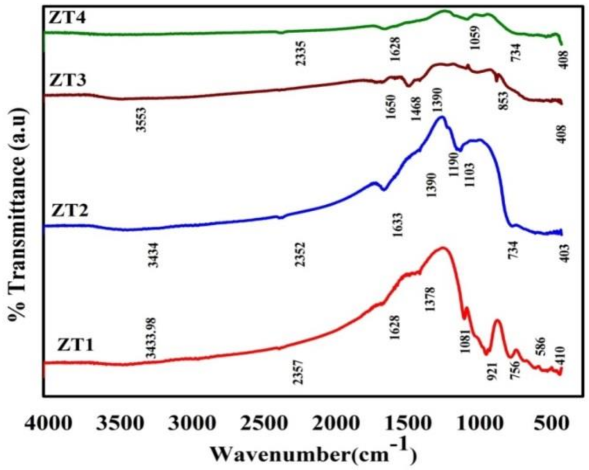

Figure 2. FTIR profile of ZrO_2 nano particle when ZT1) 600° C ZT2) 700° C ZT3) 800° C ZT4) 900° C as reaction temperature

FTIR spectra of ZrO_2 particles using various temperatures are depicted in Fig.2 (ZT1-ZT4) in the frequency range 4000-400 cm^{-1}. The strong bands at 1635, 1382 and 757 cm^{-1} are ascribed to the stretching vibration of O-H absorption of non-bridging OH groups and characteristics of m-ZrO_2 respectively [14-16]. These peaks are moved to (1628, 1633, 1650 and 1628 cm^{-1}), (1378, 1390, 1390 cm^{-1}), (756, 734, 734 cm^{-1}) in the complexes. The peaks perceived 734 and 408 cm^{-1} endorsed to Zr-O_2-Zr asymmetric and Zr-O stretching modes, respectively, which are the characteristics bands of monoclinic phase of ZrO_2.

The particle size distribution and surface morphology of the ZrO_2 particles are studied with varying temperature by a scanning electron microscope (SEM) and the images a-d are given in Fig 3 (a-d), respectively. The SEM image of samples has an agglomerated spherical particle having a size of 40-45, 60-70, and 75-80nm respectively for sample a-c. From Fig.3d, it is observed that there is cauliflower like morphology with size of 90-95 nm. It may be due to phase segregation which is considered as a preparatory period of nucleation and can promote nucleating is more obvious due to the agglomeration of spherical ball-like substance. The method of preparation is same in all cases, particles seem to have cauliflower like morphology when the heat treatment grows and constitute multiple morphologies. With increasing heat temperature, the systematic growth of particles of cauliflower is obsereved. The process of crystal growth and morphology evolution can be described in terms of Oswald ripening [17-20]. Further, the EDX spectrum of ZrO_2 sample is shown in Fig. 3e. The result clearly exhibits the presence of Zr and O.

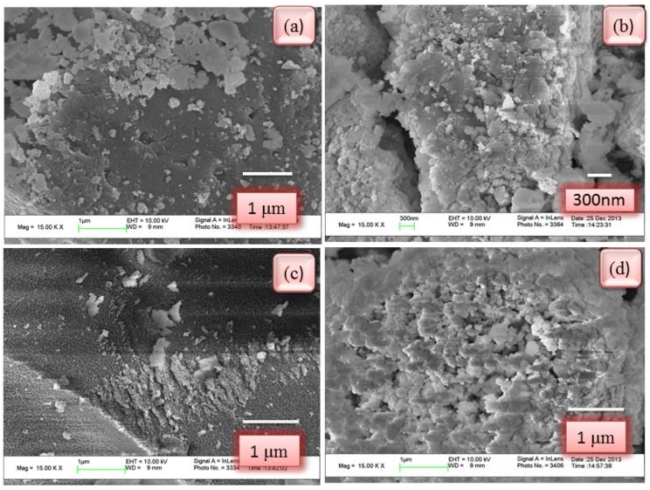

Figure 3. SEM images of ZrO_2 nano particle when a) 600° C b) 700° C c) 800° C d) 900° C as reaction temperature

The TEM images of ZrO_2 nano particles at 900° C as reaction temperature along with SAED pattern are shown in Fig. 4(a-b). It is inferred that from the fig, crystallinity could be observed based on the particles and its corresponding electron diffraction pattern. Its crystallite size is about 240-250 nm as estimated from the TEM micrographs. The particle generally revealed rounded edges, but they are not well-defined due to small size. Good crystalline phase and crystallinity could be observed. From fig 4b, it is revealed that the orientation along (221), (210), (002) and (111) directions are in accordance with the d-spacing values 1.66, 2.28, 2.62 and 3.16 Å in the XRD pattern.

