SYNTHESIS AND CHARACTERIZATION OF ALUMINIUM BASED NANOMATERIALS USING DIRECT HEATING TECHNIQUE

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By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Thesis Title'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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Date: 15 July 2022

Witness by

Supervisor: Assoc. Prof. Ts. Ir. Dr. Pung Swee Yong Signature:

Date: 15 July 2022

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ABSTRAK

Sintesis bahan nano berasaskan aluminium melalui teknik pemanasan terus telah dijalankan dalam kajian ini. Aluminium oksida (Al_2O_3) merupakan sejenis bahan seramik yang mempunyai celah jalur yang lebar (8.3 eV) dan mempamerkan pelbagai sifat seperti kekuatan tinggi, rintangan kakisan yang baik, kekonduksian haba dan elektrik yang rendah serta kekerasan yang tinggi. Oleh sebab it, Al_2O_3 mempunyai pelbagai aplikasi. Sintesis bahan nano Al_2O_3 biasanya dilakukan melalui kaedah hidroterma dan juga pemendapan wap kimia (CVD), namun kaedah ini menggunakan masa yang lama dan kos tenaga yang tinggi. Oleh sebab itu, teknik baharu iaitu teknik pemanasan terus telah digunakan untuk mensintesis bahan nano Al_2O_3 pada wayar Kanthal supaya dapat memendekkan masa sintesis dan mengurangkan kos tenaga tinggi. Bahan nano Al_2O_3 telah disintesis dengan pelbagai parameter berubah supaya dapat memilih sesuatu parameter yang optimum untuk pembentukan bahan nano Al_2O_3 melalui kaedah pemanasan terus ini. Pelbagai kaedah pencirian seperti pembelauan sinar-X (XRD), mikroskop elektron pengimbasan pelepasan medan (FESEM), mikroskop elektron penghantaran (TEM) dengan spektroskopi UV-vis telah digunakan untuk menganalisiskan bahan nano yang terbentuk. Analisis XRD pun telah menentukan bahan nano yange terbentuk merupakan AlOOH dan $Al(OH)_3$ yang mempunyai saiz purata 568.3 ± 235.7 nm berdasarkan keputusan FESEM dan 98.4 ± 35.8 nm berdasarkan keputusan TEM. Batang nano dan partikel nano yang terbentuk melalui paramter optimum mempunyai jurang jalur masing-masing 3.03 eV dan 3.57 eV. Kerja-kerja lanjut perlulah dilakukan untuk mengubahsuai lagi keadaan sintesis teknik pemanasan terus ini bagi mendapatkan bahan nano Al_2O_3 pada masa hadapan.

ABSTRACT

The synthesis of aluminium based nanomaterials via direct heating technique was carried out in this research. Aluminium oxide (Al_2O_3) is a ceramic material with a wide bandgap (8.3 eV) that exhibits many unique properties such as high strength, good corrosion resistance, low thermal and electrical conductivity as well as high hardness, hence having a wide range of applications. Synthesis of Al_2O_3 nanomaterials were usually done through hydrothermal and chemical vapour deposition (CVD) methods, however these methods are mostly high energy consumption and time consumption. Hence, direct heating technique was developed in order to synthesize Al_2O_3 nanomaterials on kanthal wire with a much lower energy consumption rate and shorter duration. Synthesis parameters such as change in precursors, concentration as well as synthesis duration were systematically studied to determine the optimum parameter for Al_2O_3 nanomaterials formation. Various characterization methods such as X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and UV-vis spectroscopy were used to characterize the as-grown nanomaterials. Nevertheless, the XRD analysis indicates that as-grown nanomaterials were Al-based, i.e. AlOOH and $Al(OH)_3$ with average size of 568.3 ± 235.7 nm based on FESEM and 98.4 ± 35.8 nm based on the TEM result. The optimum synthesis parameter were determined to be 30 min synthesis duration using 0.008 mol of $Al(NO_3)_3$ precursor. The nanorods and nanoparticles formed have bandgaps of 3.03 and 3.57 eV respectively. Further works need to be done to further improve the synthesis condition of direct heating technique in order to obtain Al_2O_3 nanomaterials.

CHAPTER 1 INTRODUCTION

1.1 Background

Aluminium oxide (Al_2O_3) is a ceramic material with wide bandgap (8.3 eV) (Uchikoshi et al., 2014). It exhibits many unique properties, for instances, good mechanical strength (300 - 630 MPa), good corrosion resistance as well as low electrical conductivity (10^{-13} $\Omega^{-1}m^{-1}$) and thermal conductivity (30 $Wm^{-1}K^{-1}$) (Coderman, 2022). As a results, Al_2O_3 has been used as electrical insulator (Ceramics, 2022), pigment in paint to improve reflectivity (Hughes, 2022), composite fiber (Mallick, 2007) and body armor (Coderman, 2022). Also, it poses good hardness value (54 HRC) and thus it is also used as abrasive materials and as a component in the cutting tools (AZoM, 2022). The production of Al_2O_3 is commonly based on Bauxite process. In this process, a mixture of mineral ores such as gibbsite, bauxite, diaspore and sodium hydroxide are melted in furnace. The [$Al(OH)_3$] precipitates, which is the main component from the melting, will be calcined at 1100 ^oC to produce Al_2O_3 (Worldofchemicals.com , 2022). The whole production of Al_2O_3 incurs high equipment and operational cost.

Synthesis of Al_2O_3 nanomaterials is getting research focus recently. It is noted that addition of Al_2O_3 nanomaterials into the coatings allows increase in the corrosion resistance, scratch resistance, abrasion resistance and UV-resistance of the coating (Dhoke et al., 2009). Furthermore, Al_2O_3 thin films have been used as electrical insulator in integrated circuits as well as insulating barrier in capacitors thanks to its properties of being a dielectric material (Belkin et al., 2017). Besides, Al_2O_3 particles

are used as an effective catalyst in Claus process for production of sulphur from H_2S attributed to its high specific surface area (> 100 m^2/g) and activity associated with defects that enhanced its catalytic properties (Busca, 2014).

Due to the fact that Al_2O_3 nanomaterials having a wide range of applications, multiple approaches of synthesizing Al_2O_3 nanomaterials had been done throughout the years by different researchers to obtain Al_2O_3 nanomaterials with suitable size and properties for the meant applications. Despite the fact, most synthesis methods of Al_2O_3 nanomaterials involve in either having long synthesis duration (> 1 hour) or being very costly, or even both. For example, atomic layer deposition (ALD) method is one of the method of synthesizing Al_2O_3 thin film (Avci et al, 2011). This method despite of its capability of forming films that are as thin as atomic scale, it would require a long period of time, costly operating conditions and costly chemicals for the entire process just to form a single layer. Hence, this project focuses on developing an alternative synthesis method that is capable of forming Al_2O_3 nanomaterials with a much simpler set up, rapid synthesis process as well as less costly.

Direct heating technique is the method that was used in this project to synthesize the Al_2O_3 nanomaterials. As the name implied, this synthesis technique directly heats a solution containing the precursors by using a highly resistive wire that is connected to an AC power supply. The highly resistive wire used in this project was kanthal with electrical resistivity, ρ of 1.45 Ωm. The composition of kanthal consists of 20-30% chromium, 4-7.5% aluminium and 62.5-76% iron. It displays good resistant to oxidation and corrosion. It is a common substrates use as a heating element.

