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Study of the Photocatalytic and Antibacterial Activity of TiO_2 Powder Synthesized by Microwave-Assisted Sol-Gel Method

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Abstract

TiO_2 powder was prepared by microwave-assisted sol-gel method. The powder was refluxed at 180 W for 1, 2 and 3 h and dried at 180 W for 1 h by a conventional microwave oven. Several analytical techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) and surface area measurement (BET) were employed to characterize the synthesized powder. Photocatalytic activity of the powder was examined via the degradation of methylene blue (MB) solution under UV irradiation for a certain time. The efficiency of antibacterial activity was evaluated by the inactivation of *Staphylococcus aureus (S. aureus)*. The results showed that only anatase TiO_2 was observed and the as-prepared powder exhibited the agglomeration of spherical nanoparticles with crystallite sizes of 20.7, 13.8 and 9.3 nm when the refluxed time was 1, 2 and 3 h, respectively. The highest efficiency for the photocatalytic and antibacterial activities was 66.68 and 91.67%, respectively, belonging to those powders using the reflux time of 3 h.
Keywords : TiO_2 powder, Photocatalytic activity, Antibacterial activity, Microwave-assisted

1. Introduction

In recent years, titanium dioxide (TiO_2) is used for a wide range of applications such as photocatalyst, self-cleaning surfaces, solar cells, water and air purification, gas sensing and optical coating (1-3) because of its unique properties including good photocatalytic activity, chemical stability, non toxic nature, large band gap and low cost (4-6). TiO_2 has three different crystal structures: anatase, rutile and brookite (7-9). Anatase and rutile phases possess superior photocatalytic activity to the brookite one (10-11) and hence they are good candidates for photocatalysis applications.

Many efforts have been carried out to modify morphology and phase structure of TiO_2 powder using various methods such as hydrothermal synthesis, sol-gel, anodization, template and microwave-assisted (12-14). However, the conventional sol-gel method usually suffers from high processing temperature and long reaction time leading to grain growth and phase transition (15). It is therefore necessary to consider an alternative technique to overcome those drawbacks. In the last few years, microwave irradiation has been reported to effectively enhance the efficiency of sol-gel method on the preparation of inorganic materials. The microwave-assisted sol-gel method has unique advantages of uniform and rapid heating in comparison with the conventional one. In addition, this method can significantly reduce the processing time and simplify the preparation procedures as well as improve the nanometer size fraction of particles (16). In addition, the method saves energy and appears today as a new technology for green chemistry development by means of solvent-free and/or less reactant needed. Recently, the microwave-assisted method has been used to synthesize different morphologies of TiO_2 powder (17).

In this study, a facile method for synthesizing TiO_2 powder via microwave-assisted sol-gel technique using titanium (IV) isopropoxide as a Ti precursor was developed. The prepared powder was refluxed at 180 W for 1, 2 and 3 h and dried at 180 W for 1 h by a conventional microwave oven. The physicochemical characteristics of the powder including crystallization, morphology and specific surface areas were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and surface area measurement (BET), respectively. The photocatalytic activity was also examined via the degradation of methylene blue (MB) solution under UV irradiation. Finally, antibacterial activity efficiency was evaluated by the inactivation of *Staphylococcus aureuswere (S. aureus).*

2. Experimental and Details

2.1 Powder preparation

All chemicals used were of analytical research grade and employed without further purification and obtained from Fluka. Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, TTIP, 97%) and hydrochloric acid (HCl, 97%) were used as a starting material and a peptizer, respectively [18]. TiO_2 powder was prepared via a conventional sol-gel method [19]. Firstly, to prepare TiO_2 sol, TTIP (10 ml), ethanol (150 ml) and water (250 ml) were mixed and stirred for 15 min at room temperature. The solution was acidified to pH = 3 by adding few droplets of 2 M HCl into the solution and stirred for 45 min. The treated solution was refluxed at 180 W for 1, 2 and 3 h using a domestic microwave oven (Samsung, ME82V) to produce a milky solution. The obtained solution was then dried using the microwave oven at 180 W for 1 h to receive TiO_2 powder. The powder product, however, was agglomerated and so grinding process was further required to reduce the agglomeration. In this work, TiO_2 powder refluxed at 180 W for 1, 2 and 3 h was designated as T1, T2 and T3, respectively.

