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Synthesis of Zinc Oxide (ZnO) Nanoparticle using Non-Transferred DC Thermal Plasma Method: A Morphology Review

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ABSTRACT

The increase of nanomaterial usage such as nano-ZnO application in developing countries is a type of progress that is beneficial from the engineering standpoint. Being able to control the results of nanomaterial production is crucial in this development. To control the outcome is to obtain ZnO nanomaterials properties which are suitable and in accordance to its intended application. This study focuses on the morphology of ZnO nanomaterials which are synthesized by non-transferred DC thermal plasma method. In this review, parameters of the apparatus regulating the outcomes of the synthesis is studied and analyzed to find certain guidelines that affect nanomaterial morphology. Some of the findings include the influence of non-transferred DC thermal plasma torches main variables such as gas output and power input which are involved in plasma jet production. It also finds precursor input techniques in which affects the ZnO nanomaterial production outcome. The study indicates that each production parameters on the DC thermal plasma device have different ways in affecting the morphology of the synthesized nanomaterial and it is possible to control them.

Key words : nanomaterial, thermal plasma, zinc oxide

1. INTRODUCTION

The use of nanotechnology in Indonesia is growing and we are now able to feel the presence of nanotechnology to meet the needs of Indonesian society. Nanotechnology is employed in computers, electronic products, cosmetics, fertilizers, polymers, supplements, and herbal medicines in the nation [1]. Nanotechnology however, is a technology that is still in its infancy for the nation. In the last fifty years, nanotechnology has undergone tremendous developments internationally indicated by thousands of nano designs that have been applied in various studies [2]. The presence of nano technology has an important role in the utilization of a material, especially in nano size which have advantages over materials that have a larger size [3]. The formation of nanomaterials can be done through various methods, several methods are used, but in general the formation of nanomaterials is carried out through bottom-up and top-down methods [4]. In the bottom-up method, nanomaterials are formed by collecting atoms and molecules to form atomic clusters to form nanoparticles. This method generally involves chemical reactions, while the top-down method is the formation of nanomaterials by breaking bulk materials to be made into nanomaterials which can be done by mechanical methods.

One material synthesized into nanomaterial is Zinc Oxide. It is an inorganic compound which has wide band gap (3.37 eV) and large free exciton binding energy (60 meV) and other characteristics that can be applied in various fields [5]. These include fields for the development of piezoelectric, thermoelectric, photoelectric, anti-bacterial, and optical purposes, it also has an ability as a catalyst with non-toxic properties at certain concentrations [6], [7]. Some applications that are used using zinc oxide materials include: solar cells, antibacterials in polymers, medical purposes, cosmetics, coatings, piezoelectric sensors, and biosensors [7].

The method of manufacturing ZnO nanoparticles based on the production capacity is divided into two methods, namely Pyro metallurgical synthesis and Hydrometallurgical synthesis. Pyrometallurgical is further divided into indirect or French process and direct or American process. Small-scale production can be done by aqueous zinc salt solution, zinc nitrate solution extraction and pyrolysis, thin film deposition, gas phase synthesis, sol gel, hydrothermal plasma, chemical vapor deposition (CVD), and plasma methods [8].

A plasma method called DC Thermal Plasma (DCTP) method has some of the shortest processing time, fast chemical reactivity, and can be used with temperatures above 10000 K. It uses the high temperature and powder density which has a strong effect on the rate of nanoparticle production and coating processes. The approach of this technique is that it brings larger sized precursor materials to the nano size in matter of seconds. This is done by injecting it into the plasma flame by means of flow of gas. When passing through the plasma flame, the material undergoes evaporation due to high plasma enthalpy. The material will vaporize and be rapidly cooled or quenched in the reactor tube with a drastic decrease in temperature [9]. The high quenching process causes the vapor to become highly saturated, which leads to the rapid and large number of nanoparticles produced through homogeneous nucleation, heterogeneous condensation and coagulation among the nanoparticles themselves. Nanoparticles synthesized are then collected by filters or directly deposited on the substrate to make nanostructured films or coatings [10]. Figure 1 shows the process on how the nanomaterials form from being fed to the plasma flame until the particles continue to build up and grow to particular nanostructures of zero to three dimensions. This demonstrates potential for both the synthesis of nanoparticles and the deposition of layers of nanoscale structures.

