

Synthetization of Nanostructured Titanium Dioxide by Atmospheric-Pressure Plasma Jet for Bacteriological Applications

Ghada A. Kadhim[†], Najwa J. Jubier[†], Ahmed Abed Anber[‡]

[†] Department of Physics, College of Science, Wasit University, Wasit, Iraq

[‡] Department of Renewable Energy Science, College of Energy and Environmental Sciences, Al-Karkh University of Science, Baghdad, Iraq

*Corresponding Author Email: ahmedkrm88@gmail.com; ahmed.abed@kus.edu.iq

ABSTRACT

Highly pure nanostructured titanium dioxide was synthesized from a titanium foil via atmospheric-pressure plasma jet technique with electrolyte medium. The structures and morphology have been investigated and approved by X-ray diffraction, field emission scanning electron microscopy (FESEM) and energy dispersive x-ray diffraction (EDX). X-ray diffraction shows approve the titanium dioxide nanoparticles have a domain peak of crystallinity structure (anatase and rutile phase). Application of Titanium dioxide has been actively explored during last several years, the products of this nanoparticles were used to decontaminate and inactivate of *Escherichia coli*, *Staphylococcus strain*, and *Pseudomonas aeruginosa* clinical isolates as the alternative sterilizing approach. The main constituents include reactive oxygen species. These species can be useful to synthesize biologically important nanomaterials or can be used with nanomaterials for various kinds of biomedical applications to increase human health. *Escherichia coli*, *Staphylococcus strain*, and *Pseudomonas aeruginosa* were verified by applying the disk diffusion method, with titanium dioxide nanoparticles addition and found that the inhibition zone.

KEYWORDS

Titanium oxide nanoparticles, Atmospheric pressure plasma jet, Electrolytic system, Antibacterial activity

INTRODUCTION

In recent years, nanomaterials synthesized by plasma technology have received great attention due to their exclusive characteristics compared to their bulk counterparts. Atmospheric-pressure plasma jet is important for nanotechnology development for biomedical applications, which is gaining great attention as a prominent synthesis method for nanomaterials, due to its distinguishing properties when compared to solid, liquid and gas phase synthesis approaches [1, 2]. It is very suitable for inner surface modification in a needle since plasma can be generated inside the needle at atmosphere (1000 mbar), and it has several remarkable features. Non-equilibrium plasma is generated due to the large surface/volume ratio of the plasma. The densities are High (Ion and radical) because of the gas pressure discharge is extraordinary. In addition, the plasma can be localized under the excitation electrodes since the mean free path of the charged particles is reduced to be on the order of a submicron. The application of this technique for various oxide thin film coatings on the surfaces of the strip is very promising for developing novel functional devices.

However, currently, there is very little knowledge of the reaction mechanism of PECVD using Atmospheric-pressure plasma jet. Plasma usually consist of ultraviolet radiation, excited and charged particles species, which interact with the surface of electrolyte media. Plasma at liquid interface becomes a reaction region when the many particular chemical and physical processes occur under the electron and positive ion irradiation from the plasma. The plasma liquid process in atmospheric pressure represents a novel nanoparticle synthesis plan in previous years because of the simplicity and environmental friendliness at a low cost. Plasma is sustained at atmospheric pressure and room temperature by decreasing the dimensions under to micrometer range. Caused by several benefits

presented by titanium oxide nanoparticles, the interests in fabrication and characterization of such structures have recently increased and considered a has strong interest for its potential use in gas sensor [2-3], photocatalysis, solar cell [3, 4, 5,6], electrochromic devices [7, 8], water cleaning [9, 10] also biological improvements [11, 12].

The properties and performance of titanium oxide rely strongly on its structure and surface morphology like the nanoparticles [13,14,15] nanotubes, nano-rods [16], nanowires [17], nano leaves [18], in a mesoporous layer [19], and also it has tunable of fascinating characteristics such as shape, size, morphology and so on. In this work, it was reported a large scale and one step continuous flow atmospheric pressure plasma jet to prepare nanoparticles of titanium oxide. The influence of change electrolyte system concentration on the structure of titanium oxide particles size was investigated. The synthesis of nanoparticles may cause adverse environmental and health effects. There are different methods for the synthesis of TiO_2 nanoparticles such as hydrothermal, plasma sputtering and so on. The production of nanoparticles was demonstrated practically using the above technique to employ in killing bacteria. The biological method for nanoparticle synthesis is simple, ecofriendly and allows for getting controlled size nanoparticles which can be used as catalysts with specific composition, which is not possible by classical methods. The inhibition zone of bacteria with addition titanium oxide nanoparticles was also studied. Titanium oxide nanoparticles and their antibacterial activity via using the atmospheric pressure plasma jet were not yet reported. It was exhibited good antimicrobial activities against selected microbes. Hence, biogenic synthesized of this nanoparticles can possibly be employed for diverse clinical applications [20].

