Fabrication of ultrafiltration membranes by repurposing dental zirconia waste

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Abstract

This thesis focused on the repurposing of dental zirconia waste combined with commercial zirconia to fabricate zirconia membranes on silicon carbide supports suitable for ultrafiltration. DLS and DSC analyses were conducted to determine the behaviour of the zirconia powders under the influence of various pH environments and temperatures, which will be used to optimise the subsequent coating procedure and thermal treatment. XRD analyses were performed to characterise the crystalline structure of the zirconia powders before and after calcination.

Preface

The project was created by a chemical engineering student from Aalborg University as a master's thesis and the project is about *Fabrication of ultrafiltration membranes*. A prerequisite for reading the paper is the knowledge acquired from a B.Sc. in chemistry. The help and funding from the supervisor Vittorio Boffa and the external supervisor Linfeng Yuan has been greatly appreciated in making the project.

Reading guide

The references in the project are made using the Vancouver system, and appear in chronological order in the report. The reference is placed at the end of a sentence or paragraph, where it refers to the preceding piece of text. The complete bibliography can be found at the end of the report, with all references in chronological order of appearance.

References to figures, tables, and equations appear with chapter number followed by the reference number for the chapter. Each figure and table has a caption with additional information below or above, respectively. The figures have been made by the author unless otherwise specified. A list of the different abbreviations used can be found in the following section.

List of abbreviations

DLS - Dynamic light scattering
DSC - Differential scanning calorimetry
MF - Microfiltration
NF - Nanofiltration
RO - Reverse osmosis
SEM - Scanning electron microscopy
UF - Ultrafiltration
XRD - X-ray diffraction
YSZ - Yttria-stabilised zirconia

Contents

1 | Introduction

Membrane technology is a rapidly growing field due to its variety of applications in separation processes across various industries. Compared to conventional wastewater treatment, membrane filtration presents several advantages such as high retention of contaminants, high energy efficiency, low maintenance, low environmental footprint, and low operating expenses [1]. Two prominent categories of membranes are polymeric and ceramic. Although polymeric membranes are dominant in the market due to their low production cost, established manufacturing processes, and flexibility to be customised to meet different needs, ceramic membranes are preferred under certain circumstances such as harsh environments with elevated temperatures and extreme pH, in addition to their superior fouling resistance and longer lifespan, favouring them in conditions in which polymeric membranes are inappropriate [1, 2].

Common materials applied in ceramic membrane fabrication are alumina, silica, silicon carbide, titania, zeolites, and zirconia [3]. Although membranes fabricated with alumina, silica, and zeolite are dominant commercially, considering their cost-effectiveness and optimised fabrication processes, their poor chemical and thermal stability under corrosive conditions and hydrothermal environments limit the applications of these membranes [4]. On the other hand, zirconia is a promising material for developing ceramic membranes due to its refractory features and high mechanical strength, in addition to its high chemical stability, making it suitable for working in conditions where other materials may fail.

Another application of zirconia is in the orthodontic industries. Its advantageous properties such as hardness, whiteness, chemical stability, and biocompatibility have been utilised to optimise the size and composition of nanoparticles, achieving excellent chemical and mechanical robustness of the restoration material and improving the fabrication of dental prosthetics. However, as the implants are shaped by milling, only a small part of the material is used, where the generated waste correspond up to 80% of the original mass, estimating more than 2000 tons of zirconia waste being treated and disposed of as non-hazardous waste annually [5, 6]. Potential recycling and/or repurposing of this waste is a prompt to reduce waste in addition to saving the resources otherwise required to produce the nanoparticles used in membrane fabrication.

The focus of this thesis is to fabricate an asymmetric composite membrane in which an ultrafiltration selective layer of a mixture of a commercial zirconia and the dental zirconia waste is coated on commercial silicon carbide supports. Different fabrication parameters will be investigated to optimise the fabrication processes. This leads to the thesis statement:

How can dental zirconia waste be repurposed to fabricate membranes suitable for ultrafiltration? What fabrication parameters can be optimised to improve the quality of the membrane?

