Tailoring the Interfacial Reinforcement Efficiency of Polyvinyl Alcohol Matrix using Refractory Ceramic Nano-fillers

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ABSTRACT: This paper explores polymeric nanocomposites based on refractory ceramic oxides with special emphasis on polyvinyl alcohol (PVA) as the host matrix. The aim of the study is to synthesizing nanoparticles and their nanocomposite membranes for improving the structural, optical and morphological characteristics of nanocomposite membrane. This establishes the foundation by giving an overview of refractory materials and highlighting their important for withstanding high temperatures in a variety of industrial processes along with the literature survey. The area of focus is the incorporation of nanoparticles into a polymer matrix, which provides improved chemical and physical properties. The use of PVA as a host matrix is justified by highlighting its remarkable properties, including mechanical strength, flexibility, and film-forming ability. A thorough explanation of PVA's hydrophilic properties and its wide range of uses from food packaging to sensors, supercapacitors, catalysts, and more is then discussed. It has been noted that the optical properties of nanocomposites have improved with the addition of both organic and inorganic constituents. These nanocomposites therefore have potential applications in a variety of fields, such as gas sensors, solar cells, super capacitors, and flexible electronics.

[Dr Jyotsna Chauhan, akansha mehto, Shaswat Chauhan. Tailoring the Interfacial Reinforcement Efficiency of Polyvinyl Alcohol Matrix using Refractory Ceramic Nano-fillers. *Nat Sci* 2026,24(11):26-35]. ISSN 1545-0740 (print); ISSN 2375-7167 (online). http://www.sciencepub.net/nature 03. doi:10.7537/marsnsj241126.03

Keywords: Tailor; Interfacial; Reinforcement; Polyvinyl Alcohol Matrix; Refractory; Ceramic; Nano-fillers

Introduction: There are different experimental methods utilized for the preparation of nanoparticles and their composite membranes. Sol-gel method was used for producing TiO_2 and ZrO_2 nanoparticles, while solution casting approach was used to prepare PVA and PVA/nanoparticles composite membranes. The solution casting technique is the simplest and most effective technique to get the best possible dispersion of nanoparticles within nanocomposite.

Synthesis of refractory ceramic nanoparticles:

1.1.1. Top-down synthesis methods:

Top-down synthesis methods refer to approaches used in nanotechnology and materials science to create nanoparticles and nanostructures from larger bulk materials. Figure 1.1 illustrates the both top -down and bottom-up processes employed for synthesis of nanoparticles. In these techniques, the starting point is a bulk material, typically a larger solid piece, and the goal is to reduce or modify it to achieve nanoscale dimensions or structures. Common top-down synthesis techniques include etching, lithography and ball milling. Li et al. (2018) synthesized extremely small α-Al_2O_3 nanoparticles of 8 nm through direct ball-milling technique [9]. Wet-chemical etching technique was used by Han et. al. (2012) to prepare spiral shape ZnO nanoparticles [10]. Kim et al. (2014) reported top-down synthesis TiO_2 nanowires by the modified hydrothermal process [11]. Khashan et al. (2021) also reported the Colloidal solutions synthesis containing TiO_2 nanoparticles through the laser ablation performed on a Titanium plate immersed in deionized water [12].