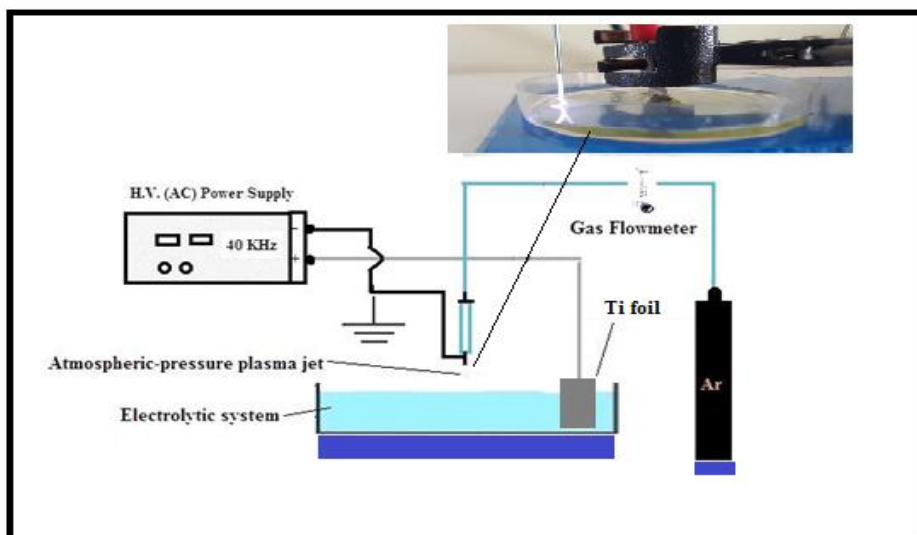


Figure 1: The schematic diagram of an atmospheric plasma jet electrochemical synthesis of titanium oxide nanoparticles

EXPERIMENT

Titanium dioxide nanoparticles were synthesized by using atmospheric pressure plasma jet. Fig. 1 shows the set-up and a photograph of an atmospheric plasma jet electrochemical synthesis of TiO_2 nanoparticles. The tube acted as the cathode with length is 7 cm and the inner diameter is 0.6 mm which was made of stainless steel. The anode made of a titanium foil (6 cm length, 3 cm in width) and it was located 1.5cm onward from the cathode. The distance between the surface of the electrolyte medium and the needle was 4 mm. A discharge gas (Argon) was joined at the syringe by using a glass flow meter, to control the gas flow at 60 ml/min. The reaction was take placed in a glass petri dish (diameter is 5cm and depth is 2.5cm). The anode was submerged into an electrolytic medium that was involved in ethylene glycol (supplied by Sigma-Aldrich), hydrofluoric acid. Distilled water has been used at all times during the experiment. The first electrolyte was contained 10 wt. % HF and 5 wt. % ethylene glycol with different preparation time (5, 10, 15, 20 and 25 min), then and there the color of electrolyte was altered as presented in Fig. 2, which is shows changing color at different concentrations with different preparation times. 2ml of titanium oxide liquid nanoparticles were added into *Escherichia coli* and *Staphylococcus strain* and

Pseudomonas aeruginosa, and then cultured on a plastic petri dish. After that, the inhibition zone of bacteria was measured.