2 | Theory

2.1 Membranes

Fundamentally, a membrane serves as a barrier that separates two distinct phases and selectively restricts the passage of undesirable particles. Typically, in a membrane filtration process, a feed of solution is inserted into a system, where upon applying a driving force, the membrane divides the feed solution into a permeate and a retentate. The permeate is the desired product that passed through the membrane uninterruptedly, and the retentate is the element that is blocked by the membrane. An example of the process is where wastewater passes through treatment plants, in which clean water is obtained, while sludge and other biowastes are disposed of. The driving force applied across the membrane is usually pressure, but depending on the process can also be a concentration gradient, a chemical potential, or an electric potential.

The applications of membrane filtration are determined by the types of filtration processes, categorised as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). In addition to the classification of the filtration processes, membranes are also distinguished between symmetric and asymmetric. Symmetric membranes are characterised by the uniform particle size distribution throughout the entire membrane structure, providing homogenous pore sizes across the membrane layer. On the other hand, asymmetric membranes are composed of two or more layers with different membrane structures. During a filtration process with an asymmetric membrane, as the feed penetrates the membrane, it is met with varying pore sizes, resulting in higher permeability and selectivity compared to those of a symmetric membrane.

2.2 Zirconia

Zirconia is an oxide of zirconium metal, which occurs in three temperature-dependent crystal structures. Regarding pure zirconia, the monoclinic phase is the most stable structure at room temperature up to 1170°C, while the tetragonal and cubic phases are stable at temperatures of 1170°C to 2370°C and above 2370°C, respectively [7]. Because of the smaller ionic radius of zirconium compared to that of oxygen, zirconia consists of seven-fold coordinated zirconium centres in the monoclinic phase.

However, producing flawless pure zirconia ceramics is impossible, as the phase transformation between the aforementioned phases is accompanied by volume changes. Upon structure transition from tetragonal to monoclinic, the cooling process causes an increase in volume of 4% to 5%, generating internal stresses and inducing sample cracking [7]. To address the issue, a certain amount of yttria is added as a dopant to stabilise the tetragonal and cubic phases of zirconia at room temperature. When zirconia is doped with yttria, some of the zirconium ions are substituted by yttrium ions, creating oxygen vacancies to maintain charge neutrality in the resulting yttria-stabilised zirconia (YSZ). The formation of oxygen vacancies reduces the coordination number of zirconium centres to less than seven, while also decreasing the repulsive forces of oxygen-oxygen bonds, resulting in the arrangement of zirconium and oxygen ions in a more symmetrical order, thus obtaining a stabilised tetragonal or cubic crystal of zirconia at low temperatures [7].

2.3 Membrane fabrication

When preparing a coating solution for membrane fabrication, several aspects should be considered to optimise the approach and achieve the best results.

2.3.1 Particle dispersion

By default, when particles are suspended in a liquid medium, they tend to aggregate due to the van der Waals attractive forces. An approach is to add a dispersant, acting both through electrostatic and steric repulsion, stabilising the dispersion by counteracting the van der Waals forces and preventing particles from aggregating [8].

Similarly, the impact of different pH values on the particle dispersion can be determined by the zeta potential, correlating to the stability of the colloidal dispersion. Zeta potential is defined as the electrical potential difference between the dispersion medium and the outermost layer of fluid attached to the dispersed particle. The electrostatic repulsion between similarly charged particles in a dispersion is determined by the magnitude of the zeta potential, regardless of whether it is positive or negative. A high magnitude indicates stability and thus high electrostatic repulsion, causing the particles to repel each other and preventing aggregation. The commonly measured zeta potential and the stability behaviour thereof are shown in Table 2.1.

Table 2.1: Stability behaviour of a colloid depending on zeta potential [9].

