Study on size control of TiO$_2$ nanoparticles synthesized using solution plasma process

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Abstract The research was conducted to study the size control of TiO$_2$ nanoparticles synthesised. The TiO$_2$ nanoparticles was formed using the solution plasma process. This method is an electrolysis of water-based experiment. When compared to other methods, the solution plasma method offers both a shorter synthesis time as well as a simple setup. Researches conducted on nanomaterials have proven that these materials tend to have varying properties when compared to bulk metals. With this, being able to vary the sizes of the TiO$_2$ nanoparticles meant being able to study its possible future applications. One being using these nanoparticles for the fabrication of solar cells. Varying the sizes of these nanoparticles could bring a difference in the reactivity which can help enhance the performance of the solar cells. In order to vary the sizes of the nanoparticles, the concentration of the electrolyte was varied. During the research, it was found that the sizes of the TiO$_2$ nanoparticles decreases with the increase in the concentration of the electrolyte.

1. Introduction
There are multiple ways to synthesize nanoparticles which includes methods such as sol-gel method, high energy milling and pulse laser ablation [1]. Although these methods can synthesize and control the size of the nanoparticles, there are limitations for the methods mentioned as different researcher is situated in a different environment. One of the few limitations is that the methods mentioned would require specialty equipment such as vacuum chambers and high-powered lasers [1]. Nanomaterials have the tendency to exhibits different properties from their bulk counterparts. Such properties include a change in thermal, optical, reactivity etc. An example of varying properties can be seen from the copper when bulk copper is opaque and copper nanoparticles exhibits transparency. By exploiting the unique properties of nanomaterials, it can be utilized in fields such as medical, aerospace, biotechnology etc. [2].

For this paper, the study revolves around the use solution plasma process for synthesizing titanium dioxide (TiO$_2$) nanoparticles and size control of the particles. Some benefits of solution plasma over other methods are that it has a simpler setup and can be conducted in small sized laboratories. In addition, the preparation time is shorter than any other methods stated above. The novelty of this research is to device a sustainable technique of producing various size ranges of TiO$_2$ nanoparticles, which consequently, improve the overall outcomes of its application, otherwise, it is able to provide new ways to synthesis different applicable outcomes. For example, TiO$_2$ nanoparticles can be used as substitute for the fabrication of solar cells and its reactivity in terms of its plasmonic resonance, helps to enhance the efficiency of the cells.

2. Theory
2.1 Correlation between the size and properties of nanoparticles
As particles micronize, the behavior of the particles tends to be affected in some manner and exhibits
different physical properties. The variation in the physical properties is caused by the change of the molecular and atomic bonding states which construct the particles [3]. One of the corresponding effects of reducing the particle size is the change of the number of atoms present on the surface of the particle. This could increase the reactivity of the atoms as the higher number of exposed atoms available for reactions directly corresponds to the higher reactivity. The relationship between particle size and percentage of surface atoms are illustrated in Figure 1.

![Figure 1. Percentage of surface atoms vs diameter of the particles [3]](image)

Apart from reactivity, the optical and thermal properties are also affected when the size of the particles were reduced. For optical properties, nanoparticles tend to absorb light with a specific wavelength and emit the energy as the electrons returns to its original state. Such property could be exploited and used as pigmentation and light scattering applications because nanoparticle paint pigments is reported to be 100 times greater than ordinary pigments.

As for thermal properties, when metal particles are reduced to the nano spectrum, the melting point greatly reduces as the size gets smaller [3]. This phenomenon is called the melting point depression as nanoparticles have a larger surface-are-to-volume ratio which enables the particles to receive more energy and result in a lower melting point. The melting point depression is shown in Figure 2.

2.1 Method of synthesis – Hydrothermal method

Some common methods to synthesize metallic nanoparticles are shown here. One common method to synthesize fine particles of metal oxides is the hydrothermal method. It involves condensation and hydrolysis process to produce ultrafine particles. The condensation process involves the condensation of metal salts in a high temperature and pressure atmosphere while in contact with a hydrothermal medium.

The high temperature and high-pressure atmosphere are normally achieved in an autoclave which it could produce a controlled pressure and temperature condition where the reaction could occur. Due to this elevated pressure and temperature, the hydrothermal medium could exhibit properties such as viscosity and dielectric constant when compared to normal atmospheric conditions. These changes in properties could lead to better solubility of the metal complexes and thus enables better particle formation and growth [4].
Another method of nanoparticle synthesis is the electrochemical method. The electrochemical method involves an external circuit and chemical reactions similar to electrolysis process. The external circuit contains the anode and cathode. The anode contains the bulk metal that will be oxidized and the metal cations would be migrated to the cathode. The electrochemical method causes a reduction along with the formation of metal oxides which are normally present in the zero oxidation states [5]. An additive is normally added to prevent the agglomeration of the metal powders. In addition to that, this method of synthesis is normally conducted in a special nitrogen filled atmosphere and therefore a need for a special gas chamber arises in order to synthesize nanoparticles via electrochemical method.

