Synthesis of Titanium Dioxide Nanoparticles

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Abstract

Different techniques such as hydrothermal, co-precipitation, chemical vapour deposition, microemulsion and sol-gel among others have been used for the synthesis of titanium dioxide nanoparticles (TiO_2-NPs). Among these, the sol-gel synthesis is a promising method because of its mild experimental conditions. This review summarized this commonly used technique (sol-gel) and other steps via this, for the synthesis of TiO_2-NPs and also facile factors which include pH and calcination temperature that affect synthesized TiO_2 nanoparticles. It was found that these factors affect the agglomeration of titanium nanoparticles.

Keywords: Sol-gel, synthesis, calcination temperature, TiO_2 nanoparticle

1. Introduction

Nanotechnology is a field of science and technology for the production of nanoscale materials with unique properties which are widely used in modern material sciences research. The synthesis involved in the production of these nanoscale-based materials using different techniques including chemical, physical, irradiation, and biological methods have resulted in environmental pollution [1]. Therefore, the quest for clean, safe, eco-friendly, and less or non-toxic techniques for the synthesis of nanoparticles is insatiable. However, through academic and technological research approach, the use of non-toxic, inexpensive, highly photoactive, and easily synthesizable nanoparticles could be obtained.

Titanium oxide (TiO_2) has been considered a non-toxic nanomaterial that possesses a high concentration of hydroxyl groups, stability and catalytic efficiency [2]. Titanium dioxide is also known as titania naturally exists in three forms namely anatase, rutile, and brookite. Both the anatase and rutile forms have tetragonal shapes while brookite has orthorhombic shape. Other phases that can be produced synthetically are TiO_2B, TiO_2H (hollandite-like form), TiO_2R (ramsdellite-like form), TiO_2II (α-PbO_2-like form), akaogiite (baddeleyite-like form, 7 coordinated Ti), TiO_2O, cubic form, and TiO_2 OII (cotunnite $PbCl_2$ like) [3].

There are copious methods of preparing titanium oxide nanoparticles, including sol-gel, hydrothermal, precipitation, chemical vapour deposition, microemulsion, laser ablation and thermal decomposition of organometallic precursor etc. The commonly used methods were hydrothermal, co-precipitation, sol-gel and microemulsion. Among these, the sol-gel method has been found to be the most outstanding due to the generation of high-quality surface morphologies [4].

Titanium dioxide nanoparticles (TiO_2-NPs) have been utilized in industrial and commercial applications for solar cells, memory devices, adsorption of pollutants and wastewater purifications [5-7]. Although, numerous investigations have been carried out on the practical applications of these nanoparticles. The major setbacks have been the cost of the preparation processes. The production of TiO_2 nanoparticles equally faced with these problems. Here, we reported a short review on the commonly used technique for the synthesis of TiO_2 nanoparticles.

2. Methods for TiO_2 Nanoparticles Synthesis

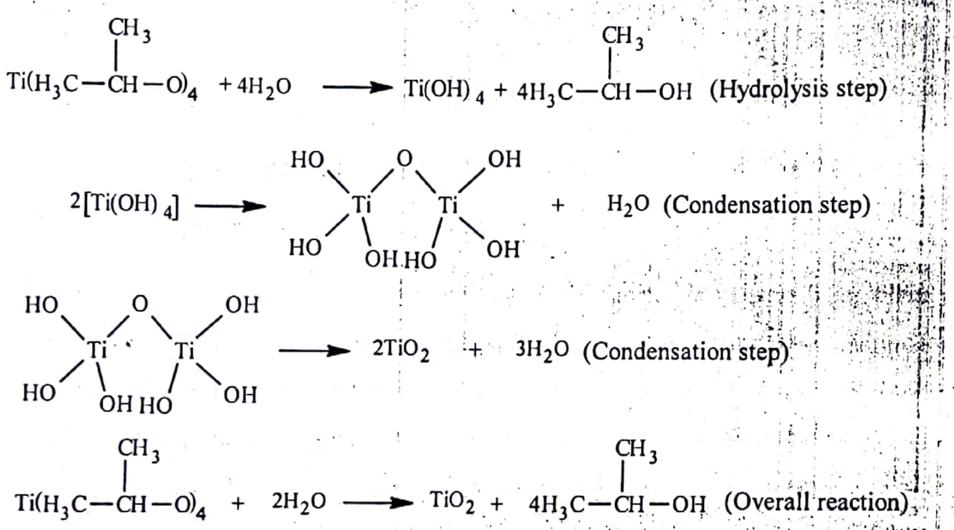
Several techniques have been employed for the synthesis of titanium oxide nanoparticles which include laser ablation, solvothermal, precipitation, sol-gel, hydrothermal, hydrolysis, microemulsion and chemical vapour deposition. These methods have been categorized into three major classes: (1) liquid phase (2) gas phase and (3) vapour phase.