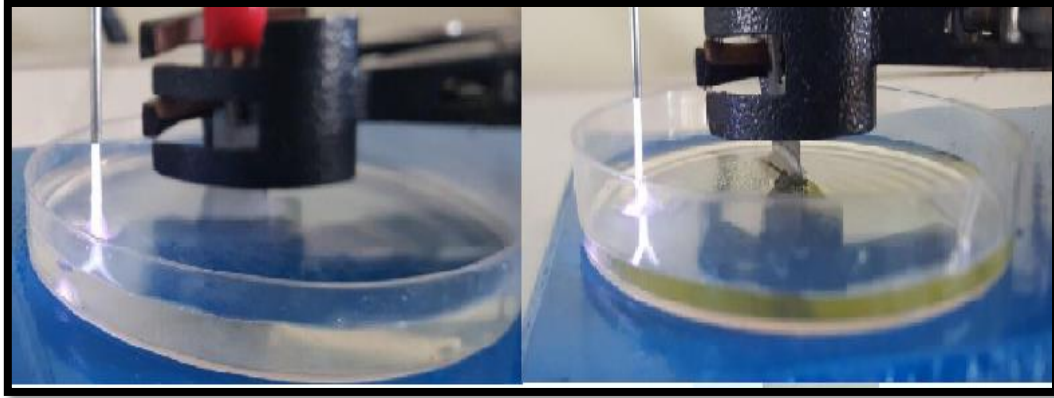


Figure 2. (Color online) at different concentrations with different preparation times

RESULTS AND DISCUSSION

The x-ray diffraction XRD patterns of the titanium dioxide nanoparticles formed on Ti surfaces at different preparation times with annealing temperature at 250 °C for 1 h are shown in Fig.3. The mixture of the anatase and rutile phase were observed in the XRD investigation of TiO₂ NPs. The phase changes after increasing time at 15 min, that is just anatase phase peaks. The increasing preparation time at 25 min, also rutile phase peaks were observed. The experimental XRD pattern agrees with the JCPDS card no. 21-1272 (anatase TiO₂) and the XRD pattern of TiO₂ nanoparticles other literature [21]. The 2θ at peak 25.4° confirms the TiO₂ anatase structure [22]. Strong diffraction peaks at 72° indicating TiO₂ in the anatase phase [22]. The intensity of XRD peaks reflects that the formation of nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite. The EDX measurements extracted from SEM results of samples prepared with TiO₂ nanoparticles at different preparation times are shown in Fig. 4. As seen, the nanoparticles were composed of Ti and O which played a dominant in the structure of TiO₂ NPs. EDX results displayed that the atomic ratio of oxygen cleared with increasing of titanium.

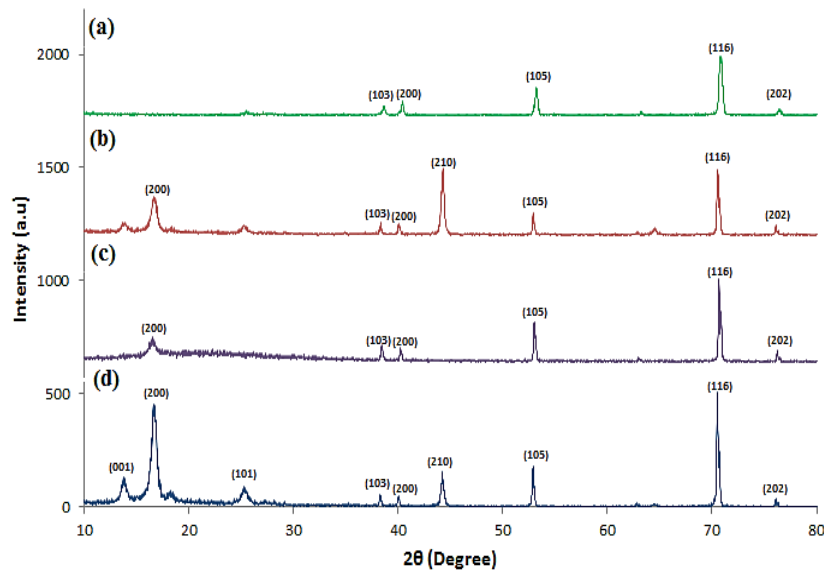


Figure 3. X-ray diffraction patterns of TiO₂ nanostructure after annealing at temperature 250 °C for 1 h, and different preparation time: (a) 10 min, (b) 15 min, (c) 20 min and (d) 25 min.

