

Non-aqueous sol-gel derived calcia partially stabilized zirconia: Synthesis and characterizations

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Abstract

Temperature dependence of the phase transformation of zirconium oxide (ZrO₂) retards the overall performance of zirconia in dentistry. This shortcoming can be overcome by using stabilizer such as calcium oxide (CaO). This study highlighted the synthesis of calcia partially stabilized zirconia (CPSZ) prepared by sol-gel method in ethanol and characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Brunauer-Emmett-Teller (BET) for the determination of phases, chemical bonding, surface morphology and surface area analysis, respectively. From XRD, the highest occurrences of ZrO₂ in the form of cubic and tetragonal can be detected at $2\theta = 50^\circ$ and 31° , respectively while CaO occur at $2\theta = 28^\circ$ suggesting the existence of CPSZ. The FTIR peaks at 482 cm^{-1} is allocated for Ca-O bond, while peaks at 585 and 765 cm^{-1} are assigned for Zr-O bond, suggesting the successful preparation of CPSZ by using sol-gel method in ethanolic medium. Furthermore, lower surface area of the CPSZ as compared to commercial ZrO₂ powder indicative of incorporation of CaO nanoparticles onto the surface of ZrO₂, suggestive of the success in using sol-gel method in preparing CPSZ nanocomposites.

Keywords: Spherical CPSZ, sol-gel method, dental restoration

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Introduction

As we age, the problem of tooth loss becomes a major issue that needs to be addressed. In dentistry, restorative materials such as crowns, bridges and implants are some of the common ways to overcome the lost tooth structure. Basically, the restorative material used is contingent with the degree of destruction of the tooth where their functions and appearances must be similar to that of the natural tooth. Fixed dental prostheses (FDPs) which refer to crowns and bridges have previously been done with metals or metal substructures veneered with porcelain for aesthetic purposes. Several laboratory steps are involved in this type of crown construction. Currently, with chair side computer-aided design/ computer-aided manufacturing (CAD/CAM) technology, the construction of FDP, especially crown can be prepared chairside, during a single visit using ceramic ingot.

Zirconia-based ceramics have been used to replace non aesthetic dental alloy as framework underneath the brittle veneering porcelain in the fabrication of fixed dental prostheses (FPD) [1]. Lately, as the aesthetic properties of zirconia based ceramics improve, they have also been used to construct the whole crown and bridge rather than just as framework.

Zirconia (zirconium dioxide, ZrO_2) is the most studied ceramic material in the field of dental science for specific aims and reasons in the later part of the 20th century because of its decent esthetics, in addition to the worries regarding allergic and toxicity effect of certain alloys [2]. However, due to its peculiar arrangements of atoms, ZrO_2 tends to be very hard [3]. The addition of stabilizing oxides to the pure zirconia will obtain a multiphase material, which makes it completely or partially stabilized zirconia, thus enables it to be used for dental application [4].

Typically, pure zirconia has three polymorphic forms in nature namely monoclinic (room temperature - 1170 °C), tetragonal (1170 – 2370° C) and cubic (2370 – 2680 °C) [5]. Pure zirconia encounters setback upon cooling where large volume change occurs leading to cracking of the material. Incorporation of small percentage of metal oxide stabilizers such as yttria (Y_2O_3), ceria (CeO_2), magnesia (MgO), and calcia (CaO) to zirconia would be able to delay the phase transformation [6, 7]. Zirconia-containing ceramic systems used to date in dentistry are yttrium cation-doped tetragonal zirconium polycrystals (3Y-TZP), magnesium cation-doped partially stabilized zirconium (Mg-PSZ), zirconium-toughened alumina (ZTA) and ceria-stabilized zirconia-alumina (CeTZP/A) [8, 9].