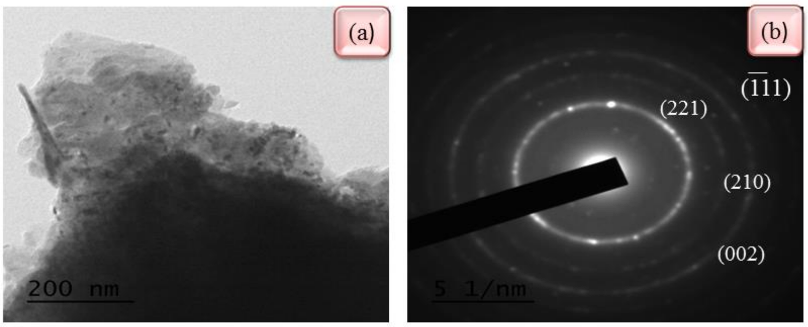

Figure 4. a) TEM image b) SAED pattern of the ZrO2 nano particle when temperature fixed as 900°C

IV. CONCLUSION

ZrO_2 particles are synthesized using a co - precipitation method at various reaction temperatures. XRD pattern for as-synthesized samples agree well with the standard XRD pattern of ZrO_2 with a cubic structure (JCPDS. 89-9069) for 600 and 700° C, and monoclinic structure (JCPDS.89-9066) for 800 and 900° C. The average crystalline size is 9.38- 30.6nm, increased with increasing temperature. Depending on the reaction conditions, ZrO_2 nanoparticles could be produced in the form of pure monoclinic and pure cubic polymorphs. Under the reaction conditions used in this work, the crystallinity and morphology of the resulting ZrO_2 nanoparticles can be adjusted. Further, the presence of Zr, O was confirmed through FT-IR, EDX analyses. The well dispersed spherical morphology with particle diameter of 240-250 nm in TEM analysis is observed. As a consequence, 900° C is observed as effective temperature to the formation pure monoclinic phase of ZrO_2 nano particles. Consequently, the as prepared ZrO_2 nano particles could be used as filler in the polymer electrolyte fabrication.

REFERENCES

[1] K.Gupta, P.C.Jana, A.K.Meikap; *J.Phys. Sci*., 16(2012) 209-216.
[2] K.Anandan, V.Rajendran; *J.Phys.Sci.*, 14(2010) 227-234.
[3] Liangronge Li, Wenzhong Wang; Solid state communi. 127 (2003) 639-643.
[4] A.P.Naumenko, N.I.Berezovska, M.M. Billy, O.V.Shevchenko; *Physics and chemistry of solid state* 9 (2008) 121-125.
[5] Y.W.Zhang, Z.G. Yan, F.H.Liao, C.S.Liao, C.H.Yan; *Mater.Res.Bull*. 39(2004) 1763.
[6] H.Ranjan sahu, G.Ranga rao, *Bull.Mater.sci.*, 23(2000) 349-354.
[7] I.Ganesh, R.Johnson, G.V.N.Rao, Y.R. Mahajan, S.S.Madavendra, B.M.Reddy; *Ceramics international* 31(2005) 67-74.
[8] G.Xu, Y.W.Zhang, C.S.Liao, C.H.Yan; *Soild state ionics* 166 (2004) 391.
[9] Z.Tang, J.Zhang, Zh.Cheng, Zh.Zhang; *Materials chemistry and physics* 77(2002) 314-317.
[10] Razaei. M, Alavi.S.M, Sahebdal far.S, Feng yan.Zi, *J.of porous mater*. 15 (2008) 171-179.
[11] K.Anandan, V.Rajendran, J.*Phy.Sci* 17 (2013) 179-184.
[12] Dong Feng, Kelong Huang, Zhiping Luo, Yue Wang, Suqin Liu and Qiguon Zhong, *J.Mater.Chem*, 21(2011), 4989.
[13] M.Ramachandran, R.Subadevi, Wei-Ren Liu and M.Sivakumar, *J. Nanosci.Nanotechnol*, (2018), 18(1), 368-373.
[14] Zhanxia Shu, Xiuling Jiao and Dairong Chen; *CrystEngComm*, 2013,15, 4288-4294.
[15] Shivam Bajpai, Sundaram Singh, Vandana Srivastava; *RSC Adv.*, 2015, 5, 28163-28170.
[16] Mohamed A. Ebiad, Dalia R. Abd El-Hafiz, Radwa A. Elsalamony and Lamia. S. Mohamed; *RSC Advances*, 2012, 2, 8145–8156.
[17] D.Kistamurthya, A.M.Saiba,D.J.Moodley, J.W.Niemantsverdriet, C.J.Weststrateb; *Journal of Catalysis*, (2015), 328, 123-129.
[18] Mengjin Yang, Taiyang Zhang, Philip Schulz, Zhen Li, Ge Li, Dong Hoe Kim, Nanjie Guo, Joseph J. Berry, Kai Zhu, Yixin Zhao; *Nature Communications* (2016), 7, 12305.
[19] Kristina Wettergren, Florian F. Schweinberger, Davide Deiana, Claron J. Ridge, Andrew S. Crampton, Marian D. Rötzer, Thomas W. Hansen, Vladimir P. Zhdanov, Ueli Heiz, and Christoph Langhammer; *Nano Lett.*, (2014), 14 (10), 5803–5809.
[20] Tomasvan Haasterecht, MartenSwartaKrijn P. JongaJohannes, HendrikBitter; *Journal of Energy Chemistry*, (2016), 25(2), 289-296.