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OPTIMIZATION OF pH ON THE SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA (ZrO_2) NANOPARTICLES

[1,2]M.Ramachandran,[3]M.Shanthi, [2]R.Subadevi, [2*]M.Sivakumar

[1]*Department of Physics, ArumugamPillaiSeethaiAmmal College, Tiruppattur 630211 India.*
[2] *Energy Materials Lab, School of Physics, Science block, Alagappa University, Karaikudi. India.*
[3]*Department of Physics, Kamaraj College of Engg. And Tech, Virudhunagar 626001, India.*

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. The effect of pH such as 9,10,11 and 12 on the synthesis of ZrO_2 nano particles had been analysed. 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-O2-Zr asymmetric vibrations were confirmed through FT-IR analysis. The different morphology was obtained through SEM analysis. The band gap of the ZrO_2 nano particles was estimated through PL analysis. The optimized sample was examined 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 dioxide (ZrO_2), particularly in the powder form, is one of the auspicious material broadly used as solid electrolytes, catalyst, optical coating and dielectric. Commonly, different morphologies and size are essential when ZrO_2 nano powder is engaged for different applications. Pure Zirconia exhibits three polymorphs of which monoclinic phase is thermodynamically stable up to 1100°C and tetragonal phase occurs in the temperature range 1100-2370°C and cubic phase is found above 2370°C [1-3]. Several methods including sol-gel [4], Hydrothermal [5], Micro-wave assisted [6] and chemical precipitation method [7] were used to synthesize the ceramic oxide nano powders. Among these, chemical precipitation method is humble, viable and dimension adapting and cost effective. Beena Tyagi et.al reported [8] that pH environment and ion concentration in the precipitant solution is significant to obtain pure phase of Zirconia. M.N.Tahir et.al [9] reported the phase selection of ZrO_2 strongly depends on the pH of the reaction medium. However, Zirconia metal oxide with pure monoclinic phase using aqueous solution is scarce in the literatures and also still challenged. Based on this issue, an inspiration towards the synthesis and analysis of pure monoclinic ZrO_2 nanoparticles using aqueous solution in absence of any ligands with varying pH and controlled morphology and crystalline nature has been found in the present study.

II. MATERIALS AND METHODS

Zirconium nitrate hexahydrate [Zr(NO3)2. 6H2O], 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-9,10, 11 and 12 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 900°C for 4h in the muffle furnace. Finally ZrO_2 nano particles were obtained.

The samples ZP1, ZP2, ZP3 and ZP4 attained 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 studied through X-ray Diffraction measurements (XPERT-PRO with Cukα radiation). FTIR study was analyzed using Thermo Nicolet 380 Instrument Corporation. The presence of monoclinic structure was confirmed through Micro Raman spectroscopy by using (STR-500) Laser Raman spectrometer. (SEKI, Japan), Optical properties of the products were carried out by photo luminescence (PL, Fluoromax-4 spectafluorometer with Xe lamp excitation light source].

III. RESULTS AND DISCUSSION

Fig.1 (ZP1-ZP4) depicts the XRD pattern of the prepared ZrO_2 nano particles of varying pH such as 9,10,11 and 12 respectively. All the diffraction peaks are corresponding to the monoclinic ZrO_2 (JCPDS: 89-9066). No obvious XRD peaks arising from impurities or other phase are identified, which undisputedly specifies the high purity of the as-prepared crystalline ZrO_2. The average crystalline size is calculated as 47.9, 46.8, 46.5 and 42.9 nm for samples ZP1, ZP2, ZP3 and ZP4 respectively, using Debye-Scherrer formula and the values are comparable with previous studies [10-12].

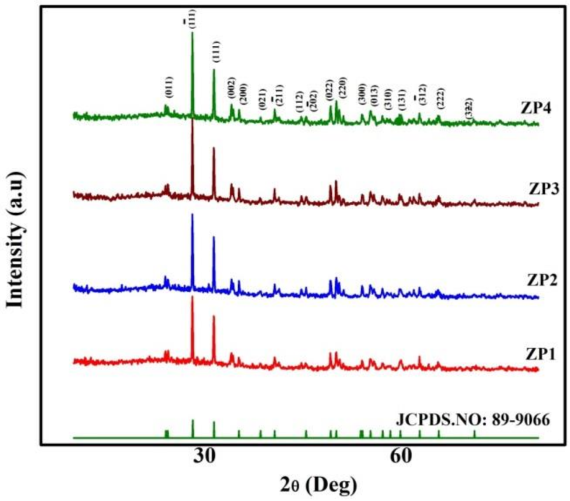

Figure 1. XRD pattern of ZrO_2 nano particles when ZP1) 9 ZP2)10 ZP3) 11 ZP4) 12 as pH

Vibrational spectroscopy has been acknowledged as a potential tool to study the interaction among the various ingredients in particles [13,14]. Fig 2. (ZP1-ZP4) shows the FT-IR spectra of ZrO2 nanoparticles using various pH. It revealed that the occurrence of band at 422, 512, 586 and 757 cm^{-1} are corresponding to the strong stretching vibration of Zr-O group. According to the literatures [15-17], these bands are the characteristic monoclinic phase of ZrO_2. The FT-IR studies are in promise with the XRD pattern of the ZrO_2 and that both endorse the existence of a monoclinic ZrO_2 phase.