2.2 Powder characterizations

Morphology and particle size of the synthesized TiO_2 powder were characterized by scanning electron microscope (SEM) (Quanta 400). Specific surface area of the powder was analyzed using quanta chrome BET surface analyzer. The phase composition was characterized using an x-ray diffractometer (XRD) (Phillips X'pert MPD, Cu-K). The crystallite size was calculated by the Scherrer equation, Eq. (1) (20-21).

$$D = 0.9\lambda/\beta\cos\theta_B \quad (1)$$

Where *D* is the average crystallite size, *k* is equal to 0.9, a shape factor for spherical particles, λ is the X-ray wavelength (λ = 0.154 nm), θ is the Bragg angle and $\beta = B - b$, the line broadening. B is the full width of the diffraction line at half of the maximum intensity and b = 0.042 is the instrumental broadening.

2.3 Photocatalytic activity test

The photocatalytic activity was evaluated by the degradation of MB under UV irradiation using eleven 50 W of black light lamps. A 10 ml of MB with a concentration of 1×10^{-5} M was mixed with 0.0375 g of TiO_2 powder and kept in a dark chamber for 1 h prior to storing in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h (20). After photo-treatment, concentration of the treated solution was measured by UV-vis. The ratio of remained concentration to initial concentration of MB calculated by C/C_0 was plotted against irradiation time to observe the photocatalytic degradation and the percentage degradation of the MB molecules was calculated by Eq. (2) (20).

$$M = 100(C_0 - C)/C_0 \quad (2)$$

Where M is the percentage degradation of the MB molecules, C_0 is the concentration of MB aqueous solution at the beginning (1×10^{-5} M) and C is the concentration of MB aqueous solution after exposure to a light source.

2.4 Antibacterial activity test

The gram-positivebacteria S. aureus were used for the antibacterial activity testing of the TiO_2 powder. The bacteria were grown aerobically in 4 ml of tryptic soy broth, at 37°C for 24 h. The bacterial solution was then diluted in 0.85% NaCl, and the initial bacterial concentration was set to 10^5 colony forming units CFU/ml. A bacterial suspension of 10 ml volume was then treated with 0.0375 g of TiO_2 powder, under UV 110 W lamp for a designated time (0, 30, 60 and 90 min). An 0.1 ml sample of the treated suspension was taken and spread onto a Nutrient agar plate and incubated at 37°C for 24 h. After incubation, the number of viable colonies of S. aureus on each Nutrient agar plate was observed and disinfection efficiency of each test was calculated in comparison with that of the control (N/N_0) (20). Percentage of bacterial reduction or *S. aureus* kill percentage was calculated according to the following equation, Eq. 3, (20).

$$S = 100(N_0 - N)/N_0 \quad (3)$$

Where S is the percentage bacterial reduction or *S. aureus* kill percentage, N_0 and N are the average number of live bacterial cells per milliliter in the flask of the initial or control and powders finishing agent or treated fabrics, respectively.

3. Results and Discussion

3.1 Powder characterizations

Figure 1 shows XRD patterns of the TiO_2 powder refluxed at 180 W for various periods of time. The peak locations and relative intensities for TiO_2 were cited from the Joint Committee on Powder Diffraction Standards (JCPDS) database. It was found that only anatase phase was seen for all samples; the peaks locating at 25.40°, 37.8°, 48.00° and 54.15° corresponded to the (101), (004), (200), (105) and (211) planes (JDPDS 21-1272) (22). The crystallite sizes of nanocrystalline anatase

TiO_2 powder that refluxed for 1, 2 and 3 h were found to be about 20.7, 13.8 and 9.3 nm, respectively, which seemed to decrease with an increase in refluxed time due to the contribution of the power from the refluxed time (18).