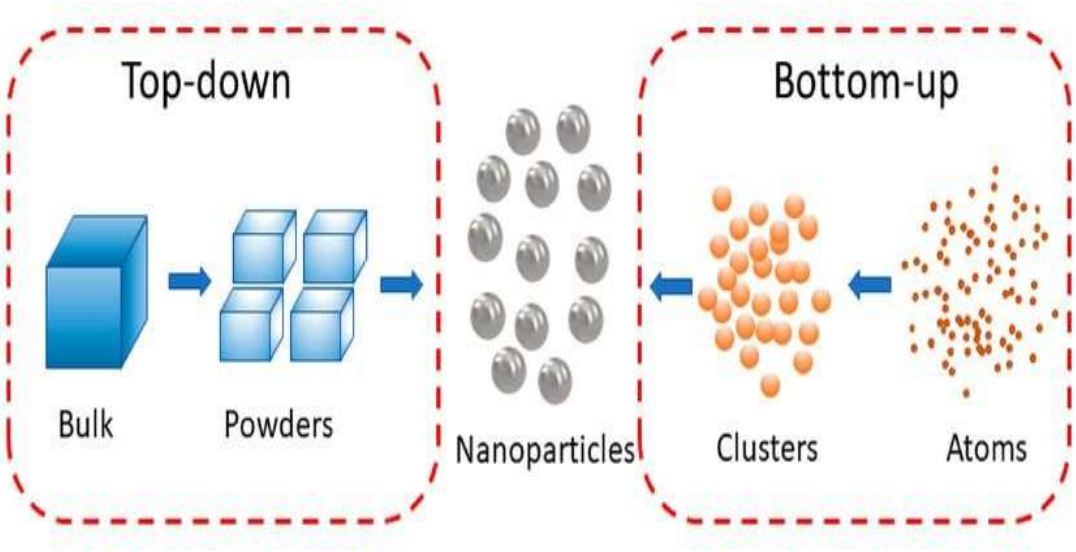


Figure 1.1: Illustrates a schematic diagram representing the nanoparticles synthesis through both top-down and bottom-up techniques [13].

1.1.2. Bottom-up synthesis methods:

Bottom-up method in nanoparticle synthesis entails the meticulously assembling the nanoparticles from their foundational elements, such as atoms or molecules. This approach allows to accurately regulate the nanoparticles dimension, composition and shape, which is essential in various applications. In this approach, nanoparticles are prepared by progressively assembling smaller units into the desired nanoparticle structure. There are two primary classifications of the bottom-up method:

1.1.2.1. Wet chemical method:

These methods typically involve the use of liquid solutions or chemical reactions in a solution or suspension. Examples of wet-chemical methods include chemical precipitation, sol-gel processes, electrodeposition, chemical synthesis, hot-solution decomposition and microemulsion. These techniques enable the controlled assembly of nanoparticles from precursor materials in a liquid medium. Examples of the use of this method include MgO nanoparticle synthesis using a wet chemical technique [14]. The co-precipitation method was utilized Yousaf et al. [2020] to synthesize NiO with its Cu^{+2} and Zn^{+2} derivatives [15]. Through the utilization of ultrasonic-assisted wet chemical process, ZnO and composite of ZnO-ZrO_2 were prepared [16].

1.1.2.2. Sol-gel technique:

Sol-gel technique is a versatile and extensively employed method for fabricating materials, including metal oxides, ceramics. It involves the conversion of a chemical solution (sol) to gel-like material, which eventually into a solid material, such as ceramics. A sol refers to fluid containing dispersed solid particles, while a gel represents a state wherein both solid and liquid elements are evenly diffused in one another, forming a solid framework that contains liquid components. This process is primarily employed for fabricating nanoparticles, thin films, powders, and bulk materials with controlled properties.

The schematic diagram illustrating the Sol gel technique are shown in Figure 1.2. Refractory ceramics nanoparticles, such as TiO_2, SiO_2, Al_2O_3, and ZrO_2, have been successfully synthesized using this technique. Jeevanandam et. al. (2014) utilized sol-gel technique to synthesize TiO_2-MgO nanoparticles with varying magnesium contents [17]. Ahmed et al. (2012) successfully synthesized NiO/TiO_2 nanocomposite through the sol–gel technique, using cetyltrimethylammonium bromide [18]. The synthesis of nanocomposites Al_2O_3–SiO_2–MgO and Al_2O_3–SiO_2 was carried out using the sol–gel technique [19].