Zeta potential (mV)	Stability behaviour
0 - ±5	Rapid aggregation
±10 - ±30	Incipient instability
±30 - ±40	Moderate stability
±40 - ±60	Good stability
>±60	Excellent stability

Membrane fabrication by applying a particle dispersion as the selective layer often includes binders as an additive, as they induce hydrogen bonds with the dispersed particles, leading to improved tensile strength of the membrane. Moreover, the addition of a binder prevents deformation and cracking during sintering [10]. Binders are classified as organic or inorganic, where organic binders are often preferred due to their lower decomposition temperatures compared to those of inorganic binders.

2.3.2 Coating

Various coating techniques are available for membrane fabrication. Dip coating is among the most common methods, due to the simplicity and low cost of the process. The dip coating process steps begin with slowly immersing a substrate into the coating solution, where it is held for a certain amount of time to allow the dispersion to fully adhere to the substrate. Subsequently, the substrate is withdrawn at a controlled speed and left to evaporate the solvent. The speed in which the substrate is withdrawn dictates the thickness of the coating layer, as faster withdrawn speed results in thicker layers.

2.3.3 Sintering

Thermal treatment is the final process a green membrane body undergoes before it is suitable for filtration applications. Sintering is a process of compacting and forming a solid material by heating it below its melting point. During sintering, the surfaces of the particles fuse together through diffusion, creating *necks* between the particles, while shrinkage occurs and porosity is reduced. As the process continues, the necks increase in size, the green body densifies, and the porosity is reduced further until the end of the process, where big grains form, consisting of the initial smaller grains, and pores are either shrunk drastically or completely eliminated.

3 | Experimental Setup

3.1 Processing of dental zirconia waste

The dental zirconia waste was received in lumps and must be processed before further use. The lumps of dental waste were first crushed manually and then ground into fine powder using a ball mill. As zirconia is placed relatively high on the Mohs scale [11], the container and the grinding balls that were utilised were also made of zirconia, since using equipment of softer materials could cause zirconia to scratch against it and contaminate the ground powder.

3.2 Optimisation of coating procedure and thermal treatment

Prior to the coating procedure, both zirconia powders were examined to obtain optimal conditions for preparing the zirconia dispersion and later the calcination. The particle size of the selected commercial zirconia was labelled below 1 µm, while the dental waste contributed as the smaller particle.

Dynamic light scattering (DLS) analyses were conducted individually on both powders in various pH environments to determine their influence on particle size distribution. Nitric acid or ammonium hydroxide was used to adjust the pH of the samples. The prepared dispersions were diluted tenfold compared to the coating solution to avoid possible aggregation.

Differential scanning calorimetry (DSC) analyses were performed on both powders to measure changes in heat flow as a function of temperature, which were used to determine potential crystal phase transitions and dictated the temperatures at which calcination would be conducting.

3.3 Membrane fabrication

The coating solutions were a mixture of an equal mass ratio of the commercial zirconia and the dental waste, a dispersant, and a binder, dispersed in demineralised water. The amounts of zirconia varied between 14% and 16 wt%, and the dispersant and the binder were both 2 wt%. All amounts were in relation to the total quantity.

The following method was applied to prepare all solutions. First, demineralised water and dispersant were mixed and the pH was adjusted to 10 using ammonium hydroxide under continuous stirring. Then both zirconia powders were added and the pH was adjusted to 10 again. Afterwards, the solution was homogenised using probe sonication for 10 minutes. Finally, binder was added under stirring.

The prepared zirconia dispersion was coated on tubular silicon carbide supports using a lab-made setup, as seen in Figure 3.1.