The production of TiO_2 is being certified by their properties, economical operations, and environmental friendliness during application. Thus, among these techniques, wet chemical methods have been known to be the best and these include microemulsion, hydrothermal/solvothermal, precipitation and sol-gel which have been well studied. But the sol-gel method is reported to be simple, economical and most often used to synthesize TiO_2 nanoparticles. However, there are still ongoing researches on the synthesis of TiO_2 using sol-gel. Scholars came up with logical steps in the production of these nanoparticles and were found indomitable in various forms of applications.

2.1 Sol-gel method

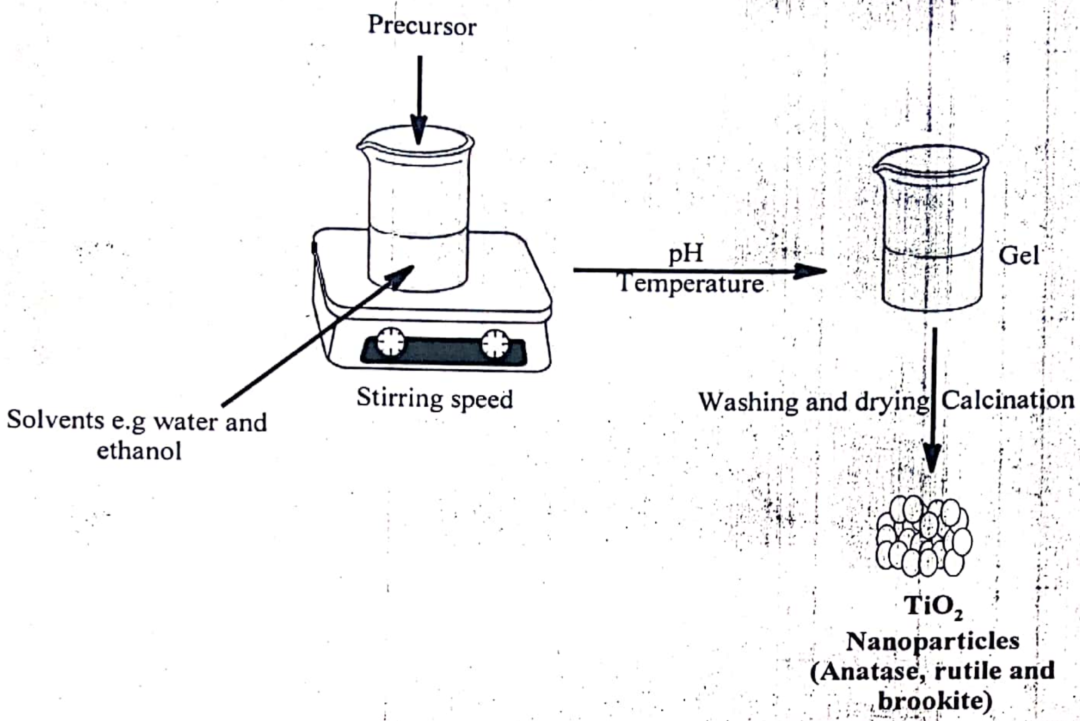
Among the wet chemical methods, sol-gel is a sophisticated method for the production of titanium dioxide. The method helps to control the stability and phase formation of the precursor. During this process, an integrated network gel is produced while the metal alkoxides serve as the typical precursor on the addition of water to form a colloid. The formation of colloid is as a result of hydrolysis and polycondensation reactions. However, the four stages that occur during sol-gel formation are hydrolysis, condensation, growth, and agglomeration of particles.

This process proceeds by hydrolytic polycondensation of titanium precursors being alkoxides or chlorides in the presence of solvents, modifiers, and organic templates. The reaction starts with hydrolysis, which is the formation of Ti-OH moieties by the substitution reaction of water with Ti-OR groups. The precursors undergo condensation reactions to produce Ti-O-Ti by oxolation or Ti-OH-Ti bonds by olation[8]. The mechanisms for the formation of TiO_2 nanoparticles are presented as follows:



Scheme 1: Hydrolysis and condensation reactions of titanium isopropoxide for TiO_2 production [9].

In general, the sol-gel method consists of the transformation of a system from a liquid phase (sol) toward a solid phase (gel).The various precursors such as organic alkoxides and acetates, in addition to inorganic salts like chlorides, are utilized for the synthesis of nanoparticles. Alcohols are greatly used among various kinds of solvents, although some other solvents could be used for some alkoxides as depicted in scheme 2.