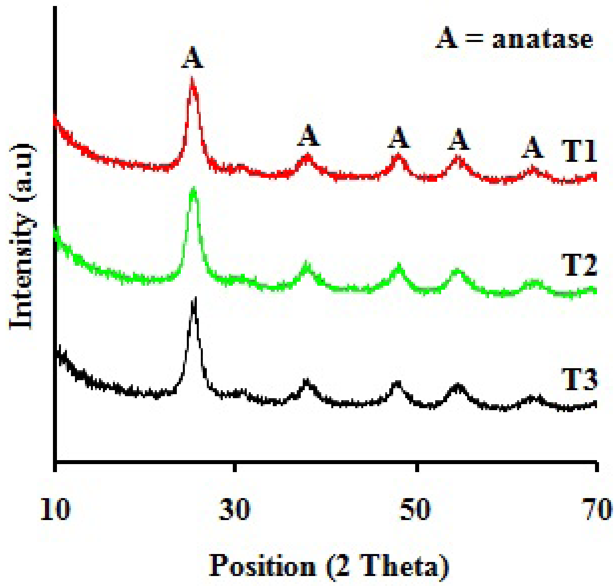

Figure 1. XRD patterns of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h

Figure 2 displays SEM images of the synthesized TiO_2 powder at different hours of the refluxed time. Spherical TiO_2 with narrow size distribution and nice dispersibility can be prepared at different refluxed time. Refluxed time only influences particle size. As Fig. 2(c) shows that, small size particles are obtained at long refluxed time. As Figure 2(a) and Figure 2(b) show that big size particles are obtained at short refluxed time. The main reason is that solution can get a fast heating rate at long refluxed time can be hydrolyzed in a short time. The relationship between quantity of crystal nucleus and delivery of precursor solute presents a positive correlation according to nucleation mechanism (14), so particles have small size and a large amount in long refluxed time. The results revealed that T1, T2 and T3 powders were spherical nanoparticles but agglomerated. As compared to T1, reduction in particle size was obviously observed in T3 suggesting particle size reduction with increasing refluxed time. The specific surface areas of T1, T2 and T3 powders were 17.78, 20.17 and 23.48 m^2/g, respectively. The results revealed a significant effect of refluxed time on the crystallite size and specific surface area of the synthesized TiO_2 powder that the 3 h refluxed time (T3) induced the synthesized powder to possess the smallest crystallite size and so the largest specific surface area.