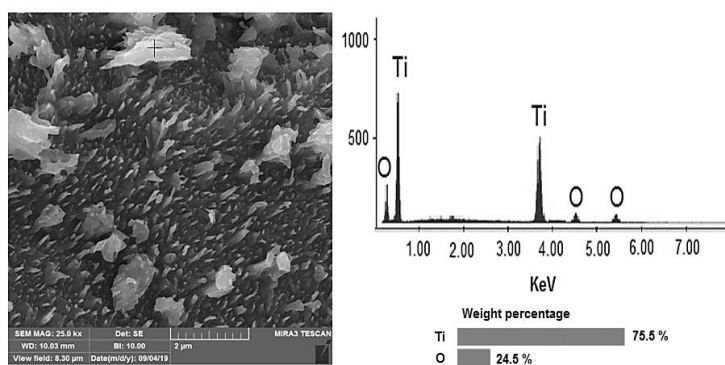


Figure 4. SEM based EDX spectra of the TiO₂ nanoparticles at different preparation time

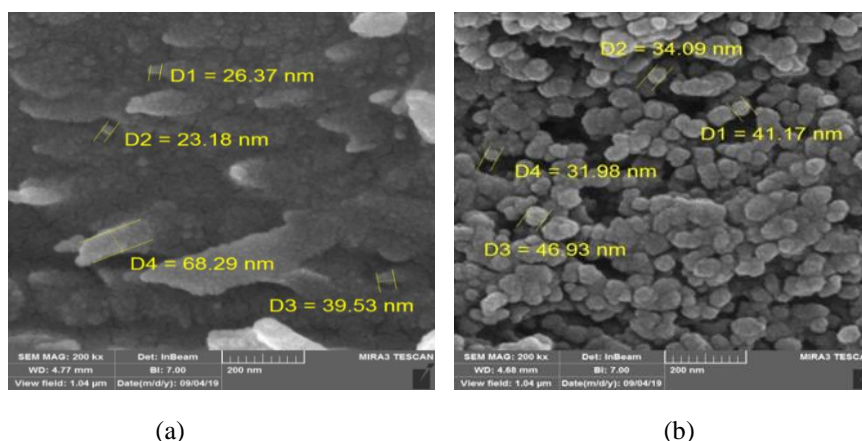


Figure 5: FESEM images of plasma-treated samples at annealing temperature 250 °C for (1 h) with different preparation times: (a) 5 min, (b) 25 min.

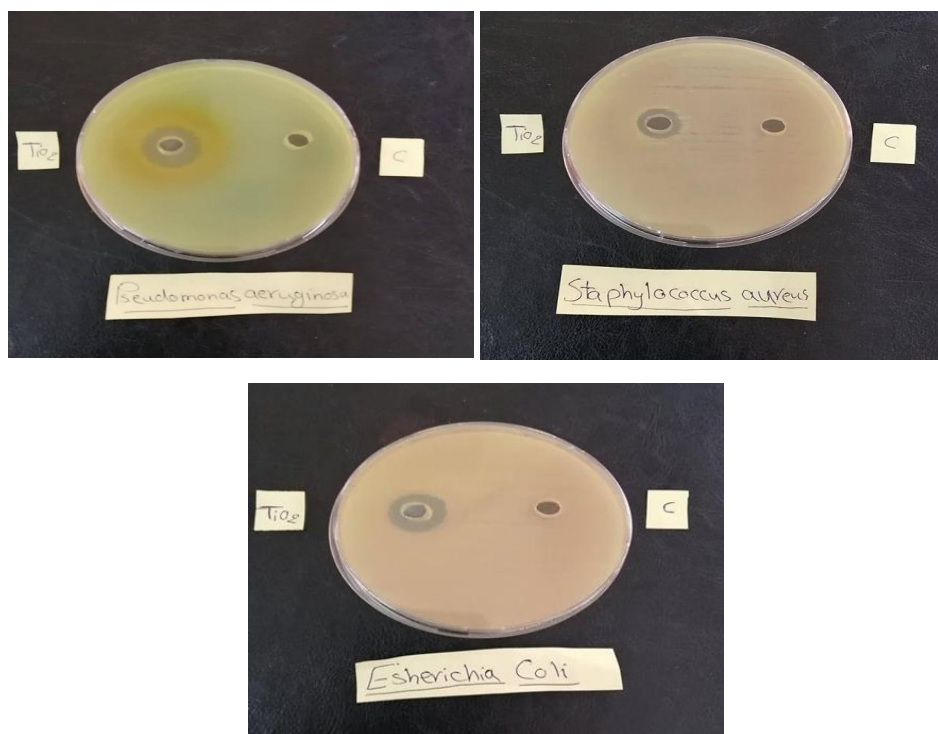


Figure 6. Diffusion disks showing the antimicrobial activity of silver nanoparticles toward (a) *Pseudomonas aeruginosa*, (b) *Staphylococcus*, (c) *Escherichia coli*.