In direct heating technique, the heat that is generated from the wire and subsequently transfer to the precursor solution via conduction and convection. The general idea of the method is very similar to a heating coil in a boiler, where the heating coil would be generating heat and boil the water as the heat energy was transferred from the coil to the water. Unlikely other synthesis techniques such as CVD and hydrothermal, there is minimum loss of heat energy to the environment. The heat generated by the wire would directly heat up the precursor solution. This would provide sufficient energy for the precursors in the solution to overcome its activation energy and trigger the chemical reactions to grow Al_2O_3 nanomaterials (a) on the surface of kanthal wires and (b) in the precursor solution (as by-product). Till now, this technique has not been widely explored for the growth of nanomaterials. For instances, Lee et al. (2017) had used this method to synthesize vertically aligned ZnO nanorods on stainless steel meshes; Chiam et al., (2021) produced TiO_2 particles and MnO_2 particles (Chiam & Pung, 2021) by this technique. There is no report on the synthesis of Al_2O_3 nanomaterials using Direct Heating technique. Hence, the potential of Direct Heating technique would be studied to grow Al_2O_3 nanomaterials in this project.

1.2 Problem statement

Long synthesis duration and high synthesis cost to produce Al_2O_3 nanomaterials

Al_2O_3 nanomaterials were synthesized by many methods as summarized in Table 1.1. For examples, Park and Choi (2014) produced Al_2O_3 nanotubes using CVD method. It took 7.5 hrs to complete the whole synthesis process. The tube furnace was costly, ranging from RM 60,000 to RM 160,000. The operational cost was high as a typical tube furnace would consumed 22.5 kWh electric power for one cycle of synthesis process. Bell et al. (2017) synthesized Al_2O_3 nanorods using hydrothermal method. It took them 10 hrs up to 80 hrs in order to complete the synthesis duration. Similar method was used by Wang et al. (2013) to synthesize Al_2O_3 nanorods that took 24 and 36 hrs synthesis duration. The equipment for hydrothermal process was also costly. The autoclave uses in this process is from RM 150 to RM 2,000. The operational cost was high as normally autoclave would consume 1.5 kW to 6 kW depending on its size and the specific heat of the solution in the autoclave. In another example, Kusama et al. (2020) synthesized Al_2O_3 nanoparticles using sonochemical route. The synthesis duration was 1 hr and the power consumption was estimated to be 0.5 kWh. Although this process took shorter synthesis duration and lower operation cost, the equipment used in sonochemical method was estimated to be range from RM 4,800 to RM 40,000. Tok et al. (2006) had also synthesized Al_2O_3 nanoparticles using spray pyrolysis method, although the synthesis duration is not specified, however, the equipment that were used cost a fortune of RM 9,000 up to RM 80,000 depends on the scale of the equipment that were used. Electrospinning method of synthesizing nanorods would incur a cost of RM 75,000 to RM 270,000 for the equipment used for the synthesis. On

the other hand, sol gel method for synthesis of nanomaterials although did not incur much cost on the equipment, they are known for their long synthesis duration, taking an example, Shojaie-Bahaabad and Taheri-Nassaj (2008) took over 52 hrs just to synthesis Al_2O_3 nano powder via sol gel method from aluminium chloride hexahydrate, aluminium powder and hydrochloric acid.

Table 1.1 : List of cost and power consumption of various synthesis methods

Synthesis method	Duration (hrs)	Equipment cost (RM)	Estimated electricity consumption (kWh)	Electricity cost per synthesis* (RM)	References
Hydrothermal	10 - 80	150 - 2,000	15 - 120	5.7 - 45.60	Bell et al. (2017)
Hydrothermal	24 - 36	150 - 2,000	36 - 52	13.68 - 19.76	Wang et al. (2013)
Sol gel	52	-	-	-	Shojaie-Bahaabad & Taheri-Nassaj (2008)
Sonochemical	1	4,800 - 40,000	0.5	0.19	Kusama et al. (2020)
Chemical vapour deposition	7.5	60,000 - 160,000	22.5	8.55	Park and Choi (2014)
Spray pyrolysis	-	9,000 - 80,000	-	-	Tok et al., (2006)
Electrospinning	0.5	75,000 - 270,000	0.013-0.04	~0.01	Kang et al. (2011)
Direct heating	< 2	~ 900	< 0.12	0.05	-

*Taking RM 0.38 per kWh industrial rate for electricity bill (TNB, 2022).

Hence, a simpler set up, rapid synthesis and less energy consumption of Al_2O_3 nanorods fabrication method is proposed. The direct heating technique seems to be a promising method as it has a relatively simple set up compared to the CVD method and it would theoretically require lesser electrical power in order to synthesize nanostructures in a shorter duration. The cost of equipment is RM 900 (regulator and multimeter). The heating power is 50-60 W. It is estimated the synthesis of Al_2O_3 nanomaterials would take less than 2 hrs. Till now, no report has been found on the synthesis of Al_2O_3 nanorods using direct heating technique.

1.3 Research objectives

1. To develop direct heating technique for the synthesis of Al based nanomaterials, and

2. To characterize the structural and optical properties of Al based nanomaterials that grown on kanthal coils and nanoparticles (by product).

1.4 Scope of study

In this research, Al based nanomaterials were deposited on kanthal coils using direct heating method. The effects of types of precursors, heating power and heating

duration on the growth of Al based nanomaterials on kanthal wires were systematically studied. In addition, the nanoparticles (by-products) that was collected at the bottom of beaker after direct heating process would be analysed. The structural and optical properties of these products were characterized using various characterization techniques such as X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM) / Energy dispersive X-ray (EDX), Transmission electron microscopy (TEM) and UV-Visible light spectroscopy respectively. Next, the photocatalytic performances of these Al based nanomaterials in degradation of methylene blue dye was accessed.

1.5 Thesis outline

This thesis comprises 5 chapters. Chapter 1 introduces the research background, problem statement, research objectives and the scope of study. Chapter 2 presents the literature review in details on the topics related to structural and crystal properties of Al_2O_3 and its oxyhydroxides, synthesis methods and applications of Al_2O_3 nanomaterials and the dye removal application via photodegradation. Chapter 3 states the materials, synthesis and characterization methods used for the synthesis of Al based nanomaterials in this project. Chapter 4 discusses the experimental results that are obtained from this research. The data analysis and findings in relation to the theoretical body of knowledge are addressed in this part. Finally, Chapter 5 summarizes the highlights of this research as well as recommendation for future works

CHAPTER 2 LITERATURE REVIEW

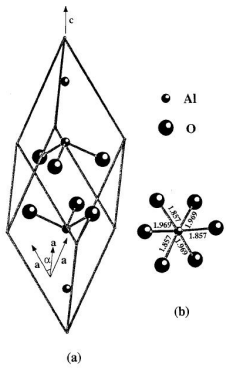
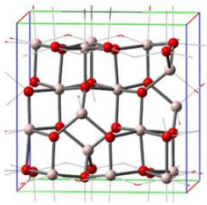
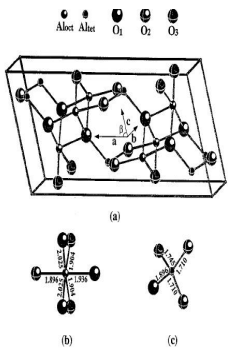
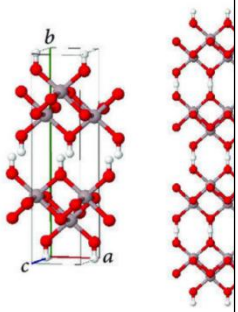
2.1 Aluminium oxide (Al_2O_3) and AlOOH