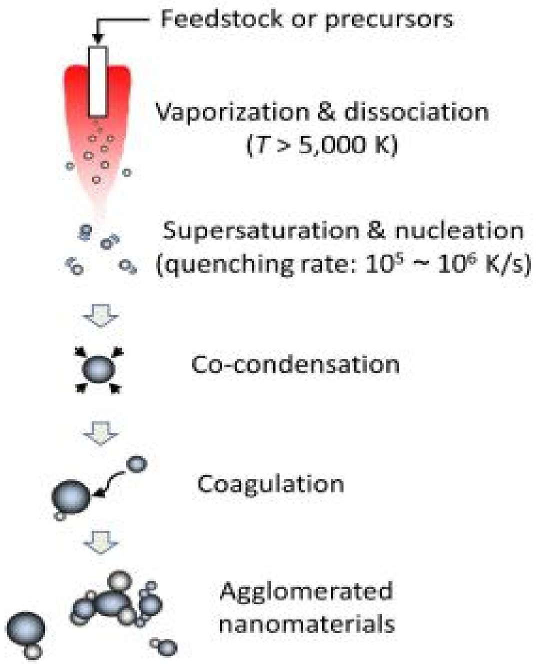


Figure 1. Nanofabrication using DCTP method [11]

After the period of nucleation and development, the ZnO crystallites would mainly develop into three dimensional objects with low index crystallographic faces [3]. There are also possibilities for zero- and one-dimension growth if the conditions are favorable. Crystals have different kinetic parameters for each crystal planes. The relative surface activities on the growth of facets are affected by many different conditions which are outlined in the next chapters.

2. PLASMA JET

One of the most important if not the most important component in the synthesis method is the plasma flame jet. As it is the subject that essentially transforms the materials and vaporizing it to be treated. The DC is usually chosen because the DC type plasma arc from the generator is stable in operation, with good control, low electrode consumption, fairly low refractory wear and low power consumption [12]. The DCTP method utilizes active substances found in plasma energy including ions, electrons, and radicals with high temperature and energy density. The energy is from the jet itself which is also dependent upon other variables that contribute to the conditions of the plasma such as the torch properties and the input gas properties.

2.1 Torch Properties

Plasma jets are generated using the torch apparatus. There are several types of plasma arc torches that can be used in DC thermal plasma device, namely transferred arc, non-transferred arc and hollow electrode plasma. In the non-transferred plasma type, a plasma jet is generated by two electrodes and chemical reaction from the input gasses which ignites and produced downstream. DCTP nozzles have electrodes that are relatively small in diameter and limit the plasma jet produced thereby increasing the temperature and maximum velocity at the torch axis. The disadvantage of this method lies in the frequent erosion at the base of the fire which causes contamination by nozzle electrodes [11], [13]. The contamination may cause changes in nanomaterial production and ultimately its morphology such as increasing the size and increasing lattice parameters [14]–[16]. Cathodes are typically made of thoriated tungsten which can erode with oxide based gases in where zirconium and hafnium is used [17]. Electrode selection such as the use of graphite electrodes can also be applied, but it is considered costly for using the material [18].

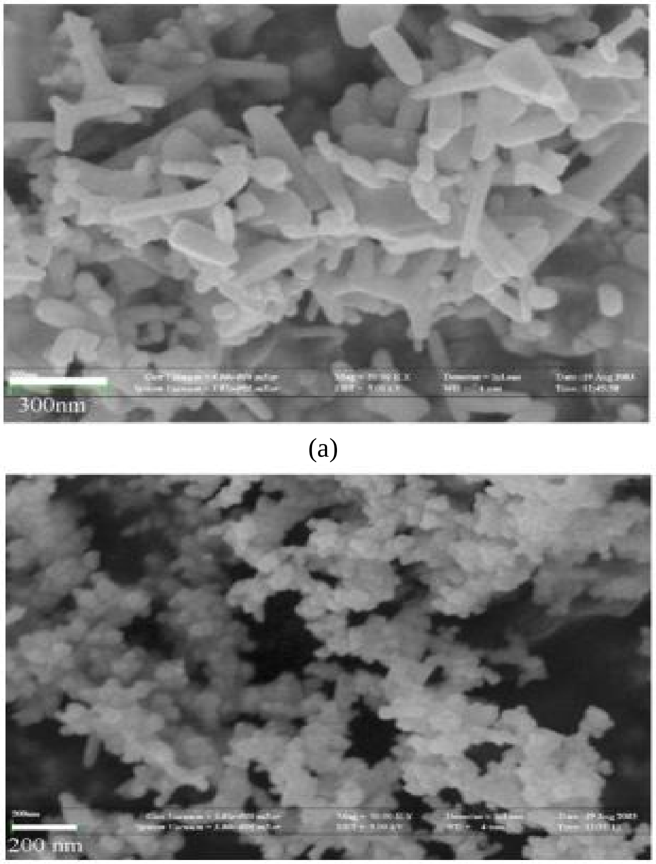
Besides the torch nozzle material, the designs are also influential in the production of the nanomaterials. Jet conditions such as temperature, velocity and species fields are possible to be customized using this parameter. These factors can make the manufacturing process speed shorter and use these energies efficiently. Even with the loss of thermal energy in the electrode section due to radiation, convection and electron condensation of 35-50 percent [11].