However, some issues such as low temperature aging degradation, lower reliability, low mechanical properties, large grain size and high porosity retard its performance for dental purposes. For example, yttrium partially stabilized tetragonal zirconia polycrystalline (Y-TZP) with a high fracture toughness, from 5 to 10 $MPa\ m^{1/2}$, and a flexural strength of 900–1400 MPa [10, 11] which can be fabricated by milling either fully sintered blocks or partially sintered blocks/green blocks using CAD/CAM procedures suffered from low-temperature aging degradation (LTAD) caused by phase transformation [12]. Ce-TZP/A which is the toughest dental ceramic material available, with a fracture toughness of 19 $MPa\ m^{1/2}$, and a flexural strength of 1400MPa [9] causes wear to the milling machine. Mg-PSZ which contains 8 – 10 mol % of magnesia seems to be unsuitable for dental application due to the presence of high porosity, large grain size (30 – 60 μm) that can cause wear to the opposing structure, low stability and low mechanical properties [13].

Other than the of the above aforementioned stabilizers, calcia (CaO) also has been widely used to stabilize ZrO₂ for various applications such as solid electrolyte for battery [14], sensor [15], solid oxide fuel cell [16] and in biomedical applications [17]. In medical applications, the usage of CaO is paramount due to CaO biocompatibility, and is one of the compositions of hydroxyapatite in human bone. Research on hip replacement implant utilizing Ca-PSZ by Nath *et al.*, (2008) [18] exhibits Vickers hardness of 8–10 GPa, and a modest fracture toughness (6 MPa m^{1/2}). These properties are better than commercial grade alumina, but lower than Y-TZP and CeTZP/A. The moderate mechanical properties of Ca-PSZ in their studies are indicative that Ca-PSZ is a suitable material for dental application as compared to commercially available bioceramics.

Furthermore, the morphological shape and particle size of CPSZ are scarcely reported in the literatures especially for dental purposes. Therefore, this current study will focus on synthesizing spherical and nanosized CPSZ using sol-gel method. Incorporation of CaO into zirconia by sol-gel technique, can shorten the processing time due to high contact surface area, and will produce material properties such as lowering the hardness of ZrO₂, as well as minimizing phase transformation of ZrO₂.

Materials and Methods

Materials

Ammonia solution (NH₃) was purchased from Merck, zirconium oxide (ZrO₂) nano powder was purchased from US Research Nanomaterials, Inc. (99+ %, 40 nm), absolute ethanol was purchased from Sigma-Aldrich, and calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) was obtained from Sigma-Aldrich.

Preparation of CaO-ZrO₂

CaO-ZrO₂ nanoparticles were prepared using sol-gel method in ethanolic solution at ambient temperature. 10-15 mmol of calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) was dissolved in ethanol, followed by addition of 5-10% ammonia solution (NH₃) and 50-55 mmol of zirconia dioxide (ZrO₂) powder. The solution mixture was then washed with distilled water and ethanol. The solid was dried and ground into a fine powder before subjected to calcination at 750°C for 30 minutes to obtain CaO-ZrO₂. Then, the as-prepared CaO-ZrO was used for further characterizations.

Characterization

X-ray diffraction (XRD) were obtained between 25° and 70° on a PAN analytical EMPYREAN diffractometer with CuKα₁ radiation (λ=1.54060 Å), at a step size of 0.01°, with an operating current and voltage of 40 mA and 40 kV, respectively. Additionally, the Fourier transformed infrared spectrum (FTIR) was obtained between 4000 and 400 cm⁻¹ on a Perkin Elmer 400FTIR/FT-FIR spectrometer. The morphology and elemental analyses of the synthesized powder were performed using a Field Emission Scanning Electron Microscope (FESEM) (Quanta 450, FEG). The thermal stability of the material was determined from 50-900°C on a Perkin-Elmer Pyris Diamond TG/DTA Thermal System under nitrogen atmosphere at a flow rate of 20 cm³ min⁻¹ and scan rate of 20°C min⁻¹.