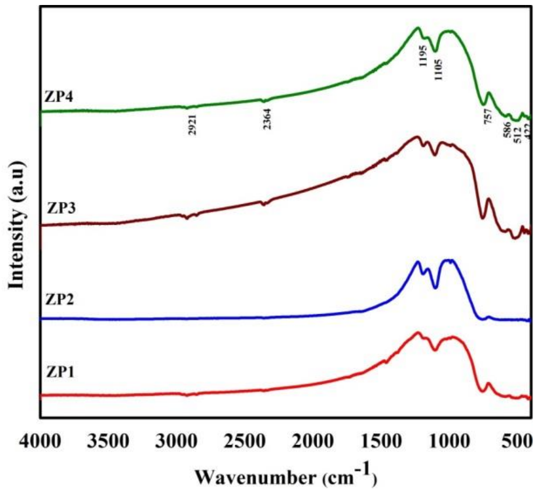

Figure 2. FTIR spectrum of ZrO_2 nano particles when ZP1) 9 ZP2)10 ZP3) 11 ZP4) 12 as pH

The Raman spectra of prepared samples are shown in Fig.3 (ZP1-ZP4). The active peaks are observed at 175, 337, 385,469,554,640 cm^{-1} in Raman spectra which belong to the monoclinic phase of Zirconium. The peaks at 337 and 640 cm^{-1} could be reliable to Ag mode. The peaks at 385 cm^{-1} could be assigned to the Bg mode. The remaining peaks at 175 cm^{-1} could identify the Raman active optical phonons that are substantiated with other findings using various methods [18-20]. The phase selection is that high symmetry structures are generally favored for high ionic materials (i.e. For those with high concentrations of surface OH- in the present case) because the coulomb potential is spherical. In agreement with these hypotheses the monoclinic poly morph is formed in the solution with the highest pH.

Fig4. (ZP1-ZP4) displays the SEM micrograph of ZrO_2 samples prepared using co-precipitation route with the magnification of 10 K. When the chemical environment is less basic in nature, irregular particles observed in fig.4 may be due to soft agglomerated particles. The agglomerated particles varied in size from 0.6 to 0.8 µm. From Fig. 4 (ZP3 & ZP4) when the chemical environment is in high basic nature, it obviously revealed two kinds of morphologies such as spherical shape (approximately 350 nm and 300 nm for ZP3 and ZP4 respectively) and rod like morphology (approximately 1.15×0.5 µm and 1.05×0.4 µm for ZP3 and ZP4 respectively) were observed in fig 4. It is concluded that the pH has played a pivotal role in the surface morphology of the powder.

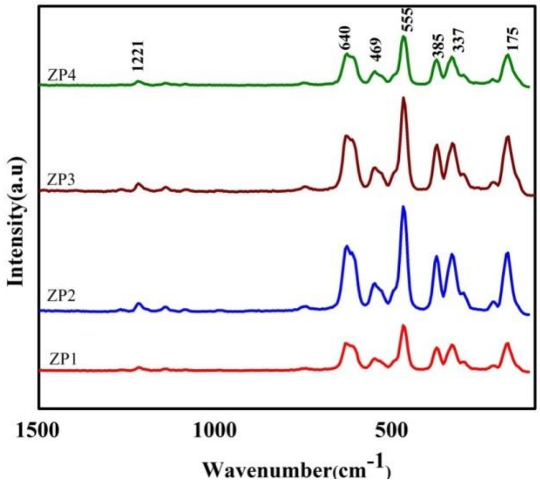

Figure 3. Raman spectrum of ZrO_2 nano particles when ZP1) 9 ZP2)10 ZP3) 11 ZP4) 12 as pH