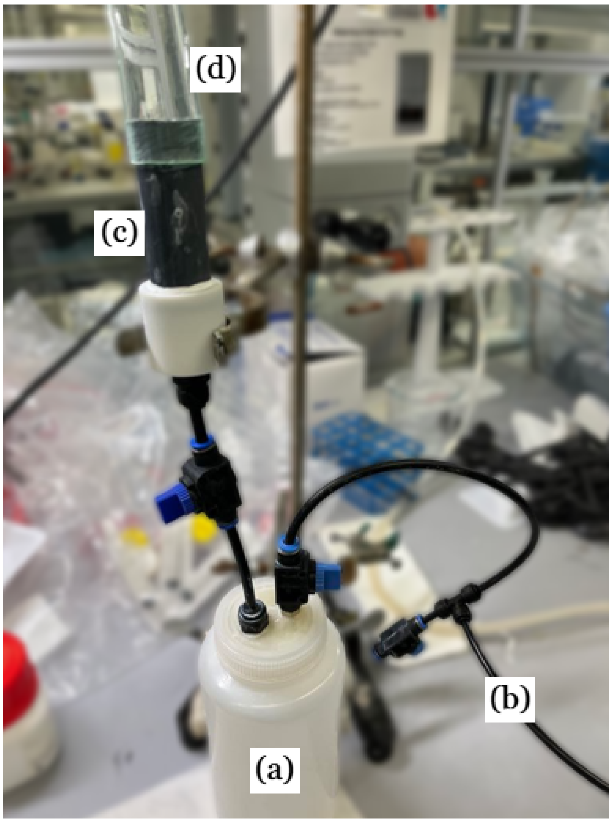


Figure 3.1: Membrane coating setup. (a) Container for coating solution, (b) entry for compressed air, (c) membrane support, and (d) plastic tube.

The coating solution was loaded into the airtight container, in which compressed air was filled in the system, forcing the dispersion to rise and coat the support channels. The pressure of compressed air was increased at a controlled speed until the solution can be seen leaking into the plastic tube, in which the pressure was kept for an additional 5 seconds before being released. Afterwards, the membranes were dried overnight at room temperature and the coating process was repeated with the membrane supports upturned. The reason was to ensure that the zirconia dispersions were deposited as evenly as possible.

Once dried, the membranes were calcined to remove water and organic impurities and solidify the membrane layer. The increase in temperature in the furnace was 2°C / min, the set point temperatures were obtained from the DSC analyses, and the holding time at the set point temperature was 1 hour. Pure dental zirconia waste was also calcined for later analysis.

3.4 Characterisation

The morphology of the final membranes and the crystalline structure of both zirconia powders and the thermally treated dental zirconia waste were analysed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM analyses were performed using a microscope equipped with a backscattered electron detector. XRD patterns were collected with a diffractometer in the diffraction angle range of 20° to 80°, operated at 20 kV and 25 mA with Cu-Kα radiation.

4 Results and Discussion

4.1 Dynamic Light Scattering

To characterise the particle size of both zirconia powders in dispersion under various pH environments, DLS analyses were performed. The examined pH values were in proximity to the value applied in another similar study [2]. Figure 4.1 and 4.2 illustrate the particle size distributions of both zirconia powders dispersed in pH 9, 10, and 11 in addition to the corresponding average particle size.

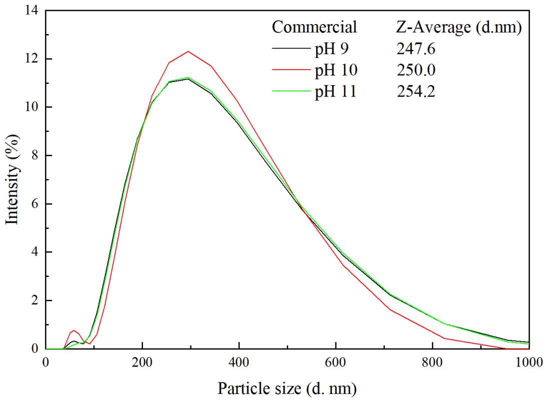


Figure 4.1: Particle size distributions and average particle sizes of commercial zirconia in various pH.