Aluminium oxide (Al_2O_3) consists of multiple crystalline phases, namely α-, β-, γ-, δ-, η-, θ-, χ- and κ-phase. Despite Al_2O_3 may consist of many different polymorphs, the most important and common polymorphs are the α-, γ-, θ- and κ-phase (Andersson, 2005). The α-phase is the most thermodynamically stable polymorph. It has a rhombohedral corundum crystalline structure, while all the other crystal phases are metastable in bulk form. Nevertheless, these crystal structures can still be produced in minor scale, where thermal equilibrium is not reached. According to Andersson (2005), the α- and the κ-phase are widely used as wear resistant coatings due to their high hardness and thermal stability, whereas the γ- and θ-phase are mostly used for catalytic applications due to their low surface energies, which also leads to having larger active surface areas that are available for catalytic reactions. Besides that, aluminium oxyhydroxide such as boehmite (AlOOH) is also used for applications such as catalyst and adsorbent due to its high specific surface area of 43.5 m^2 g^{-1} (Wang et al., 2021). Oxyhydroxide of aluminium is the precalcination form of Al_2O_3 and it is usually synthesized via similar methods with the Al_2O_3 just without the calcination step. Some intrinsic properties of these Al_2O_3 polymorphs and aluminium oxyhydroxide are shown in the Table 2.1.

In this project, the Al_2O_3 nanomaterials were synthesized for wastewater treatment usage, hence only γ- and θ-phase of Al_2O_3 as well as aluminium oxyhydroxide are of interest as they are the only few common polymorphs of Al_2O_3 that

are used in catalytic purposes. However, in this project, γ-phase Al_2O_3 was chosen to be primarily focused to produce as it was the first intermediate state during phase transformation of Al_2O_3 from boehmite (AlOOH) which makes it the easiest to be formed. Besides, the lower temperature (450 °C) required for calcination of γ-phase Al_2O_3 when compared to θ-phase Al_2O_3 (1000 °C) also allows it to be obtained at a much lower cost. The phase transformation temperatures of various polymorphs of Al_2O_3 is shown in Figure 2.1.

Table 2.1 : Intrinsic properties of Al_2O_3 polymorphs and aluminium oxyhydroxide (Ching & Xu, 1994; Mei et al., 2019; Mo & Ching, 1998; Smrcok et al., 2006; Jbara et al., 2019; Abram et al., 2016; Fankhanel et al., 2016).

Phases	α-phase	γ-phase	θ-phase	Boehmite, AlOOH
Crystal structure	Rhombohedral 	Spinel 	Monoclinic 	Orthorhombic 
Lattice constant (Å)	a = 5.128	a = 7.938	a = 11.795 b= 2.910 c = 5.621	a = 3.693 b= 12.221 c = 2.865

Refractive index	1.774	1.806	1.922	1.655
Dielectric constant	3.86	3.259	3.694	5.5-6.5
Density (g/cm^3)	3.984	3.65	3.615	3.07

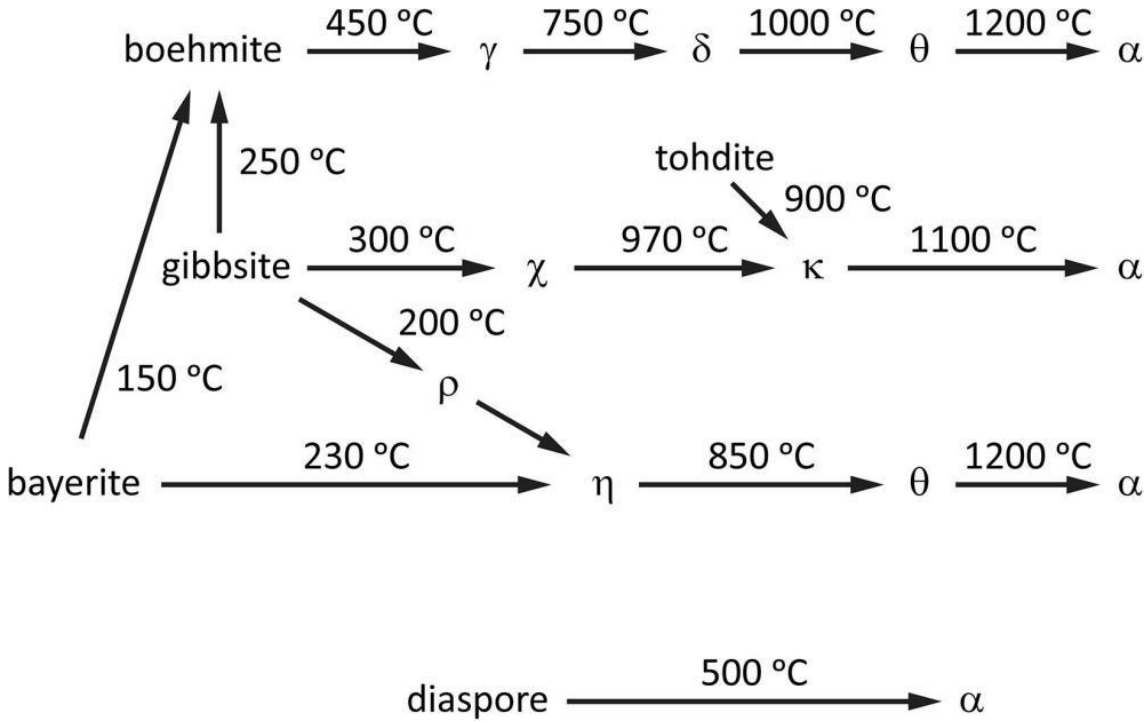


Figure 2.1 : Phase transformation temperatures for Al_2O_3 (van Gog, 2021).

2.2 Synthesis methods of Al_2O_3 nanomaterials

Various techniques have been used by researchers in order to synthesize nanostructured Al_2O_3 throughout the past few decades. Among the nanostructures

produced are nanorods (Wang et al., 2013), nanofibers (Han et al., 2007), nanoparticles (Kusama et al., 2020) and also nanoporous (Farahmandj and Golabiyan, 2015) which can be seen from Figure 2.2.