Results and Discussions

Structural analysis

The phase identification of the prepared CPSZ was identified using XRD as indicated in Fig. 1. The diffraction pattern of cubic ZrO_2 was obtained at $2\theta = 35^\circ, 49^\circ, 50^\circ, 60^\circ, 61^\circ, 62^\circ,$ and 63° which corresponds to (110), (022), (112), (121), (113), (113) and (222) diffraction planes respectively (ICDS no. 98-006-2899). Moreover, the tetragonal ZrO_2 was obtained at $2\theta = 31^\circ, 44^\circ, 45^\circ, 56^\circ$ and 66° resembles to (011), (012), (021), (012) and (122) diffraction plane (ICDS no. 98-010-8644). Calcium oxide with a cubic structure was identified at $2\theta = 28^\circ, 34^\circ, 41^\circ, 42^\circ, 57^\circ$ and 58° which corresponds to the diffraction planes of (010), (111), (002), (002), (022) and (022) and matches with ICDS no. 98-008-6047. Calcium hydroxide ($Ca(OH)_2$) (portlandite) was obtained at $2\theta = 36^\circ, 52^\circ, 55^\circ$ and 64° that corresponds to (002), (110), (111) and (013) diffraction planes (ICDS no. 01-073-5492). The formation of $Ca(OH)_2$ due to absorption of moisture by CaO nanoparticles. The crystalline peaks in the XRD pattern confirmed the formation of CaO and ZrO_2 phase.

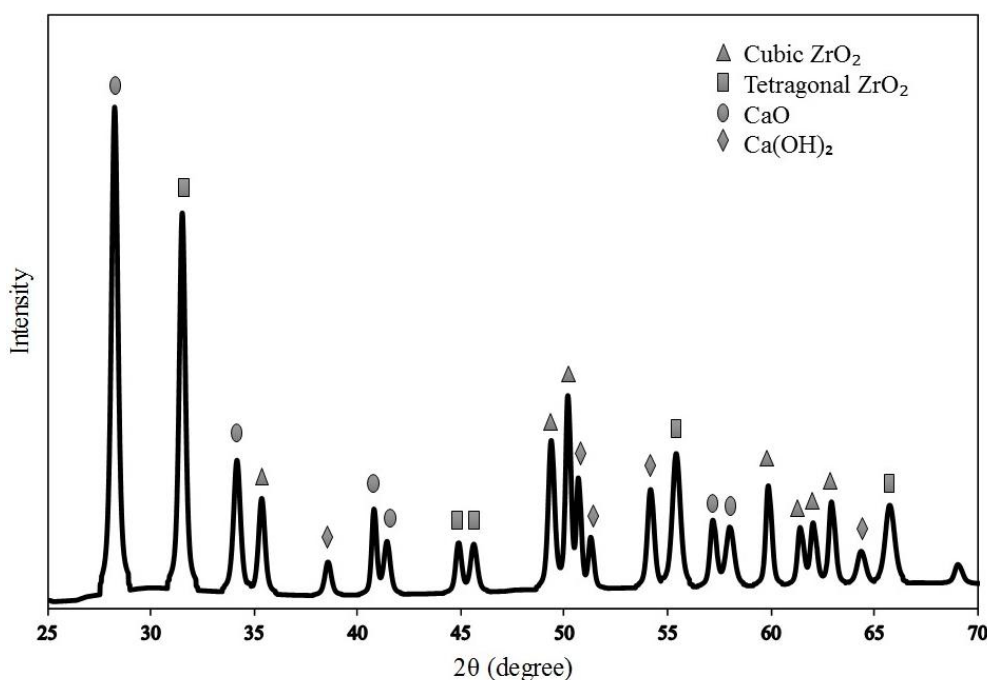


Figure 1: XRD pattern of CPSZ powder

FTIR spectrum of the as-prepared CPSZ is shown in Fig. 2. The broad absorption band at 3440cm^{-1} attributed to the vibration of OH- group in physically bonded water molecule in CPSZ matrix [19]. The broad band around 1623cm^{-1} indicate the C-O bond which is associated to carbonation of CaO [20]. The Ca-O stretching is observed at around 496cm^{-1} [21]. The spectra at the bands of 750cm^{-1} was associated to Zr-O valence vibrations [22]. The presence of CaO and ZrO_2 further ascertained that sol-gel method is suitable to synthesize $CaO-ZrO_2$ particles.