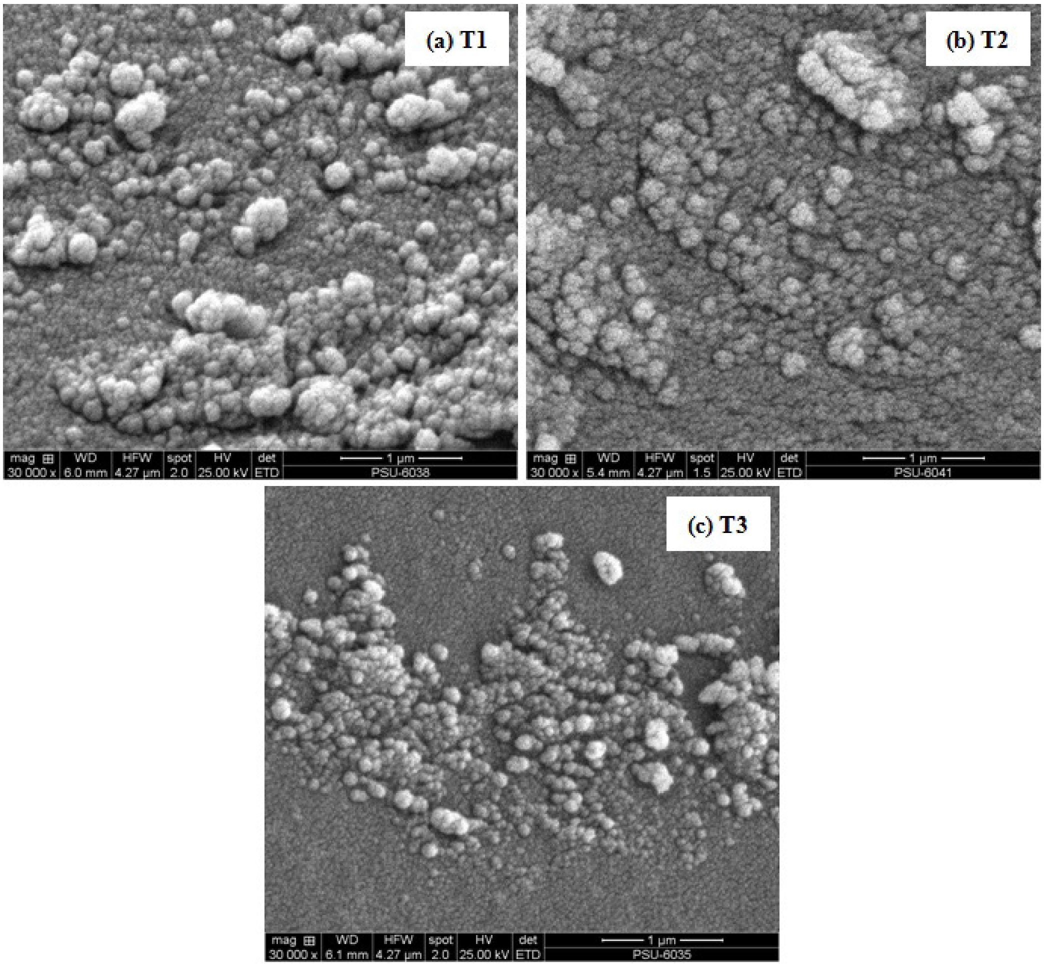

Figure 2. SEM surface morphology images of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h (magnification 30,000X)

3.2 Photocatalytic activity

Figure 3 illustrates photocatalytic activity of the synthesized TiO_2 powder in methylene blue (MB) solution under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. It was found that the photocatalytic activity TiO_2 powder increased with refluxed time, and thus T3 offered the highest photocatalytic activity. Figure 4 shows the percentage of MB degradation under the light source. After 6 h-UV irradiation, the MB degradation percentage of T3 was 68.66%, while that of T1 and T2 were 50.65 and 59.20%, respectively. Again, the results indicate a great influence of refluxed time on photocatalytic behavior and MB degradation rate of the synthesized powder that the longer refluxed time the better photocatalytic activity.

In this study, the photocatalytic efficiency caused by only UV light (without TiO_2 powder) on the MB degradation was also studied. The results revealed the fact that, after 6 h-UV irradiation, the MB degradation percentage was very low (10.65%) which was about 6 times lower than that of T3. As a result, the presence of anatase TiO_2 is a crucial factor enhancing the MB degradation under UV light. It is noted that the highest photocatalytic efficiency gained from T3 was due to its smallest crystallite size and largest specific surface area.

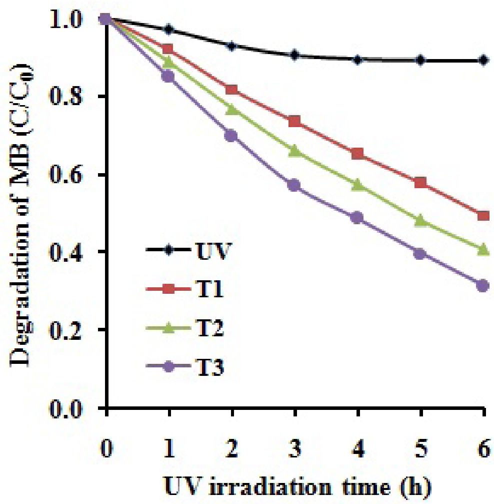

Figure 3. The photocatalytic activity of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h under UV irradiation