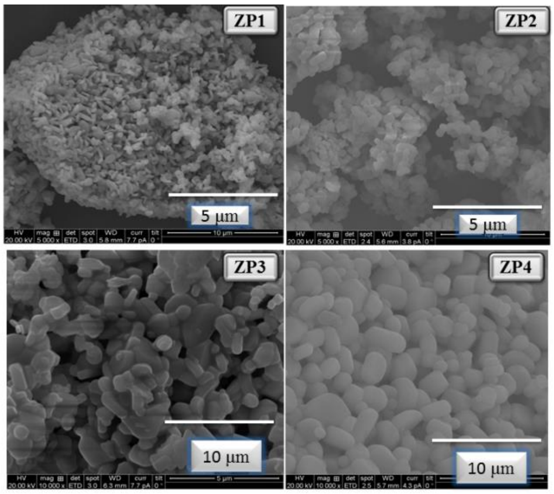

Figure 4. SEM images of ZrO_2 nano particles when ZP1) 9 ZP2)10 ZP3) 11 ZP4)12 as pH

Fig 5 (a &b) shows a typical TEM image and corresponding SAED pattern of sample ZP4 (Sample pH-12). Fig.5.a shows spherical agglomerated ZrO_2 nano particles in the range of 220-225nm. According to our previous discussion [21], in case of nanoparticles, agglomeration happens very easily, because the surface forces such as Vander-walls forces, capillary forces and electrostatic forces can astounded only against the gravitational and inertial forces for precise in size varieties. From fig 5.b, it is revealed that the orientation along (413), (411) and (121) directions are in accordance with the d-spacing values 1.09, 1.62 and 2.17 Å in the XRD pattern.

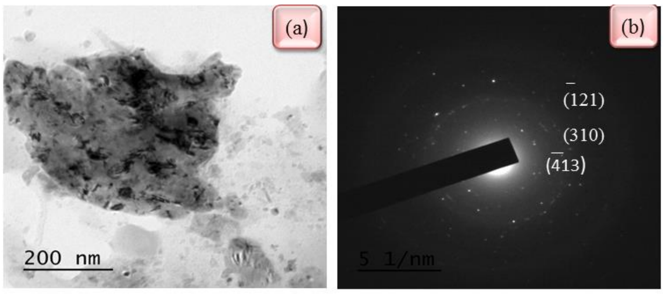

Figure 5. a) TEM image b) SAED pattern of ZrO_2 nano particles when pH -12

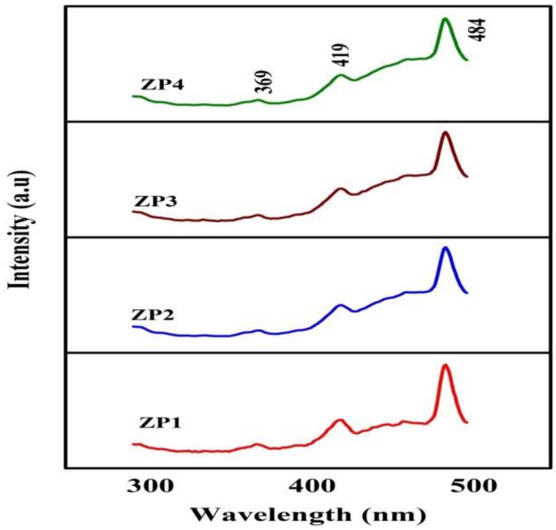

Figure 6. Photoluminescence spectra of ZrO_2 nano particles when ZP1) 9 ZP2)10 ZP3) 11 ZP4)12 as pH

Photoluminescence is one of the essential characterization tools to analyze the structural defects and quality of crystalline structure which shows essential part in the improvement of oxide nano filler. The PL spectrum of the as prepared ZrO_2 is displayed in fig.16 with an excitation wavelength of 270 nm. It is noticed from Fig.6 (a-d) that ZrO_2 has three emission bands. The emission band around 484nm (2.55 eV) can be assigned to self-trapped exciton confined on ZrO_2 monoclinic phase [22]. Band around at 419 nm (3.01 eV) and 369 nm (3.63 eV) coincide and assigned as defect due to oxygen vacancies. Especially the oxygen vacancies are responsible for the long life of the carriers [23,24].

IV. CONCLUSION

ZrO_2 nano particles have been synthesized using co-precipitation method of varying pH of the ideal reaction medium. The monoclinic phase with phase group Fm3m was confirmed through (JCPDS: 89-9066) using XRD analysis. Further the presence of monoclinic Zr, O species was ascertained through FTIR, Raman analyses. The spherical particle together with rod like morphology was clearly identified in the high basic environment rather than less basic environment through SEM analysis. It revealed that the morphology was highly dependent on the pH of the chemical environment. The well dispersed spherical particle size of 220-225 nm in TEM analysis was observed. Also, it has band gap of 2.55 eV, which was lower than bulk. Eventually, the high pH -12 is optimized in the synthesis of ZrO_2 nano particles. The as prepared ZrO_2 nano particles are used as fillers for the lithum polymer battery electrolyte fabrication.

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