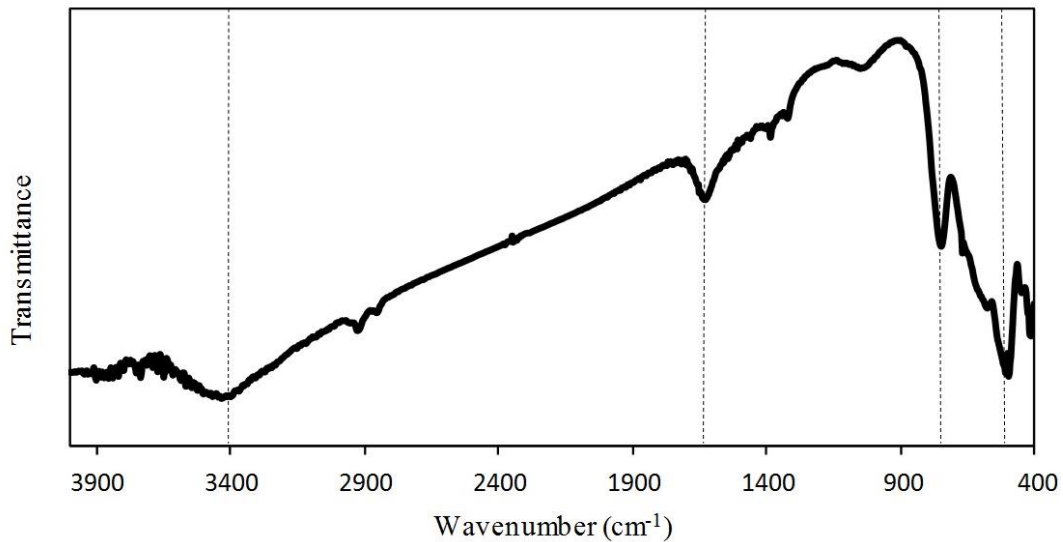


Figure 2: FT-IR spectrum of CPSZ

Surface morphology and area analysis

FESEM analysis (Fig. 3) was used to study the surface morphology and geometry of the as-prepared CPSZ nanocomposites which showed almost spherical-like structure with the particle size from FESEM analysis is about 25 to 50 nm in range suggestive that attainment of sol-gel method in preparing the CPSZ nanocomposites. The total surface area of CPSZ nanocomposites which was obtained from Brunauer-Emmett-Teller (BET) method showed the value of 29 m²/g. The surface area of the as-prepared CPSZ nanocomposites is much lower than the commercial ZrO₂ powder indicative of the successful incorporation of CaO nanoparticles on ZrO₂ surface.