Explanations of the samples morphology anodized by using this technique at different preparation times (10, 15, 20 and 25) min in an electrolyte system (ethylene glycol solvent, hydrofluoric acid and distilled water) have been examined with FE-SEM images as in Fig. 5 a and b. To achieve the procedures specific design to the work, it was used plasma jet at different times to examine the atmospheric pressure plasma assisted with electrochemical preparation of titanium oxide NPs, which are the suitable phases in the most photocatalytic activity of titanium oxide, whole samples have been annealed at 250 °C in the air for 1 hour. It is realized, the size of the nanoparticles increased from nearly 26– 68 nm to 34–46 nm when the preparation time increased from 10 min to 25 min . Fig. 6 shows the antibacterial activity of titanium oxide nanoparticles. It was a flawless inhibition zone after 24 h incubation of a dish at 37 °C. The strains susceptible to titanium oxide nanoparticles show a superior inhibition zone for three types of bacteria (*S.aureus* , *E.coli* and *Pseudomonas aeruginosa*). The inhibition zone for all samples against the declared micro-organisms is listed in Table (1).

Table 1. Zone of inhibition in mm

<i>Pseudomonas aeruginosa</i>	<i>Staphylococcus</i>	<i>Escherichia coli</i>
21mm	15mm	20mm

CONCLUSIONS

In this work, very good method to synthesize TiO₂ nanoparticles, in a versatile, non-toxic and bio-safe approach, at room temperature, and this method is simple, economic and environmentally benign which will make it suitable for various applications. TiO₂ nanoparticles can be synthesized via this technique, which can be offered a fast, low cost and simple to fabricate the large amount of TiO₂ NPs in reasonably time. XRD patterns have confirmed that the synthesized particles are anatase phase TiO₂. FE-SEM achieves a good morphology and distribution of TiO₂ nanoparticles, it may be enter inside the membranes of bacteria. To improve these results, its wanted serious hard work to use the plasma jet technique and examine many types of bacteria. Titanium oxide nanoparticles have a wide application, thus the result showed strong antibacterial against *S.aureus*, *E.coli*, and *Pseudomonas aeruginosa*. This work can be a good attempt to synthesize TiO₂ nanoparticles by this technique as a new approach and invest TiO₂ NPs in bioengineering and bacteriological application, and it is well expected that this synthesis technique would be extended to synthesize numerous other important metal oxide nanoparticles.

REFERENCES

- [1] W.T. Kim, I.H. Kim, and W.Y. Choi, “Fabrication of TiO₂ Nanotube Arrays and Their Application to a Gas Sensor”, Journal of nanoscience and nanotechnology, Vol. 15, No. 10, Pp. 8161–8165, 2015.
- [2] Y. Wang, “Nanostructured Sheets of Ti-O Nanobelts for Gas Sensing and Antibacterial Applications”, Advanced Functional Materials, Vol. 18, No. 7, Pp. 1131– 1137, 2008.
- [3] R. Daghrir, P. Drogui, and D. Robert, “Modified TiO₂ for environmental photocatalytic applications: a review”, Industrial & Engineering Chemistry Research, Vol. 52, No. 10, Pp. 3581–3599, 2013.
- [4] J.B. Joo, “Tailored synthesis of mesoporous TiO₂ hollow nanostructures for catalytic applications”, Energy & Environmental Science, Vol. 6, No. 7, Pp. 2082– 2092, 2013.
- [5] X. Wang, “Electron transport and recombination in photoanode of electrospun TiO₂ nanotubes for dye-sensitized solar cells”, The Journal of Physical Chemistry C, Vol. 117, No. 4, Pp. 1641–1646, 2013.
- [6] P. Roy, “TiO₂ nanotubes and their application in dye-sensitized solar cells”, Nanoscale, Vol. 2, No. 1, Pp. 45– 59, 2010.
- [7] G. Cai, “Constructed TiO₂/NiO core/shell nanorod array for efficient electrochromic application”, The Journal of Physical Chemistry C, Vol. 118, No. 13, Pp. 6690–6696, 2014.
- [8] P. Qiang, “TiO₂ nanowires for potential facile integration of solar cells and electrochromic devices”, Nanotechnology, Vol. 24, No. 43, Pp. 435403, 2013.