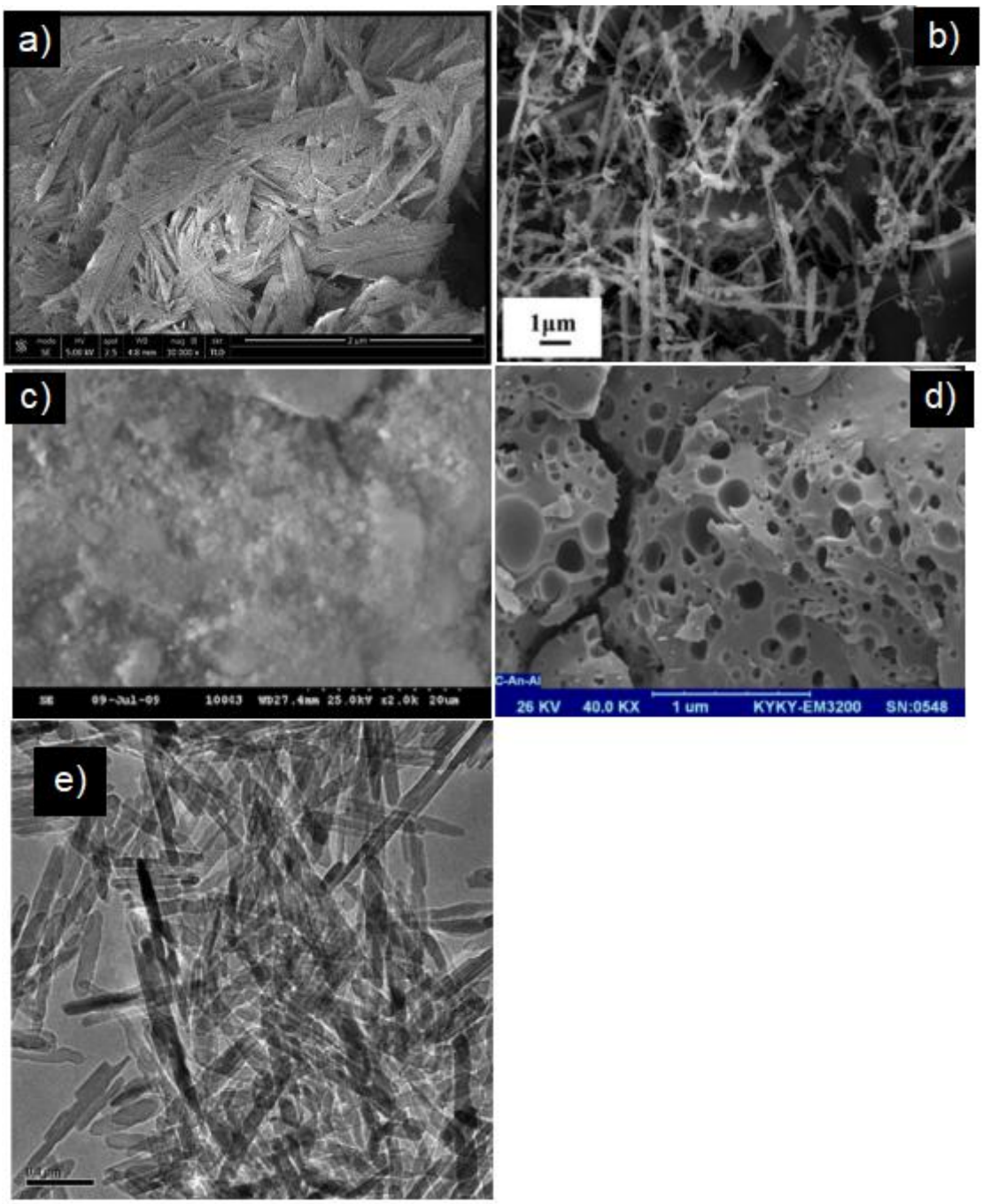


Figure 2.2 : SEM and TEM image of Al_2O_3 (a) nanorods, (b) nanotubulars, (c) nanoparticles, (d) nanoporous and (e) nanofibers synthesized by various researchers

(Wang et al., 2013; Park and Choi, 2014; Kusama et al., 2020; Farahmandj and Golabiyan, 2015; Han et al., 2007).

These synthesis methods of the nanomaterials would greatly affect the properties of the nanomaterials such as their morphology (e.g. nanorods or nanoparticles), crystal phase (e.g. α-phase or γ-phase), size (e.g. 7 nm or 200 nm) and also crystallinity (e.g. crystalline or amorphous. It is crucial as these factors would affect the properties of the nanomaterials. The synthesis methods used to produce Al_2O_3 nanomaterials are hydrothermal method (Buwono et al, 2021; Bell et al., 2017), sol-gel method (Farahmandjou and Golabiyan, 2015; Rogojan et al., 2011; Shojaie-Bahaabad and Taheri-Nassaj, 2008), sonochemical method (Kusama et al., 2020), Chemical vapor deposition method (Park and Choi, 2014), pyrolysis method (Tok et al., 2006) and electrospinning method (Kang et al., 2011). The working principles of these synthesis methods will be discussed in the following sections.

2.2.1 Hydrothermal method

Hydrothermal is a solution based synthesis method that involves in crystallization of anhydrous materials from aqueous solution at above ambient temperature (> 100 °C) and pressure (> 1 atm) (Behera et al., 2016). The synthesis is usually performed in sealed steel cylinders that are known as autoclaves. These autoclaves can withstand high temperatures and high pressures for long processing time. The main process parameters that can be controlled in the hydrothermal synthesis method are the initial pH of the medium, the temperature as well as the pressure used for synthesis. Figure 2.3 shows a schematic diagram of an autoclave setup for hydrothermal synthesis process.

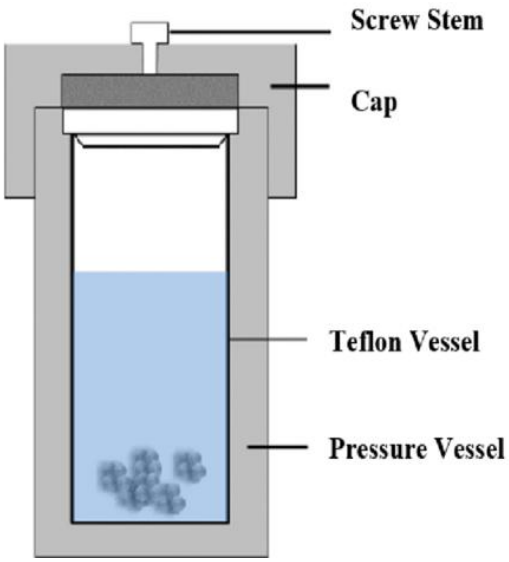


Figure 2.3 : Schematic diagram of a typical setup for hydrothermal process (Ijaola, 2020).

The γ-Al_2O_3 nanoparticles had been successful hydrothermally synthesized by Buwono et al. (2021) using aluminium nitrate nonahydrate and aqueous ammonia, with different reaction durations and temperatures in order to study their effect on the size as well as the crystallinity of the γ-Al_2O_3 nanoparticles. Similar to the above study, Bell et al. (2017) had hydrothermally synthesized γ-Al_2O_3 nanorods using different temperatures (170 to 200 °C) and durations (10 to 80 hours) to study their effect on the shape, size and structure of γ-Al_2O_3 nanorods as displayed in Figure 2.4 (a). On the other hand, Wang et al. (2013) also successfully synthesized mesoporous γ-Al_2O_3 nanorods by hydrothermal method using aluminium nitrate nonahydrate and ammonium carbonate as their precursors as shown in Figure 2.4 (b).