2.3 Solution plasma process

The solution plasma process, also known as submerged glow discharge plasma, is the focus of this research paper as it was used to synthesize and control the size of TiO\textsubscript{2} nanoparticles. As the name suggests, the solution plasma process utilizes plasma in a solution to synthesize nanoparticles. The generated glow discharge plasma acts upon the cathode and thus melting the surface of the cathode and releasing particles of molten metals into the electrolyte [6].

In solution plasma process, the electrolyte acts as a conductor and coolant. When the molten metal particles are released, the surface tension of the electrolyte forces the particles to be spherical in shape while solidifying it.

The advantages of solution plasma as a method for nanoparticles synthesis can be summarized as the time taken and the simplicity of the experimental setup. Electrochemical and sol-gel methods require several hours of preparation prior to the synthesis process. Solution plasma process requires up to five minutes for experimental setup, and up to one hour for nanoparticles synthesis depending on the amount of particles desired.

The simple setup of solution plasma process is also a major advantage compared to other methods of nanoparticles synthesis. As a comparison, hydrothermal method requires an autoclave while the electrochemical method requires a special nitrogen atmosphere. Other methods of synthesis such as pulse laser ablation technique require a high-powered laser system whereby not every laboratory houses such complex equipment. On the other hand, solution plasma process only requires a simple setup without the need for any specialty equipment and can be set up in any small sized laboratory.

Figure 2. Melting point vs particle size (nm); Melting point depression [3]
3. Methodology

3.1 Required materials and apparatus

1) Electrolyte (Potassium carbonate electrolyte, \( \text{K}_2\text{CO}_3 \))
2) Platinum wire coil
3) Titanium wire (Grade 1 titanium wire, uncoated)
4) DC power supply
5) 300ml beaker

3.2 Experimental setup

The setup is similar an electrolysis setup with an external circuit and an electrolyte. The external circuit consists of a cathode and an anode, and both electrodes were submerged into the electrolyte. The cathode holds the desired nanoparticle material, which in this case was the titanium wire and the anode was the platinum coil which acts as the counter electrode. The platinum wire used in this case was 1000mm in length [6]. As for the electrolyte, potassium carbonate with concentration of 0.1M was used initially. Both electrodes were connected to a DC power supply and both electrodes were held in place away from each other to prevent accidental short circuits.

![Schematic representation of the setup for solution plasma process](image)

The variable that was set for this experiment was the concentration of \( \text{K}_2\text{CO}_3 \) used. The initial concentration was set to 0.1M and was increased in an increment of 0.2M per iteration. A total of 5 iterations were performed, resulting in a final concentration of 1.0M. The electrolyte concentration has an effect on the plasma formation on the cathode surface. For that reason, the electrolyte concentration was chosen as a variable in this research. In addition, a graph that illustrates the relationship between nanoparticle size and electrolyte concentration was plotted.

3.3 Experimental procedure

The experiment is set up accordingly and the power supply was turned on. Prior to turning on the power supply, the cathode and anode were sufficiently separated from each other or touching each other directly. This was to prevent any short circuits that could result in a minor explosion and other damages to the equipment.

After the power supply was turned on, the voltage was increased slowly at a rate of 5V per minute. This was to enable the electrolyte to reach functional temperature by slowly warming up the electrolyte. The current reading on the DC power supply was constantly observed to ensure that the current did not exceed 4A. Exceeding this current would cause the electrodes to melt prematurely and could lead to dangerous exposure to molten metals.

The voltage was gradually increased until the formation of the discharge plasma. Immediately the voltage was reduced by 5-10V to ensure the stability of the formed plasma discharge and to sustain the plasma. The generated plasma was then sustained for one hour in order for the plasma to synthesize nanoparticles. The electrolyte volume was continuously replenished due to its evaporation.
during plasma discharge.

After the experiment was completed, the nanoparticle suspension was left to cool for 24 hours to allow for the nanoparticles to settle at the bottom of the beaker. After 24 hours, the excess electrolyte was carefully decanted, and distilled water was added to wash away the remaining electrolyte. The sample was then stored in a glass or plastic vial along with the distilled water. To obtain images of the nanoparticles, scanning electron microscopy (SEM) analysis was conducted.

4. Results

![SEM images of TiO\(_2\) for 0.1M concentration.](image1)

![SEM images of TiO\(_2\) for 0.3M concentration.](image2)

![SEM images of TiO\(_2\) for 0.5M concentration.](image3)
Figure 7. SEM images of TiO\(_2\) for 0.7M concentration.

Figure 8. SEM images of TiO\(_2\) for 1.0M concentration.

Table 1. Average particle size with the concentration and sustaining voltage

| Electrolyte concentration (M) | Average particle size (nm) | Sustained plasma voltage (V) |
|------------------------------|---------------------------|-------------------------------|
| 0.1                          | 538.6                     | 120                           |
| 0.3                          | 839.5                     | 85                            |
| 0.5                          | 869.1                     | 80                            |
| 0.7                          | 991.4                     | 80                            |
| 1.0                          | 1250.0                    | 76                            |
Figure 9. Graph of average particle size vs electrolyte concentration

5 Discussion

5.1 General discussion on the observed size and shape of the particles

Figures 4 to Figure 8 were the obtained SEM images of the synthesized nanoparticles. Observations of size and shape changes were made prior to size measurement by using GATAN Microscopy Suite software. Table 2 shows the observations obtained from the SEM images.