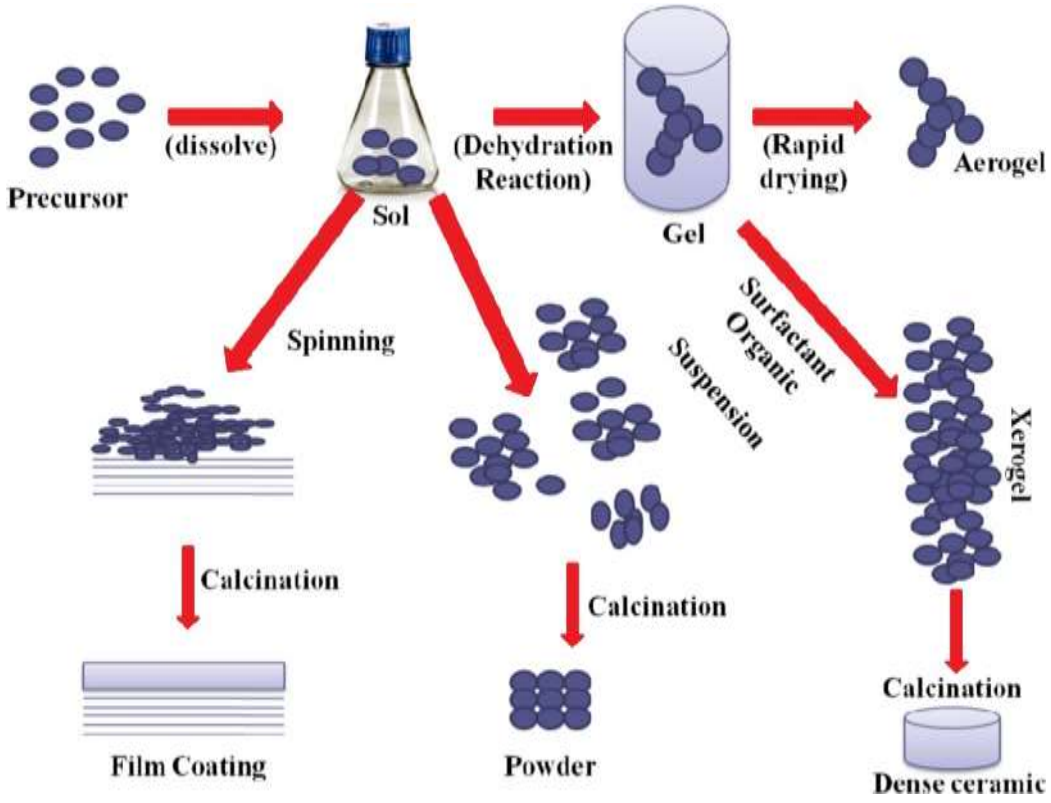


Figure 1.2: Schematic diagram illustrating the Sol gel technique [20].

1.1.2.3. Vapor-phase methods:

In vapor-phase methods, nanoparticles are formed from gaseous precursors. This category includes techniques like the self-assembly of nanostructures in materials produced using methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD), gas-phase aggregation, molecular beam

epitaxy (MBE), sputtering and liquid metal ion sources. These methods are particularly appropriate for synthesizing nanoparticles in a gas-phase environment.

1.2. *Polymer nanocomposite:*

Polymer nanocomposites are advanced materials made via incorporating nanoscale particles (commonly referred to as nanoparticles) within the polymer matrix to increase materials performance characteristics. Polymer nanocomposites formed of two constituents: polymer and nano-fillers. The characteristics of both materials are combined upon the incorporation of nano-fillers into the polymer matrix [21]. Incorporating nanoparticles in the polymer leads to fabrication of a material with exceptional characteristics [22]. A polymer coating (shell) surrounding the particle core is formed owing to filler's enormous surface area [23]. Thickness of the polymer coating layer relies on the size and concentration of the nanofiller.

The fillers' particle size directly impacts the efficient incorporation of nanofillers into polymer matrix. When the filler's particles are smaller, the filler exhibits a larger surface area relative to volume. This increased surface area promotes enhanced contact between the polymer and filler at the interface, ultimately leading to improved filler reinforcement efficiency [24].