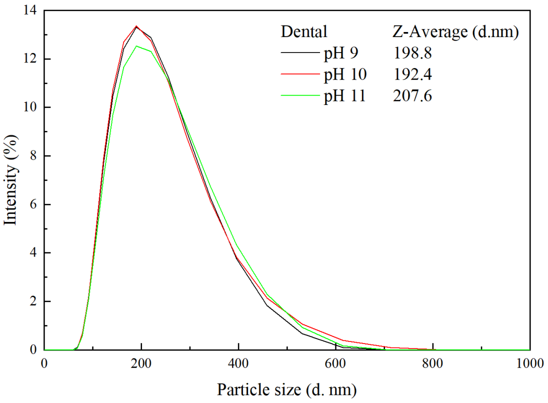


Figure 4.2: Particle size distributions and average particle sizes of dental zirconia in various pH.

For the commercial zirconia powder, a slight increase in the average particle size was detected as the pH increases, suggesting minor aggregation at higher pH, while the average particle size of the dental waste is smallest at pH 10. The changes in the Z-average of both zirconia powders were small enough to determine a stable particle suspension across the pH range. This was further verified by the shape of the distribution curve, as both powders exhibited a single strong peak, indicating uniform particle size distributions. It should be mentioned that the DLS analyses were conducted before the membrane fabrication, meaning the target pH of the coating solution in Section 3.3 was decided from the results presented here. As smaller particles combined with larger ones may produce a membrane layer with smaller pore size, which could improve the overall quality of the final membrane, the pH environment with the biggest difference between the two zirconia powders was chosen for the membrane fabrication, in this case pH 10.

Table 4.1: Difference between average particle size of commercial zirconia and dental waste in various pH. All values are in nm.

	Commercial	Dental	Difference
pH 9	247.6	198.8	48.8
pH 10	250.0	192.4	57.6
pH 11	254.2	207.6	46.6

To determine whether the zirconia powders would behave differently in an acidic setting, an additional analysis was performed at pH 3. Figure 4.3 illustrates the results.

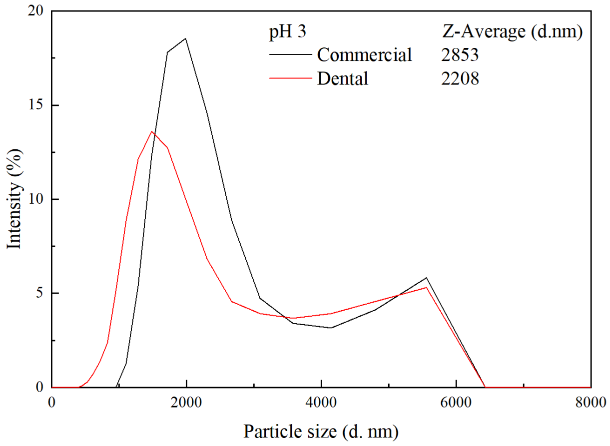


Figure 4.3: Particle size distributions and average particle sizes of both zirconia in pH 3.

In short, the Z-averages were significantly higher compared to the basic samples, indicating severe aggregation. Furthermore, two distinct peaks were observed, implying an unstable particle size distribution, thus deeming low pH to be unsuitable for membrane fabrication.

4.2 Differential Scanning Calorimetry

To identify possible phase transitions upon heating, DSC analyses were conducted on both zirconia powders. The samples were heated up to 1100°C. Figure 4.4 illustrates the results.