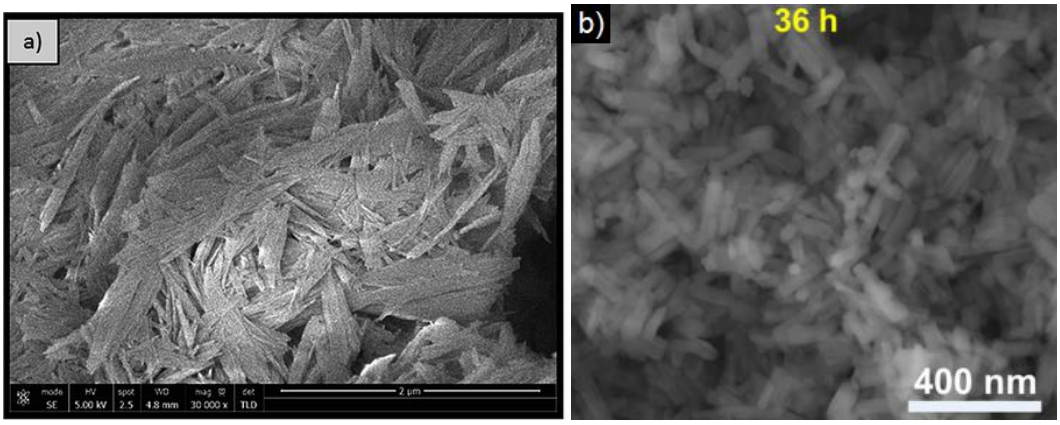


Figure 2.4 : SEM image of (a) γ-Al_2O_3 nanorods synthesized by Bell et al. (2017) and (b) γ-Al_2O_3 nanorods synthesized by Wang et al. (2013) (Bell et al., 2017; Wang et al., 2013).

2.2.2 Sol-gel method

Sol-gel method is a colloidal process involves in polycondensation reaction between the molecular precursors (sol) in order to form oxide network solid phase (gel). The sol-gel process starts from preparing a homogeneous solution of precursors and alcohols, which solvents are used to dissolve the precursors. There are 2 general kinds of precursors, which are the metallic organic precursors that need to be dissolved in a water-soluble organic solvent and the metal salt precursors that are directly soluble in water (Bokov et al., 2021). Then, it will follow a hydrolysis reaction, where water will breakdown the precursors and the metal oxide particles would form and come together to form fine solid particles that is dispersed in the solvent (sol). The homogeneity of the sol can be controlled by additives such as urea and citric acid, which will help in controlling the complexification and condensation of the precursor solution by changing its crystallization kinetics (Behera et al., 2016). Condensation reaction would then occur

to form links between the particles. At the end of the synthesis process, larger particles are formed while water is removed in the process. This slowly forms a giant molecule which has many pores. The pores traps the solvent inside, and thus it is also known as wet gel. After removal of water via various drying method depending on the solvent, a dry gel can then be formed. Lastly, calcination is done to obtain the desired metal oxide nanostructures. Figure 2.5 below shows a typical process flow for sol-gel synthesis.

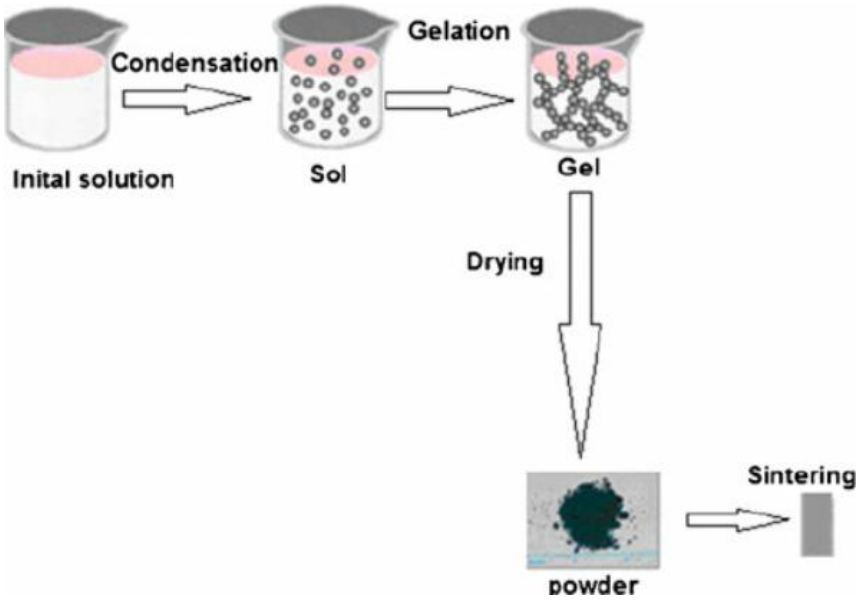


Figure 2.5 : Schematic diagram of process flow for sol-gel synthesis method (Yahia, 2013).

In the research of Farahmandjou and Golabiyan (2015), Al_2O_3 nanoporous in Figure 2.6(a) were synthesized using 18.75 g of $Al(NO_3)_3 \bullet 9H_2O$ that dissolved into 100 ml of pure water and stirred, then adding 28 g of aluminium isopropoxide. After 5 minutes, 5 ml of 2-ethilenlycole was added drop by drop into the solution as well as the synthesis temperature was increased to 90 °C. The pH of the solution was adjusted to 3 during the synthesis (Farahmandjou and Golabiyan, 2015). On the other hand, Rogojan et al. (2011) synthesized Al_2O_3 nano-powders via 2 different types of precursors, i.e.

organic (aluminium triisopropylate) and inorganic (aluminium chloride) based. They were able to obtain Al_2O_3 nanopowder in the range of 2 to 12 nm in size as shown in Figure 2.6(b) (Rogojan et al., 2011).

Al_2O_3 nano powders with size ranging from of 32 to 100 nm were synthesized by Shohaie-Bahaabad and Taheri-Nassaj (2008) via sol gel method using aluminium chloride hexahydrate, aluminium powder as well as hydrochloric acid. The precursors were produced from mixing aluminium chloride hexahydrate with aqueous hydrochloric acid and aluminium powder added gradually into the solution. The precursor solution was stirred and heated at 95 °C for 4 hrs and the gel formed was dried at 85 °C for 48 hrs before calcination.

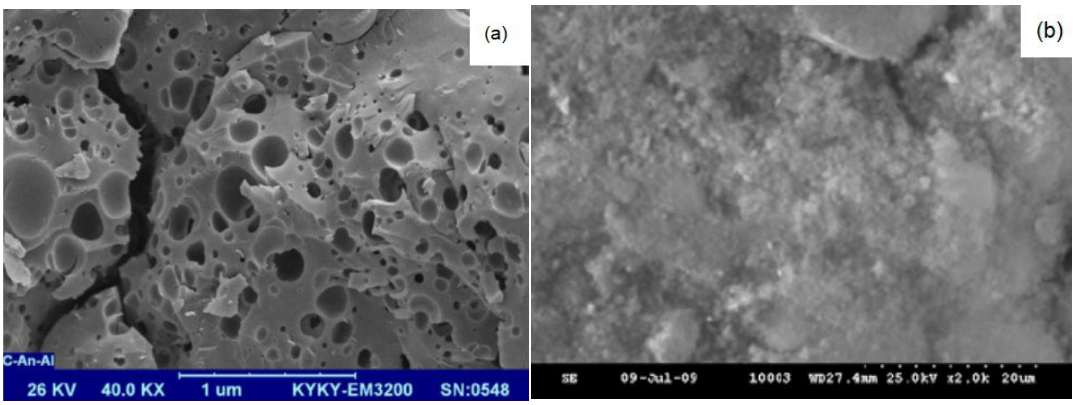


Figure 2.6 : SEM images of sol-gel synthesized (a) Al_2O_3 nanoporous, (b) Al_2O_3 nano-powders (Farahmandjou and Golabiyan, 2015; Rogojan et al., 2011).