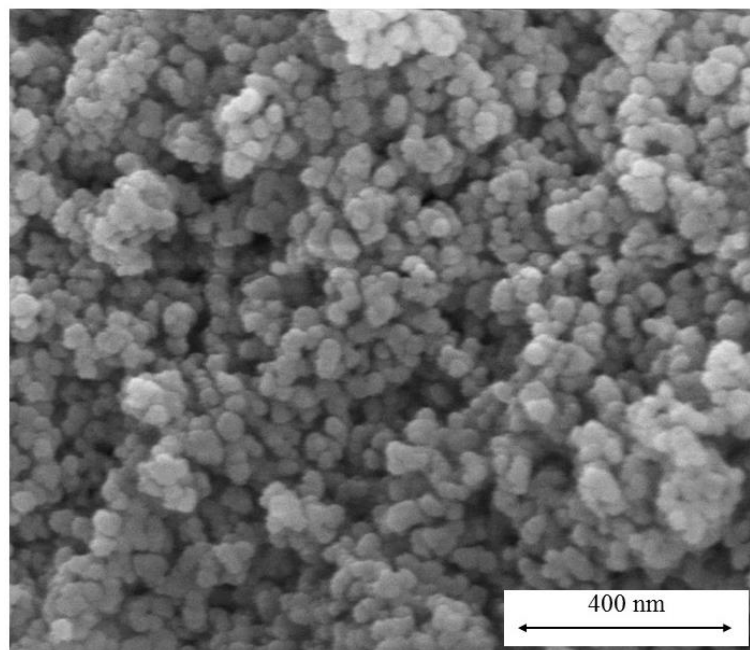


Figure 3: FESEM images of CPSZ powder

Thermal analysis

The TGA curve for CPSZ nanoparticles is represented in Fig. 4. The initial weight loss at about 50 to 120 °C was due to the evaporation of weakly bonded ammonia, water and ethanol molecules on the surface [23, 24] of the nanoparticles which contribute to 1.5% weight loss. The decomposition at 120 to 350 °C was associated to the decomposition of ammonium nitrate (NH_4NO_3) which contributes to 0.6 % of the total weight loss [25, 26]. Meanwhile, the decomposition at 350 – 600 °C was deduced to the decomposition of calcium hydroxide ($\text{Ca}(\text{OH})_2$), which contributes to 1.5 % of weight loss [27]. The complete decomposition of $\text{Ca}(\text{OH})_2$ to form CaO can be observed at the temperature of 600 °C which further produced CPSZ nanoparticles.

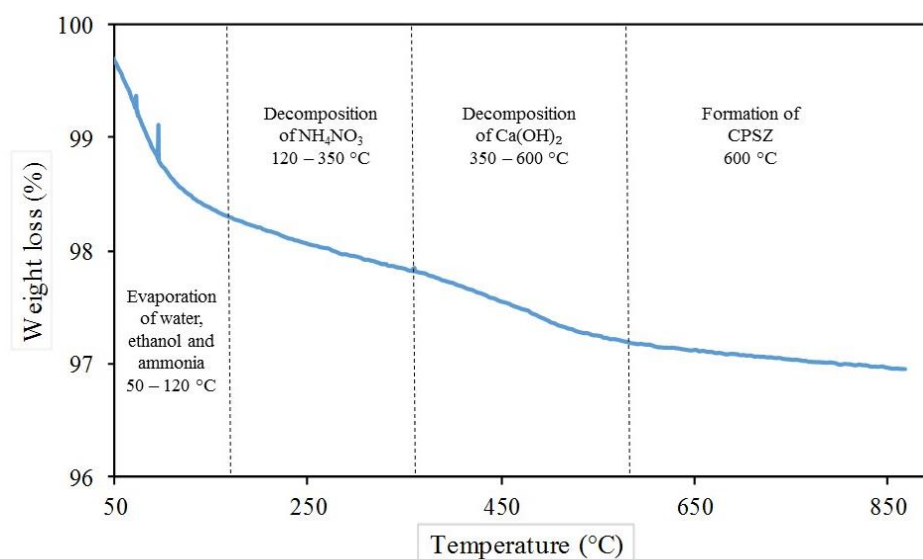


Figure 4: TGA curve of CPSZ powder

Conclusion

The spherical-like structure of CPSZ was successfully synthesized from sol-gel method in ethanolic solution in the presence of ammonia. The XRD studies revealed the crystalline nature of CPSZ nanoparticles with the presence of cubic and tetragonal phase of ZrO_2 . The FTIR analysis confirmed that existence of Ca-O and Zr-O bond indicative of successful formation of CPSZ nanoparticles. The as prepared material was thermally stable up to 600°C which is suitable for biomedical application.

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Author Contributions

Nur Atikah Ab. Ghani: Synthesis, data collection, data analysis, manuscript preparation and editing; Zuryati Ab-Ghani: Study design, manuscript preparation and editing; Yanny Marliana Baba Ismail: Characterisation, manuscript editing; Khairul Anuar Syariff: Data

analysis and manuscript editing; Ahmad Nazeer Che Mat: Synthesis, characterisation, manuscript preparation and editing; Zaihan Ariffin: Data analysis and manuscript editing; Tang Liszen: Characterisation and manuscript editing; Ahmad Fauzi Mohd Noor: Study design, manuscript editing.

Disclosure of Conflict of Interest

No conflict of interest

Compliance with Ethical Standards:

This study complies with the ethical standard and has ethical approval from the Universiti Sains Malaysia Human Ethics Committee (USM/JEPeM/17120678).

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