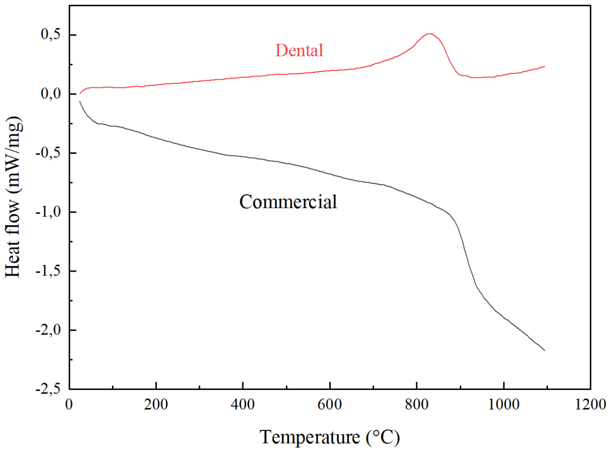


Figure 4.4: DSC curve of both zirconia.

The dental zirconia showed a relatively flat baseline until a sharp endothermic peak was observed at 830°C, suggesting a change in the crystalline structure. The overall minimal heat flow until the observed peak indicated a high thermal stability. The commercial zirconia showed a gradual exothermic behaviour throughout the analysis with a significant increase in energy released at 880°C, suggesting an upcoming phase transition from monoclinic to tetragonal. The steady decrease in heat flow indicated a lower thermal stability than the dental waste.

Further analyses were required to determine the behaviour of the dental zirconia, where the measured temperatures of three specific moments of the analysis were observed. These three points of interest were the beginning of the peak, the exact peak, and the end of the peak, corresponding to 650°C, 830°C, and 900°C, respectively. The dental zirconia and the coated membranes were calcined at these temperatures for further analysis.

4.3 Crystal Structure

The crystal structures of the different zirconia powders were examined by XRD. Figure 4.5 illustrates the XRD spectra of pure commercial zirconia and dental waste in addition to the dental waste thermally treated at 650°C, 830°C, and 900°C, respectively.