Polymer nanocomposites outperform conventional micro and macro composites when it comes to their physical and chemical characteristics [25]. In the polymer incorporating small amounts of nanoparticles leads to a remarkable enhancement in the host polymer's characteristics.
This improvement is attributed to the nanoparticles' tiny size, strong interfacial bonding, high surface-to-volume ratio and quantum confinement effect, Polymer nanocomposite properties can be enhanced through modifying the characteristics of nanofiller, its aspect ratio, and the adhesion among the nanofiller and polymer matrix [26]. The fundamentals of changing properties by incorporating fillers or salts are of interest to basic science researchers [27, 28]. Various factors such as synthesis method, morphology, nanoparticle nature, crystallinity, polymer matrix structure affects the properties of polymer nanocomposites [29, 30].

1.2.1. Properties of polymer nanocomposites:

Polymer nanocomposites have different characteristics from the conventional composite, including -

1. High surface area - Nanocomposite materials possess remarkably larger surface area relative to its volume, accompanied by higher surface reactivity due to nanometric size of particles.
2. Structural stability.
3. They have ability to tune their electrochemical, electronic, and optical properties.
4. Ease of processability.
5. The addition of nanoparticle to the polymer matrices provide the possibility to significantly enhance the optical characteristics even when nanoparticles are present in a small amount.
6. They exhibit excellent stiffness and strength, while using a smaller amount of high-density material. which makes them lighter than conventional composites.
7. Cost-effective manufacturing, robust mechanical strength, and excellent flexibility.
8. Polymer nanocomposites have the ability to significantly enhance material properties like tensile strength, abrasion resistance, conductivity and gas barrier properties.

1.3. *Polymer selection as a host matrix: Polyvinyl alcohol (PVA):*

Polyvinyl alcohol can be defined as a linear polymer, represented by the formula $[CH_2CH(OH)]_n$. Chemical structure of PVA are shown in Figure 1.3.

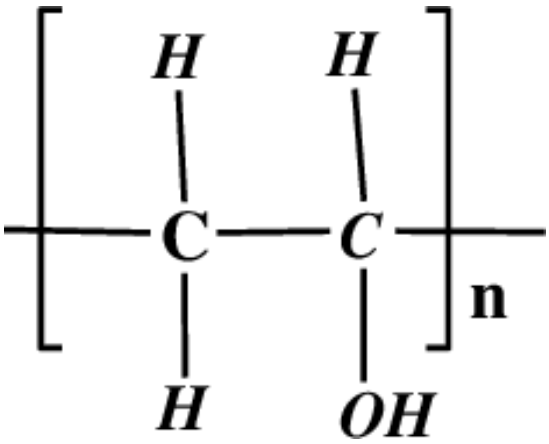


Figure 1.3: The PVA's chemical structure [31].

PVA is fully biodegradable synthetic polymer that is water-soluble, colorless, odorless and its molecule contains vinyl and alcohol groups. The adhesive properties of PVA make it a very useful polymer, PVA is commonly utilized as a glue. PVA glue is devoid of toxic substances. It is easily processable and inexpensive [32-34]. The semi-crystalline characteristics observed in PVA are typically due to the hydrogen bond formation among the PVA chains [35]. PVA exhibits excellent characteristics such as transmission of light, solubility in water and resistance to corrosion [36]. PVA finds usage in multiple applications, encompassing membranes, fuel cells, coatings, adhesives, batteries, sensors, paper making, textiles and biomedical frameworks [37-43]. To improve the structural, morphological, optical, mechanical and thermal properties, a variety of nanofillers are incorporated into the PVA matrix [44].

Additionally, it possesses excellent film forming ability. PVA films are highly optically transparent when the solution casting technique is used to prepare them [45]. As a result, it is well-suited for coating the surfaces of optoelectronic devices, electrical and electrochemical devices, as well as various multifunctional materials [46, 47].