2.2.3 Sonochemical method

Sonochemical method uses powerful ultrasound radiation that ranges from 20 kHz to 10 MHz in order to undergo chemical reaction for the synthesis of nanomaterials (Qiao, Liu and Lu, 2011). During the sonochemical process, a physical phenomenon known as acoustic cavitation occurs. Acoustic cavitation is the formation and collapse of bubbles in liquid irradiated by intense ultrasound (Yasui, 2010). As the speed of the bubble collapse, it becomes a quasi-adiabatic process where the temperature and pressure of the interior of the bubble can be raised up to thousands of Kelvin and thousands of bar. This allows high energy spots to exist in the solution and causes chemical reaction to occurs in these spots. In fact, any water vapour and oxygen that present would dissociate into the bubble and creates oxidants such as OH, O, and H_2O_2 that would then dissolve and react with the surrounding liquid and solute to undergo what we called as sonochemical reaction (Yasui, 2010). A schematic diagram of the sonochemical method is illustrated in the Figure 2.7.

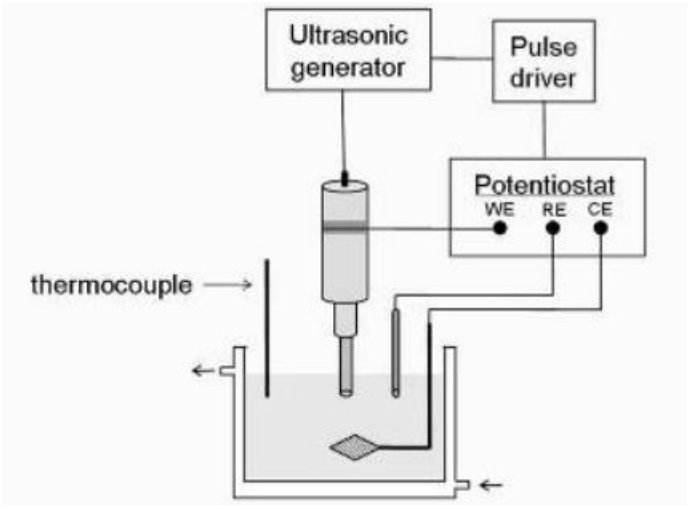


Figure 2.7 : Schematic diagram of sonochemical synthesis method (Satyanarayana, 2018).

Kusama et al. (2020) synthesized γ-Al_2O_3 nanoparticles via probe sonication method with a frequency of 20 kHz for an hour. The process was followed by drying and calcination of the product for 100 °C and 600 °C for 3 hours to get the nanoparticles as shown in Figure 2.8. The γ-Al_2O_3 nanoparticles showed a 96.4 % degradation for MB dye and 99.2 % degradation for acid green when irradiated under UV-light (Kusama et al., 2020).

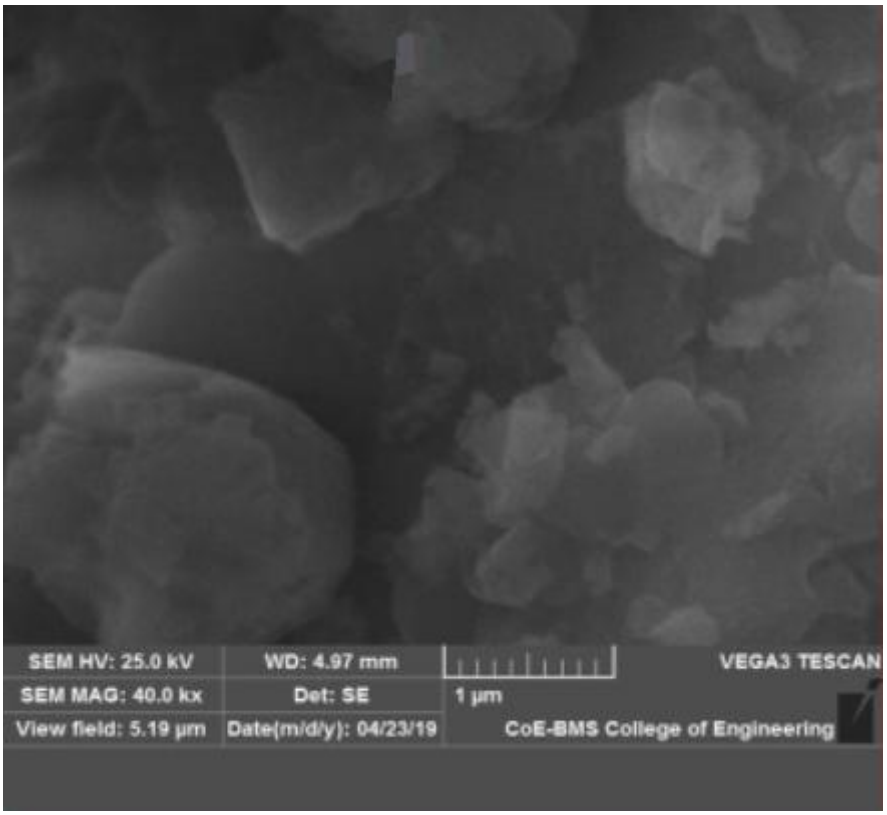


Figure 2.8 : SEM image of γ-Al_2O_3 nanoparticles synthesized via probe sonication (Kusama et al., 2020).

2.2.4 Chemical vapour deposition (CVD) method

Chemical vapour deposition (CVD) is a deposition method that involves formation of thin and thick films with thickness ranging from angstroms to millimeters. During a CVD process, a solid substrate that is heated will be exposed to volatile precursors that would react and decomposed on the substrate surface and deposited as desired phases on the substrate (Madhuri, 2020). The CVD method is commonly used for generating thin film and would need to be carried out in a closed gas chamber. The typical set up of the CVD method can be seen in the Figure 2.9, where the process flow can be seen in the set up. During the CVD process, precursors will be heated up in an atmosphere that is determined by the carrier gas input into the gas chamber. The carrier gas is input to control the atmosphere as well as to move the precursors forward to the heated substrate surface at the lower end of the gas chamber. As the precursors reaches the heated substrate surface, it reacts with the substrate surface and decomposed into a part that deposit on the surface and a by-product that will be removed by the carrier gas and into the outlet that will be connected to a vacuum pump. By precisely controlling the temperature, the duration of synthesis as well as the rate of gas input, the thickness of the thin film deposited can then be controlled.