- [9] S. Banerjee, D.D. Dionysiou, and S.C. Pillai, "Self-cleaning applications of TiO₂ by photo-induced hydrophilicity and photocatalysis", *Applied Catalysis B: Environmental*, Vol. 176, Pp. 396–428, 2015.
- [10] C. Sotelo-Vazquez, "Multifunctional P-doped TiO₂ films: a new approach to self-cleaning, transparent conducting oxide materials", *Chem. Mater.*, Vol. 27, No. 9, Pp. 3234–3242, 2015.
- [11] G.Z. Li, "Fabrication, characterization and biocompatibility of TiO₂ nanotubes via anodization of Ti6Al7Nb", *Composite Interfaces*, Vol. 23, No. 3, Pp. 223–230, 2016.
- [12] K.N. Pandiyaraj, "Improvement of Surface and Biocompatible Properties of Flexible Transparent Nano TiO₂ Films Using Glow Discharge Plasma", *Journal of Nano Science and Nano Technology*, Vol. 2, No. 1, Pp. 436–441, 2014.
- [13] B. O'Regan, M. Grätzel, and D. Fitzmaurice, "Optical electrochemistry I: steady-state spectroscopy of conduction-band electrons in a metal oxide semiconductor electrode", *Chemical physics letters*, Vol. 183, No. 1–2, Pp. 89–93, 1991.
- [14] B. Munirathinam, and L. Neelakantan, "Titania nanotubes from weak organic acid electrolyte: fabrication, characterization and oxide film properties", *Materials Science and Engineering: C.*, Vol. 49, Pp. 567–578, 2015.
- [15] P. Roy, S. Berger, and P. Schmuki, "TiO₂ nanotubes: synthesis and applications", *Angewandte Chemie International Edition*, Vol. 50, No. 13, Pp. 2904–2939, 2011.
- [16] D.M. Andoshe, "A wafer-scale antireflective protection layer of solution-processed TiO₂ nanorods for high performance silicon-based water splitting photocathodes", *Journal of Materials Chemistry A*, Vol. 4, No. 24, Pp. 9477–9485, 2016.
- [17] X. Feng, "Vertically aligned single crystal TiO₂ nanowire arrays grown directly on transparent conducting oxide coated glass: synthesis details and applications", *Nano letters*, Vol. 8, No. 11, Pp. 3781–3786, 2008.
- [18] S. Li, "Enhanced photocatalytic and photoelectrochemical activity via sensitization and doping of novel TiO₂ nanowire/nanoleaf arrays: dual synergistic effects between TiO₂-N and CdS-Mn", *RSC Advances*, Vol. 6, No. 17, Pp. 13670–13679, 2016.
- [19] Y. Dai, "High-Surface-Area Mesoporous Crystalline TiO₂: Synthesis, Characterization, and Application as Support for Making Stable Au Catalysts", *Journal of Nanoscience and Nanotechnology*, Vol. 17, No. 6, Pp. 3772–3778, 2017.
- [20] A.A. Anber, "Fabrication of Nanostructured Silver Liquid by Atmospheric-Pressure Plasma Jet for Bacteriological Applications", *Journal of Bionanosience*, Vol. 12, No. 6, Pp. 809–813, 2018
- [20] K.H. Abass, M.H. Shinen, and A.F. Alkaim, "Preparation of TiO₂ nanolayers via. sol-gel method and study the optoelectronic properties assolar cell applications," *Journal of Engineering and Applied Sciences*, Vol. 13, No. 22, Pp. 9631-9637, 2018.
- [21] M. Ba-Abbad, A.H. Kadhum, A. Mohamad, M.S. Takriff, and K. Sopian, "Synthesis and Catalytic Activity of TiO₂ Nanoparticles for Photochemical Oxidation of Concentrated Chlorophenols under Direct Solar Radiation", *Int. J. Electrochem. Sci.*, Vol. 7, Pp. 4871-4888, 2012.
- [22] K. Thamaphat, P. Limsuwan, and B. Ngotawornchai, "Phase Characterization of TiO₂ Powder by XRD and TEM", *Kasetsart.J.(Nat. Sci.)*, Vol. 42, Pp. 357-361, 2008.