2.2 Input Gasses

For the plasma to be produced it requires another variable to be taken into consideration, namely the input gas. This setting is done by controlling the input gasses to the DCTP generator with a specific flow rate. The gas itself is controlled by increasing the enthalpy and thermal conductivity of the plasma with specific gas choices [19]. Inherently, the specific enthalpy produced by the plasma generating apparatus depends on the type of input gas whether it is He, H_2, N_2, O_2, Ar or air according to the dissociation step. Changing its internal properties by mixing gases has become a common method for obtaining control of the enthalpy and thermal conductivity of plasma [6].

Oxidizing gas are not recommended with this type of torch, as previously mentioned it will damage the electrodes [13]. Argon is a gas that is chemically inert and easily ionized. This makes it suitable for use in synthesis requiring high purity. This is shown in the manufacture of sensitive devices such as semiconductors in research [20], [21]. In these studies, argon was used as a plasma gas but the resulting particles were of many types from rod, tetrapod and rod-like but differed due to reaction gasses.

The mixing of input gases such as Ar which has low thermal conductivity with gases such as H_2 which has high thermal conductivity can be seen in studies [19]. The enthalpies of various gases and their relationship to temperature can be adjusted by the mixing of other gases that will increase enthalpy and thermal conductivity [13], [22], [23]. The effects on the morphology of the nanoparticles can be seen in Figure 2 where different gas types [22] with the higher enthalpy gas of pure nitrogen has different morphologies compared to the N_2/Ar gas mix. Nitrogen plasma in this case has shown a more granular type showing agglomeration of ZnO structure due to the difference in plasma temperature and gas properties.



(a)

(b)

Figure 2. ZnO nanomaterial with input gas: (a) N_2/Ar and (b) nitrogen [22]

Compared to RF plasma jets, DC plasma jets are mostly turbulent due to the gasses which usually enhances mixing of the injected precursor [24]. This indicator can also affect the morphology of the nanoparticles. Lin's study [25] has shown the residence time of the material in the plasma zone decreased with the plasma gas flow rate. Longer residence time would increase tetrapod shape formation during synthesis.

2.3 Power Output

Large plasma power output for generating the plasma can also be another aspect to consider for the synthesis results between variations. Length of the jet and the temperature of the plasma flame, both of which will change the operating conditions and increase the working area. A research [26] revealed that a higher plasma current will affect the temperature of the plasma flame produced, a higher plasma flame temperature will support the process of heating Zn particles in a plasma flame to form ZnO nanoparticles. However, choosing a plasma current that is too high is also not allowed. This is because the high temperature that will form can cause the formation of agglomerations.

Lin's research [25] also indicated change of nano-ZnO morphology due to the effect of DC power output 70 kW to 90 kW variations in plasma gas flow rates of 90 slm. The results of the study show that the 90 kW plasma current variation contains more tetrapod nanoparticles than the 70 kW variation. The selection of higher plasma power will form a higher flame temperature as well, it supports the process of forming ZnO nanoparticles. However, the balance between plasma power and precursor carrier rate must also be considered to obtain a good nanoparticle size. Because when the carrier rate of the powder is low or less able to push and break the particles in the plasma flame, agglomeration will occur [27].

3. PRECURSOR AND REACTION GASSES

Research [28] on the synthesis of nanoparticles using DC TP Jet by varying the precursor gas carrier has shown some indication of the effects on nanomaterial morphology. Power used was of 6 kW and precursor carrier gas flow rate 15 lpm and 20 lpm. The plasma flame used an input power of 6 kW and a powder carrier gas flow rate of 15 lpm to produce a flame temperature of 6960 K. However, the flame temperature decreased to 6684 K when the injected powder carrier gas flow rate was changed to 20 lpm. The decrease in flame temperature affects the size of the resulting particles.

The method of filling particles as precursors can be a factor that has a great influence on the ability to melt particles in the plasma. As the rate of incorporation of particulates into the discharge region increases, the energy transferred from the plasma to the particles will result in a decrease in the plasma temperature and consequently the heating rate of the particles. This has been proven in several studies of nano ZnO such as [20], [21] and other materials such as nickel powder [27] and alumina [29] among others.