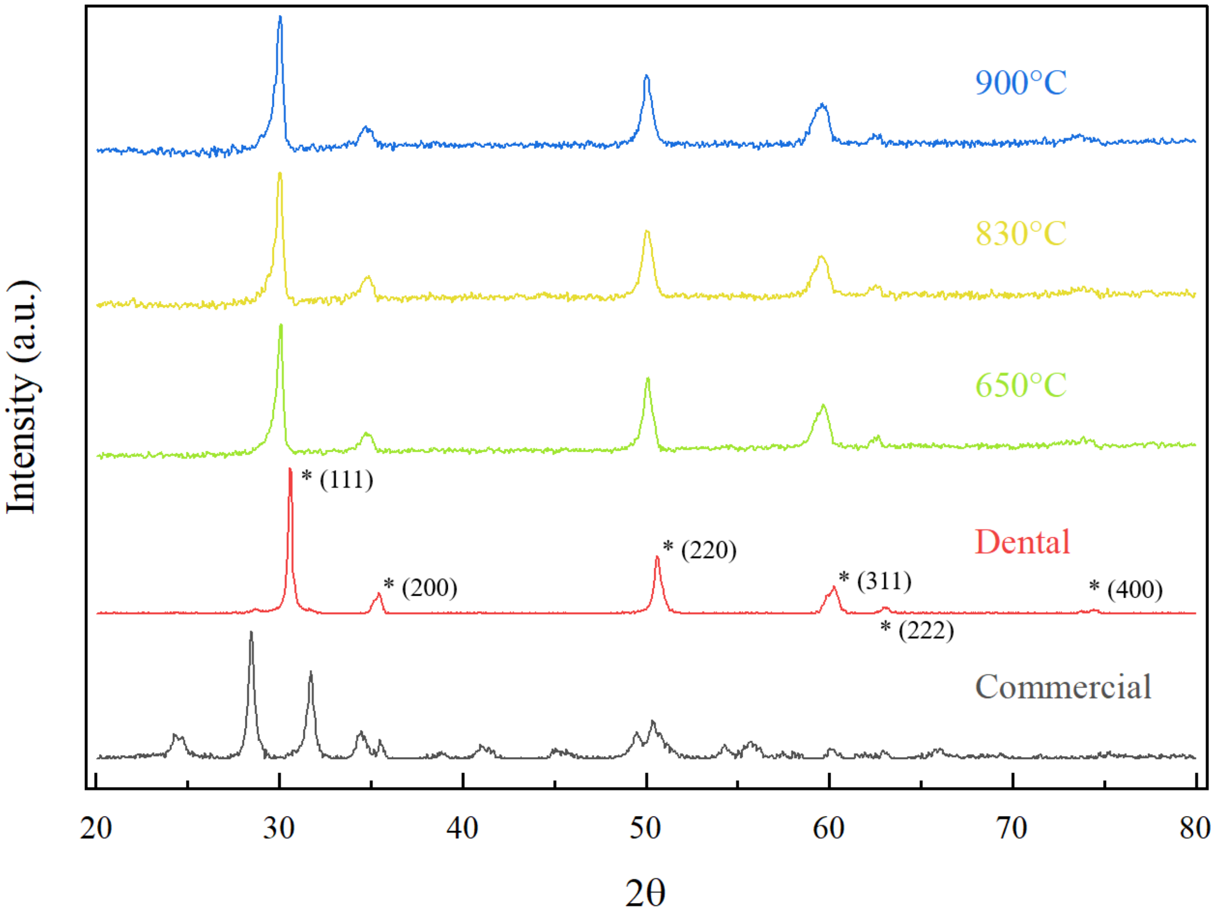
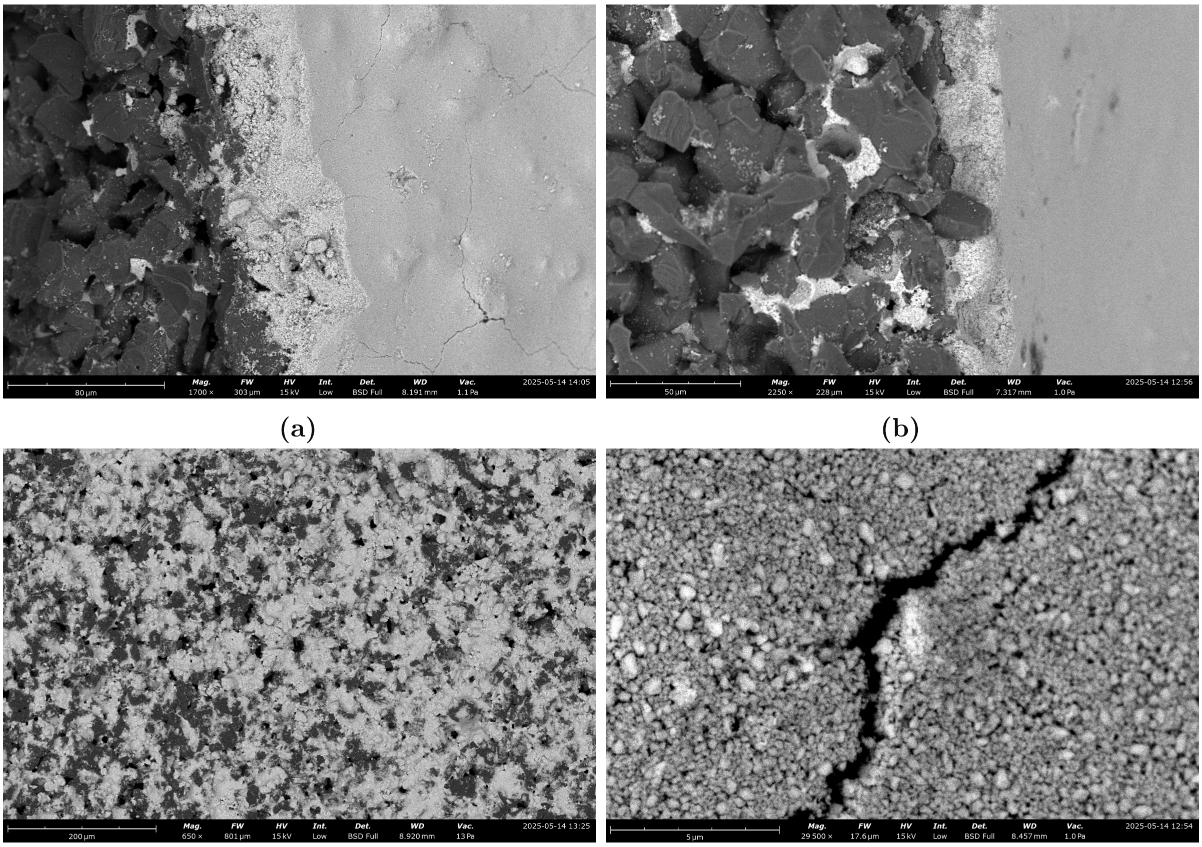