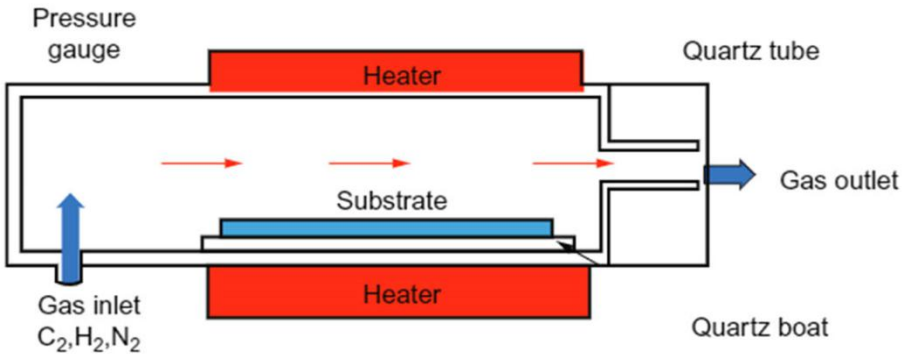


Figure 2.9 : Typical set up of the CVD synthesis method (Madhuri, 2020).

As shown in Figure 2.10, Park and Choi synthesized Al_2O_3 nanotubulars by the CVD method using aluminium, Al_2O_3 powder and oxygen gas as precursors. The synthesis parameters were 1300 °C and pressure of 100 Pa. Nanotubular structure of diameter from 90 to 300 nm was synthesized successfully without any usage of catalyst (Park and Choi, 2014).

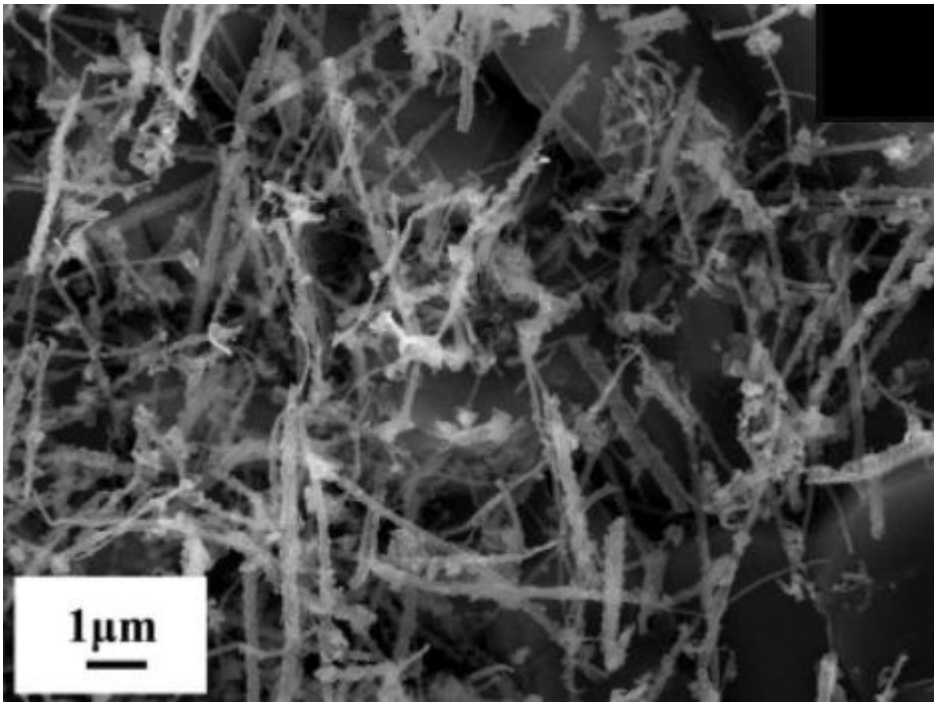


Figure 2.10 : SEM image of Al_2O_3 nanotubulars synthesized via CVD method at 1300 °C and 100 Pa (Park and Choi, 2014).

2.2.5 Spray pyrolysis method

Conventional spray pyrolysis is a process of depositing thin film via spraying a solution onto a heated surface (Mooney & Radding, 1982). Flame spray pyrolysis on the other hand is a method of using flame as the heating element that for the pyrolysis to occur. In the flame spray pyrolysis method, aqueous metal salt solution will be sprayed as a fine mist and through a capillary into a flame. The flame would then burn the solvent into small droplets and conversion of metal salt into metal oxide would occur due to pyrolysis reaction. The metal oxide atom would then be aggregated into nanoparticles that are often collected on a substrate that is placed above (Nunes et al., 2019). A schematic figure of the flame spray pyrolysis synthesis process is shown in Figure 2.11.

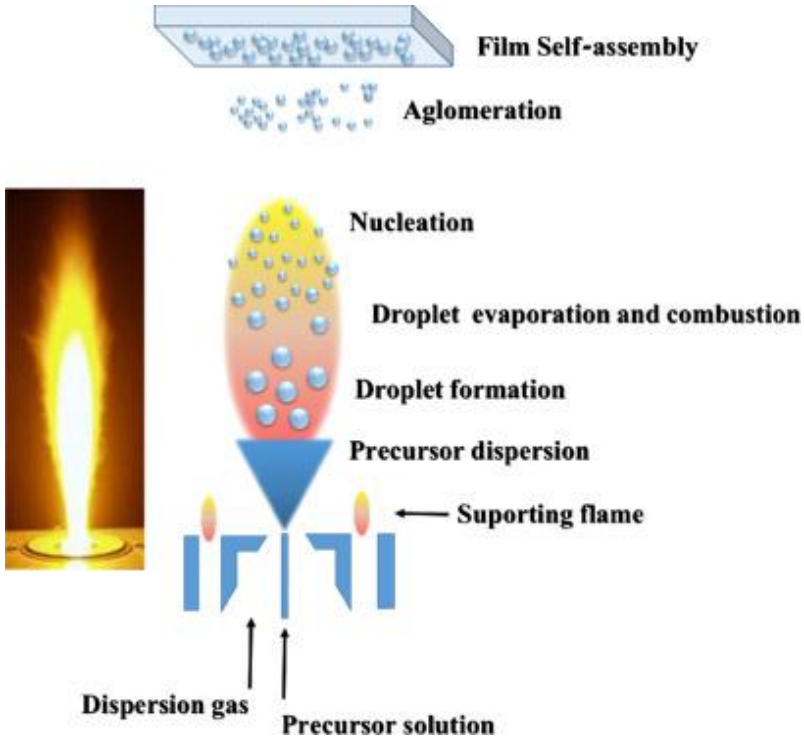


Figure 2.11 : Schematic diagram of flame spray pyrolysis synthesis (Nunes et al., 2019).

Tok et al. (2006) produced Al_2O_3 nanoparticles of size ranged from 5 to 30 nm using this flame spray pyrolysis method as shown in Figure 2.12. The nanoparticles consisted of a mixture of multiple phases which were the α- and γ-phase of the Al_2O_3. The γ-Al_2O_3 had an average size of 10 nm whereas the α-Al_2O_3 had a larger size of average grain size of 28 nm. After calcination at 1100 °C for 2 hours, all of the γ-Al_2O_3 were converted into α-Al_2O_3, while the size of the calcined powder also increased to 80 to 100 nm (Tok et al., 2006).