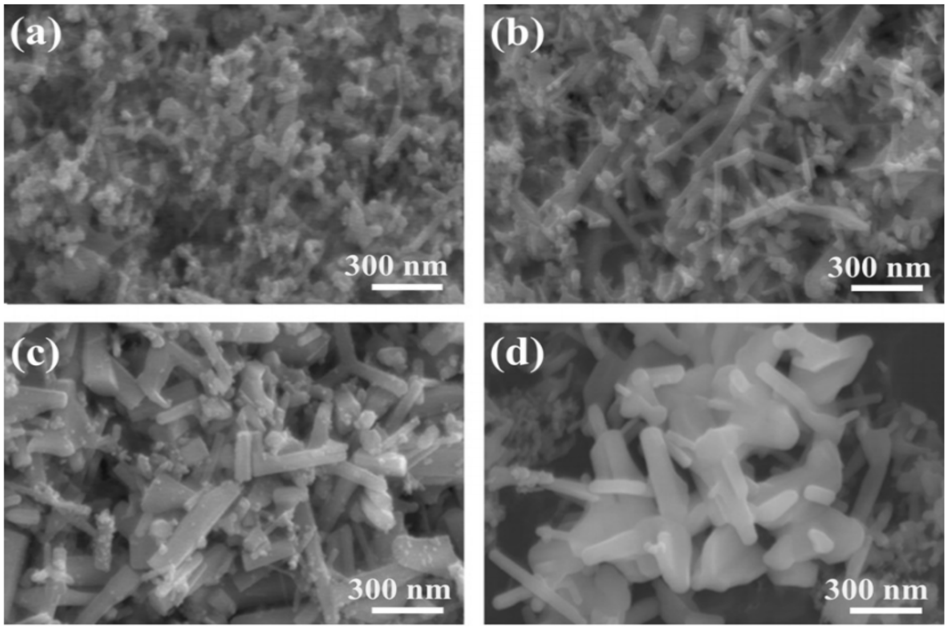


Figure 3. SEM image of ZnO nanoparticle synthesis result with gas rate variation; (a) O_2 1 l/min, (b) O_2 3 l/min, (c) O_2 5 l/min, (d) O_2 7 l/min [21]

It is shown in Lee's research [21], in terms of morphology and crystal size of ZnO particles, particles will be smaller when the reaction gas flow is lower. As the reaction gas flow rate increases, it is likely that the products will grow and become rods and the size of the clustered particles will also become larger as seen Figure 3. As the reaction gas flow rate increases, the oxygen source becomes more abundant and leads to the increase of regions for particle growth.

This phenomenon should be understood however, that the growth would only work for oxide-based gasses for carrier and reaction gasses, as it is the gas that interacts with the precursors. The concept can be seen in [30] where Ar, CO_2, and O_2 were used as carrier gases to investigate the effect. The XRD pattern is shown in Figure 4 where ZnO synthesized using carrier gas Ar (3) and CO_2 (4) had similar patterns. O_2 (5) gas had less Zn peak which indicated more efficient oxidation.

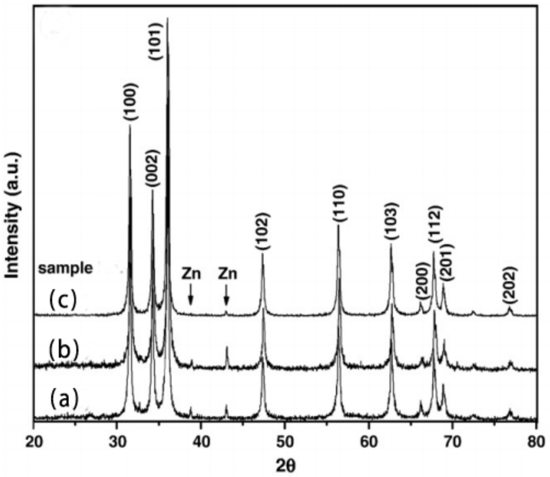


Figure 4. ZnO nanomaterial XRD with variety of reaction gas: (a) Ar; (b) CO_2 and (c) O_2 [30]

4. CONCLUSION

Many studies have successfully synthesized nano-ZnO particles with DCTP which had various characteristics. The method has shown that it is one the simplest ways in producing nanomaterials with various outcomes depending on the parameters installed. The plasma torch itself has factors such as torch nozzles, electrode type, size and materials which can change the plasma jet, resulting in plasma jet sizes or temperature that are undesirable if not controlled properly. This also includes torch input gasses that may affect the particles due to their inherent properties and can change particles morphology. From the precursor input point of view, the precursor and carrier gasses may change the output due to its reactions with the plasma jets. Different variables in this input would result in different outcome of ZnO morphology. Therefore, detailed planning of production parameters of DC thermal plasma is crucial for a desired ZnO nanomaterial morphology.

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