Figure 4.5: XRD spectra of pure commercial zirconia and dental zirconia waste, showing the characteristics of the dental waste before and subsequent to calcination at various temperatures.

The commercial zirconia XRD pattern was predictably characterised by the monoclinic phase, whereas the untreated dental waste was characterised by the cubic phase with diffraction peaks at 2θ of 30.58°, 35.39°, 50.57°, 60.29°, 62.93°, and 74.35°, corresponding to the (111), (200), (220), (311), (222), and (400) lattice planes, respectively. The position of the peaks and the corresponding lattice planes are marked in Figure 4.5. The cubic phase of the dental waste suggested that at least 8 mol% yttria was added as the stabiliser, however, compared to a similar spectrum in an XRD database, the intensities of the observed peaks were lower and the positions were slightly skewed, similar to a pattern characterised by the tetragonal phase, indicating that both crystal phases were present and the yttria content was between 5 mol% to 7 mol% [12]. When the XRD spectra of the thermally treated dental waste were compared with the untreated dental waste, both the intensities and positions of the observed peaks changed slightly in line with the pattern of the tetragonal phase, suggesting the crystals were undergoing phase transition from cubic to tetragonal.

4.4 Scanning electron microscopy

To analyse the morphology of the final membranes, SEM analyses were performed. Some selected micrographs are depicted in Figure 4.6.



(a) **(b)**

(c) **(d)**

Figure 4.6: Selected SEM micrographs.

An even thin layer of zirconia is coated on the silicon carbide membrane support, successfully creating a thin film composite asymmetric membrane, as seen in both Figure 4.6a and 4.6b. However, it is apparent that the zirconia coating has also managed to penetrate the membrane support, as depicted by the white spots intertwining the black grains. This has disastrous consequences if the membranes were used, as not only the zirconia blocking the pores, thereby reducing flux, but fouling now can also occur inside the membrane support, making the cleaning process highly improbable. In Figure 4.6c, part of a membrane is shown as not fully coated, depicted by the black spots, which indicates adjustments to the coating process are needed. Finally in Figure 4.6d, a fine mixture of small and big grains of zirconia can be seen, indicating a stable particle dispersion. However, a large crack is prominent, indicating possible errors during the sintering process.

5 | Conclusion

The findings of this study demonstrate the potential of repurposing dental zirconia waste to fabricate ceramic membranes suitable for UF. Through optimisation of the coating solution composition and calcination conditions, an asymmetric membrane structure was developed using a 1:1 mass ratio of commercial zirconia and dental waste. The DLS analyses confirmed that pH 10 produced the most favourable particle size distribution, with minimal aggregation and distinct size differences between commercial and dental zirconia. This was optimal for forming a compact, effective membrane layer. DSC and XRD revealed that the dental zirconia waste initially contained cubic and tetragonal phases. Upon sintering, these gradually transformed to the tetragonal phase, confirming its high thermal stability and suitability for membrane fabrication.

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