Scheme 2: Preparation of TiO_2 nanoparticles using Sol-gel technique

Some parameters such as the order of addition of reactants, the temperature, stirring time, the ratio of water to titanium, the solubility of reagents in the solvent and the pH affect the homogeneity of the gel. Calcination temperature and pH are paramount factors which help in giving the nanoparticles better surface areas. Among the researchers who worked on the production of TiO_2-NPs using the sol-gel method to examine some of the properties of the produced nanoparticles using various instruments such XRD (X-ray diffraction), SEM (scanning emission microscope), PL (photo-luminescence), HRTEM (high-resolution transmission microscopy), BET (Brunauer Emmett Teller), TGA (thermogravimetry analysis) and SAED (selected area (electron) diffraction) were Sharma et al. [4], Kashyout et al. [9], Phonkhokkong et al. [10], Khan et al. [11], Vijayalakshmi and Rajendra [12], Kavitha *et al.* [13], Salah et al. [14] and Bessekhouad et al.[15].

3. Factors affecting TiO_2 nanoparticles

The forms of TiO_2 depends on the arrangement of titanium and oxygen atoms in the crystal lattice. Therefore, it has been reported that the solvent, precursor type, particle size, calcination temperature, pH, additives, and stirring time affect sol-gel synthesized TiO_2 nanoparticle phases [16-17]. It has been reported that the particle sizes of the synthesized nanoparticles produced increase just as their surface areas increase [18-19].

3.1 Effect of calcination

Calcination is a thermal treatment process in the absence or a limited supply of air required for thermal decomposition. The effect of calcination temperature on the phase of TiO_2 from 100 to 1000 °C was evaluated by Pavel and Radovan [19]. The authors reported that at 500 °C, the observed peaks conform to anatase phase but as the peak grows to 800 °C, the anatase phase was transformed to rutile. They concluded that 600 °C was convenient to achieve higher efficiency nanoparticles due to the finer grains of the anatase phase of TiO_2 synthesized. Abdullahi et al. [20] demonstrated the effect of calcination temperature on nanocomposite used in the photocatalytic degradation of phenol under the visible light. The nanocomposite (ZnO/TiO_2) at 600 °C was found to be more effective in the destruction of the pollutant as a result of the formation of hydroxyl radical on the surface of the nanocomposite. They also deduced that the formation of anatase phase enhanced the degradation of the targeted pollutant.

Aphairaj et al. [21] calcined TiO_2 powder at 300-1000 °C. At a temperature of 300-500 °C, the length of the nanotubes-nanofibers structure of the calcined samples was smaller than the sample before calcination and was aggregated. As the temperature increased, the surface morphology of the calcined sample had increased particle sizes attributable to the phase transformation change from anatase to rutile.

Thus, calcination temperature controls the crystalline phase of a nanoparticle of its homogeneity and surface area. Also, the particle size of TiO_2 was found to increase with calcination temperature, suggesting that the effect of different calcination temperatures could help in the degradation of pollutant substances.

3.2 Effect of pH

The pH medium significantly affects crystal structure and surface morphology such as the size and the entanglement of TiO_2 nanostructures [22-24]. Due to the small particle size, the Van der Waals interaction is significant; this interaction increases exponentially as the particle size decreases. These facts favour the growth of clusters. Ibrahim and Sreekantan[25] reported that lower acidity promotes anatase structure while high acidity results in rutile phase formation. This shows that the degree of crystallinity of anatase is pH dependent and lower acidity enhances the crystallinity, which also promotes the formation of big crystallite size. Mutuma et al. [26] reported the formation of pure TiO_2 rutile phase calcined at 800°C and mixed phase (anatase and brookite) at 600 °C in a strongly acidic medium. While in the investigation reported by Cassaignon et al. [27], a rutile crystalline phase was formed at the pH conditions less than 4.5 and only anatase structure formed at pH greater than 4.5.

However, the possibility of anatase structure in acidic medium is apparent. Therefore, investigation of TiO_2 nanoparticles synthesized by a facile sol-gel method under acidic and basic medium is necessary for the clarification of the crystal forms, microstructure and optical properties of TiO_2 nanoparticles.

4. Conclusion

TiO_2-NPs have been extensively investigated during the last decade due to their wide view of applications. In summary, it is observed that the synthesis of this nanomaterial was mostly done using the sol-gel technique due to the high quality of TiO_2 nanoparticles produced. The sol-gel technique has emerged as a promising processing route for the synthesis of nanosized particles because of the simplicity and high purity nanopowders resulting from the availability of high purity chemicals raw materials. Changes in composition, structure, and morphology of the TiO_2 nanoparticle are strictly dependence with the pH and calcination temperature.

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