Table 2. Electrolyte concentration and the observation of the images

| Electrolyte concentration (M) | Magnification | Observation                                           | Sustained Voltage for Plasma (V) |
|------------------------------|---------------|------------------------------------------------------|---------------------------------|
| 0.1                          | 2000X         | Large numbers of spherical shaped particles         | 120                             |
| 0.3                          | 2000X         | Large and small sized particles along with irregularly shaped clumps | 85                              |
| 0.5                          | 2200X         | Large numbers of irregularly shaped clumps along with fine spherical particles | 80                              |
| 0.7                          | 3300X         | Large clumps with small amounts of fine particles | 80                              |
| 1                            | 2000X         | Large number of dispersed particles with only small amounts of irregularly shaped clumps | 76                              |

There were large clumps of irregularly shaped particles present in every conditions of the experiment. This phenomenon can be explained as an agglomeration of particles. Under normal circumstances, the nanoparticle samples would undergo filtration and are placed in a centrifuge to separate the particles from the excess electrolyte and washed with distilled water. The filtration process would filter out the large clumps of particles and leave behind the finer particles.

For this research experiment, the filtration process was skipped and due to this, there was a presence of irregularly shaped particles in all of the specimens. A comparison of SEM images between filtered and non-filtered specimens are shown below.
The agglomeration of the particles likely occurred during the synthesis process rather than during the post-processing. During the synthesis, molten metals particles were discharged into the electrolyte. The surface tension of the electrolyte forces the molten metal to solidify into spherical balls. In addition, the strong intermolecular forces between the particles act upon each other and therefore causing agglomerations which are very difficult to separate.

5.2 Correlation between the electrolyte concentration and the sustaining voltage for plasma generation

For each electrolyte concentration, the size of the nanoparticles was measured by determining the diameters of twenty particles from the SEM images, and then calculating the average diameter. According to Table 3, it can be observed that the size of the nanoparticles increased along with the concentration of the electrolyte. It is also found that the higher the concentration of the electrolyte, the lower the sustaining voltage for plasma generation.

A higher electrolyte concentration represents a higher number of dissolved ions per fixed volume of the solution. The reasoning behind the decreasing sustaining voltage for plasma generation as the concentration goes up was that the glow discharge plasma was reached when the energy filled electrons produces visible light from repeated collision of photons [6]. The sustaining voltage for the plasma generation would be lower when the concentration is higher due to the solution already yielding high amounts of dissolved ions and did not need as much energy to ionize the electrons.

5.3 Relationship between the electrolyte concentration and nanoparticles size

Table 3. The relationship of the experimental aspects

| Electrolyte concentration increases | Amounts of ions in the solution increases |
|-----------------------------------|------------------------------------------|
| 2 Amounts of ions in the solution increases | Sustaining voltage for plasma generation decreases |
| 3 Sustaining voltage for plasma generation decreases | Plasma particle intensity decreases |
| 4 Plasma particle intensity decreases | Average Particle size increases |

As the electrolyte concentration increased, the sustaining voltage decreased. However, there were still other relationships to be determined such as the plasma intensity and the size trend of the nanoparticles synthesized.

The relationship can be further discussed by noting that the plasma intensity was higher when the sustaining voltage was higher. A more intense plasma formation would yield a finer nanoparticle sizes due to the more uniform melting of the cathode surface. The increasing uniformity in the melting pattern could be further explained with the size of the plasma particles. By using a high-speed camera, it has been previously observed that a higher sustaining voltage would produce more plasma particles on the cathode surface [6]. The plasma particles produced were finer and contribute to a more uniform melting of the cathode.
6 Conclusion
This research aims to control the size of TiO₂ nanoparticles by changing the concentration of the electrolyte during plasma discharge. It was found that the average size of the nanoparticles increases along with the concentration of the electrolyte. This was mainly due to the plasma intensity that reduced as the electrolyte concentration increased. At the same time, the plasma discharge sustaining voltage was decreased as the electrolyte concentration increased. Subsequently, the plasma intensity was low at high electrolyte concentrations and low sustaining voltages.

Several issues can be considered for future work. One of it is to investigate the influence of electrolyte selection on the trend for nanoparticle size change. For example, in the case of plasma synthesis of CuO nanoparticles, it was found that the average size of nanoparticle decreased as the concentration of NaOH electrolyte increased, while the opposite occurred when using K₂CO₃. The electrolyte pH and the ionic species formed during plasma synthesis could have a major role in the resulting nanoparticles sizes.

In addition to the recommendation above, further research on controlling the plasma particles acting upon the surface of the cathode has the potential to control the yield of nanoparticles. Also, the applications of synthesized TiO₂ nanoparticles could be researched upon as they exhibit different light scattering effect in correlation to the size of the particles. The synthesized nanoparticles can then be utilized in many applications such as pigments, UV blockers and photocatalysts. It would be of great interest to study the varying properties in relation to the size of the nanoparticles as different sizes exhibit different properties.

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