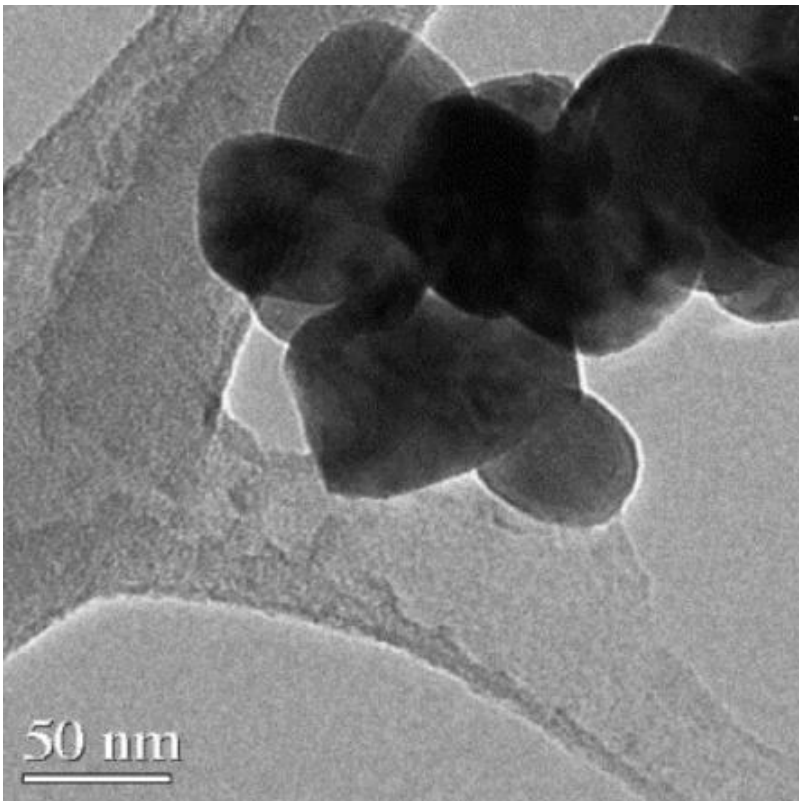


Figure 2.12 : TEM image of Al_2O_3 nanoparticles synthesized by flame spray pyrolysis and calcined at 1100 °C for 2 hours (Tok et al., 2006).

2.2.6 Electrospinning method

Electrospinning method involve generating fibers from jet of liquid droplet in a process known as electrohydrodynamic process (Xue et al., 2019). The electrospinning device consists of a liquid supply device, a needle, a high voltage supply device and also a receiving device. During the synthesis, a high voltage provided by the voltage supply device would generate an electrostatic field that is so great that it exceeds the surface tension of the liquid that is squeezed out from the needle. This causes the liquid, usually polymer to be sprayed into jet of stream and the stream will be cooled in air and collected by the receiving device. By carefully controlling the liquid viscosity and conductivity, spinning voltage applied and the liquid supply rate, nanofibers can be synthesized by this method. A schematic figure of the electrospinning synthesis process is shown in Figure 2.13 below.

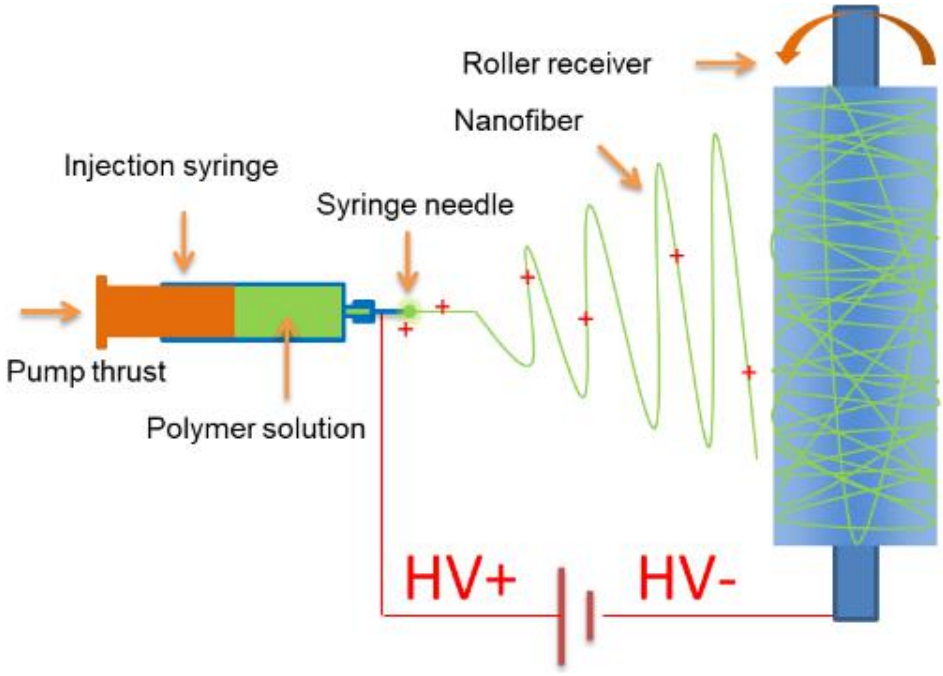


Figure 2.13 : Schematic diagram of electrospinning process (QINGZI NANO, 2022).

Kang et al. (2011) had managed to synthesize α-Al_2O_3 nanofibers with diameter ranging from 100 to 800 nm from a viscous sol-gel spinning solution of aluminium chloride / polyvinylpyrrolidone precursors. The SEM results of the nanofiber formed is shown in the Figure 2.14 below.

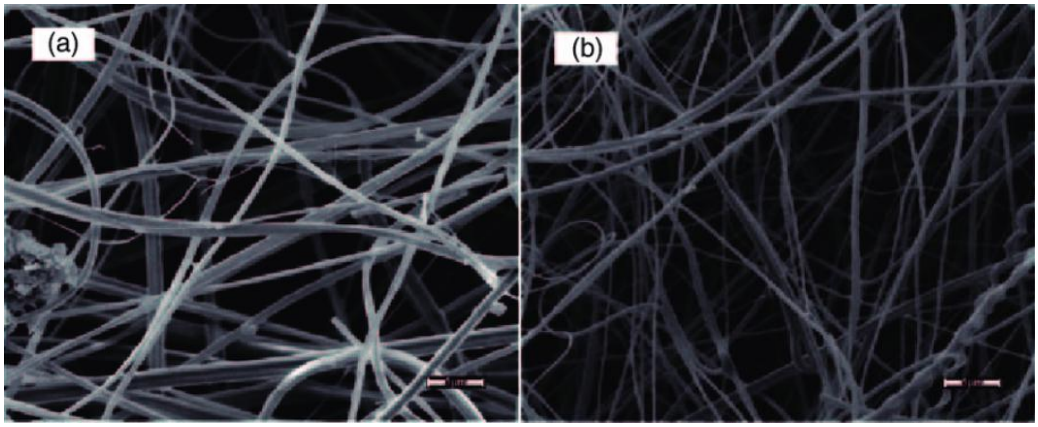


Figure 2.14 : SEM image of Al_2O_3 nanofibers synthesized by electrospinning and sintered at (a) 450 °C and (b) 900 °C (Kang et al., 2011).

2.2.7 Direct heating method

Direct heating method involves in placing a substrate directly into the precursor solution and is used to heat the solution directly through passing an electrical current on it as illustrated in Figure 2.15. During the heating process, the seeds of the crystal will naturally occur on the hot substrate surface and growth process will then carry on (Lee et al., 2017). The direct heating of the substrate in the solution also facilitates an ultra-rapid growth process and high efficiency since the heat is produced from the substrate itself. No study could be found on the synthesis of the Al_2O_3 nanomaterials using the direct heating method since it is still a newly developed method. This direct heating