1.5.1 Properties of PVA:

- It exhibits good tensile strength and flexibility.
- It demonstrates good mechanical strength and readily dissolves in water.
- It has ability to resist oils and organic solvents further enhances its utility in specific contexts.
- PVA has a high degree of hydrophilicity, which means it readily absorbs water.
- It exhibits good film-forming properties and can form transparent, flexible films.
- Its ability to form hydrogels is beneficial in biomedical and pharmaceutical field.
- It exhibits good oxygen and aroma barrier properties, making it suitable for packaging of food.

1.1. *Experimental:*

Polyvinyl alcohol (PVA) with a purity of 4 N (molecular weight = 85,000 to 124,000) purchased from Central Drug House (P) Ltd. Titanium tetraisopropoxide (TTIP) used as TiO_2 precursor obtained from Avra Synthesis Pvt. Ltd. Hydrochloric acid (HCl) and distilled water also purchased from Central Drug

House (P) Ltd.

1.1.1. Sol-gel synthesis of TiO_2 nanoparticles:

We used the sol gel method to synthesize TiO_2 nanoparticles. The synthesis procedure flow chart is given in Figure 3.1. For TiO_2 nanoparticles first we have prepared the solution of ethanol and methanol then we add TTIP in the solution while stirring continuously. The mixtures pH were maintained at 2 to 3 through the addition of drop of HCl and we have put the solution on magnetic stirrer for 2 to 3 hours. After that the reaction is stop by adding water and again stirring on magnetic stirrer for 1 to 2 hours. After Ageing at room temperature for three days the sample was dry at 85 °C, at hot plate and then grinding for 30 minutes. For obtain different phases of TiO_2 the sample was calcinated at 300 °C, 600 °C and 1000 °C for brookite, brookite -rutile and rutile phase respectively.

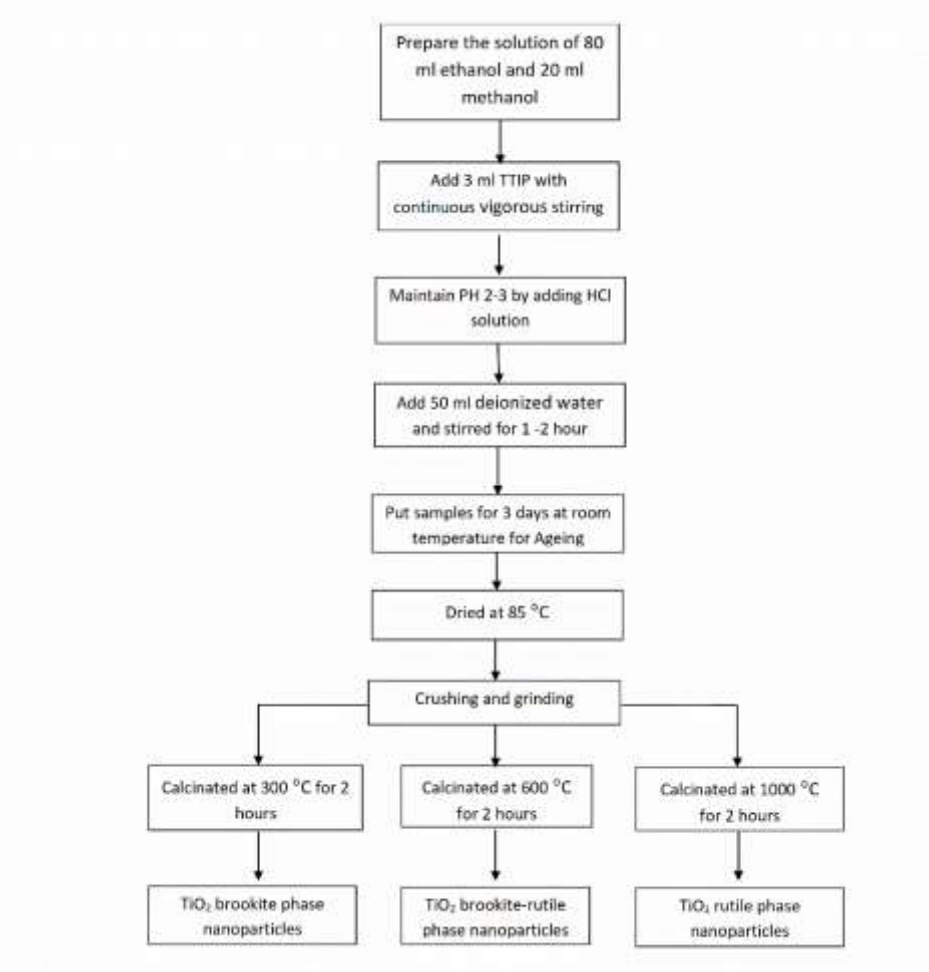


Figure. 3.1: TiO_2 nanoparticles synthesis flow chart.

1.1.2. PVA and PVA/TiO_2 membranes preparation:

Composite membrane of PVA/TiO_2 has been prepared using solution casting process. To obtain pure and homogeneous PVA solution, the process involved, 1 gram of PVA was dissolved in 20 ml of distilled water, then at 80 °C the mixture was continuously stirred until complete transparency was achieved. In

another beaker, TiO_2 (0.05 gram) were mixed in distilled water (10 ml), subsequently, sonicated for 1 h. In order to prepare TiO_2 doped PVA membranes, the two solutions were combined and sonicated the mixture for a duration of 2 hours to achieve TiO_2 nanoparticles uniform dispersion in PVA. The resultant mixture was transferred to a Petri dish then left two days for drying at ambient temperatures. After completely dried, the films were removed out of the Petri dish. The same procedure also repeated to prepare PVA/TiO_2 membrane with different phases of TiO_2 (brookite, brookite-rutile and rutile).

PVA is synthesized through a specific procedure. The key raw material employed in this manufacturing process is vinyl acetate monomer. The fundamental transformation from vinyl acetate to PVA involves a hydrolysis reaction, which entails replacing a hydroxyl group in the vinyl acetate in place of ester group. This reaction is carried out by utilizing aqueous sodium hydroxide. For the completion of reaction, the saponification agent are meticulously introduced. As the reaction progresses, it results in the formation of a tasteless, odorless, granular powder. This powder typically exhibits a white cream color. The final product is obtained through a sequence of steps, including precipitation, washing, and drying.

It is categorized in two grades that include partially and fully hydrolyzed polymers with various intended functional application. Figure 1.4 Illustrates the chemical structure of polyvinyl alcohol: (A) Completely hydrolyzed; (B) Partly hydrolyzed PVA that is partially hydrolyzed used in food. Polyvinyl alcohol has been used in cosmetics, food packaging, pharmaceuticals as well as medical field for many years [48, 49].

Summary:

The present study investigated the doping effects of different phases of TiO_2 upon the PVA membranes structural, morphological, optical and photoluminescence characteristics. TiO_2 nanoparticles prepared by sol-gel technique and different phases successfully achieved by controlling calcination temperature. PVA/TiO_2 membranes were then fabricated by solution casting method. XRD studies confirmed the existence of different phases of TiO_2 nanoparticles in PVA. TEM results indicate that the TiO_2 nanoparticles size increased as the calcination temperature increased. The XRD spectrum also shows that doping enhances the crystallinity of polymer composites. The UV-visible spectra show decrease in optical energy band gap (Eg) with different phases of TiO_2 nanoparticles. AFM results show increased RMS roughness and average roughness values of the surface with respect to the various phases of TiO_2 that affect the crystallinity. FTIR analysis shows charge transfer complex formed through hydrogen bonding among the Ti+ ions of dopant and the OH groups present in PVA. PL study shows that emission peak intensity was lower for PVA/TiO_2 (brookite) composite membrane compare to the PVA/TiO_2 (brookite-rutile) and PVA/TiO_2 (rutile) membranes. This indicates that PVA/TiO_2 (brookite) membrane has higher photocatalytic activity than the other two composite membranes. The enhanced properties of the PVA/TiO_2 composite membranes, which incorporate three distinct phases of TiO_2, offer benefits for a variety of applications.

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