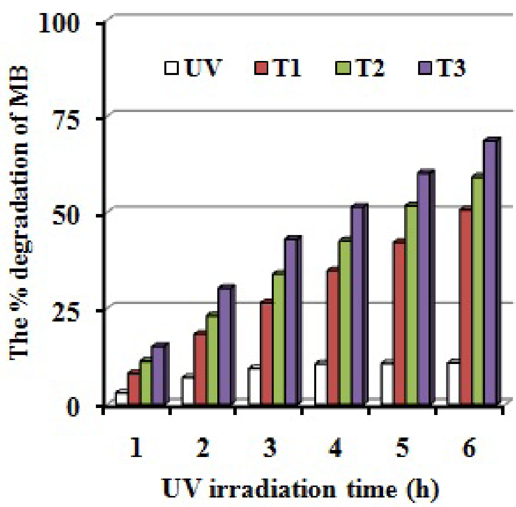

Figure 4. The MB degradation percentage of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h under UV irradiation

3.3 Antibacterial activity

Figure 5 displays the *S. aureus* survival rate (N/N_0) after UV illumination on the synthesized TiO_2 powder. The results showed that the *S. aureus* survival decreased with irradiation time and hence the highest antibacterial activity was found on T3. Figure 6 demonstrates the *S. aureus* kill percentage of the TiO_2 powder under UV light. The *S. aureus* kill percentages of T1, T2 and T3 were 75.00, 83.33 and 91.67%, respectively, under 90 min-UV irradiation. On the other hand, in the case of testing without TiO_2, the *S. aureus* kill percentage was only 5.33% under UV irradiation for 90 min. Figure 7 illustrates the photo of viable bacterial colonies (red spots) under UV light of the TiO_2 powder refluxed for 1-3 h in comparison with the control condition (without TiO_2). The results are in good agreement with those presented in Figure 6 that the *S.* aureus killing rate increased significantly with refluxed time. The killing efficiency, however, became very poor when TiO_2 was non-existent. This confirms the fact that the synthesized TiO_2 is essential for increasing the *S. aureus* killing rate under UV light.

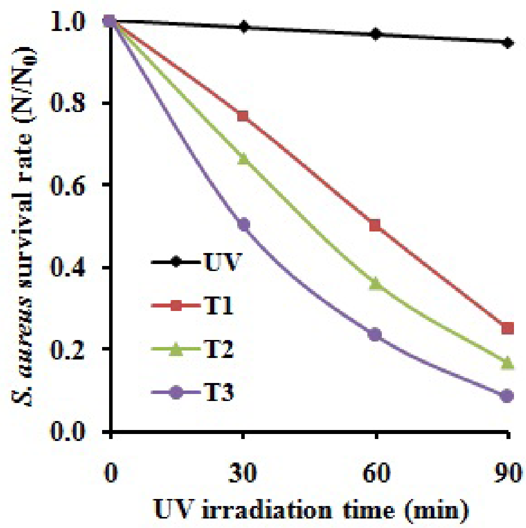

Figure 5. The antibacterial activity of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h under UV irradiation

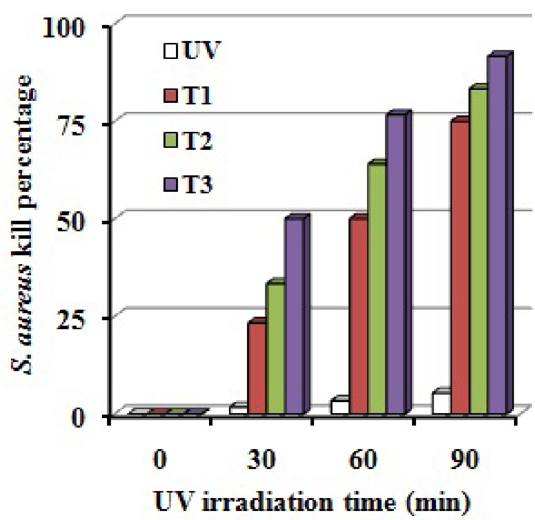

Figure 6. The *S.* aureus kill percentage of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h under UV irradiation

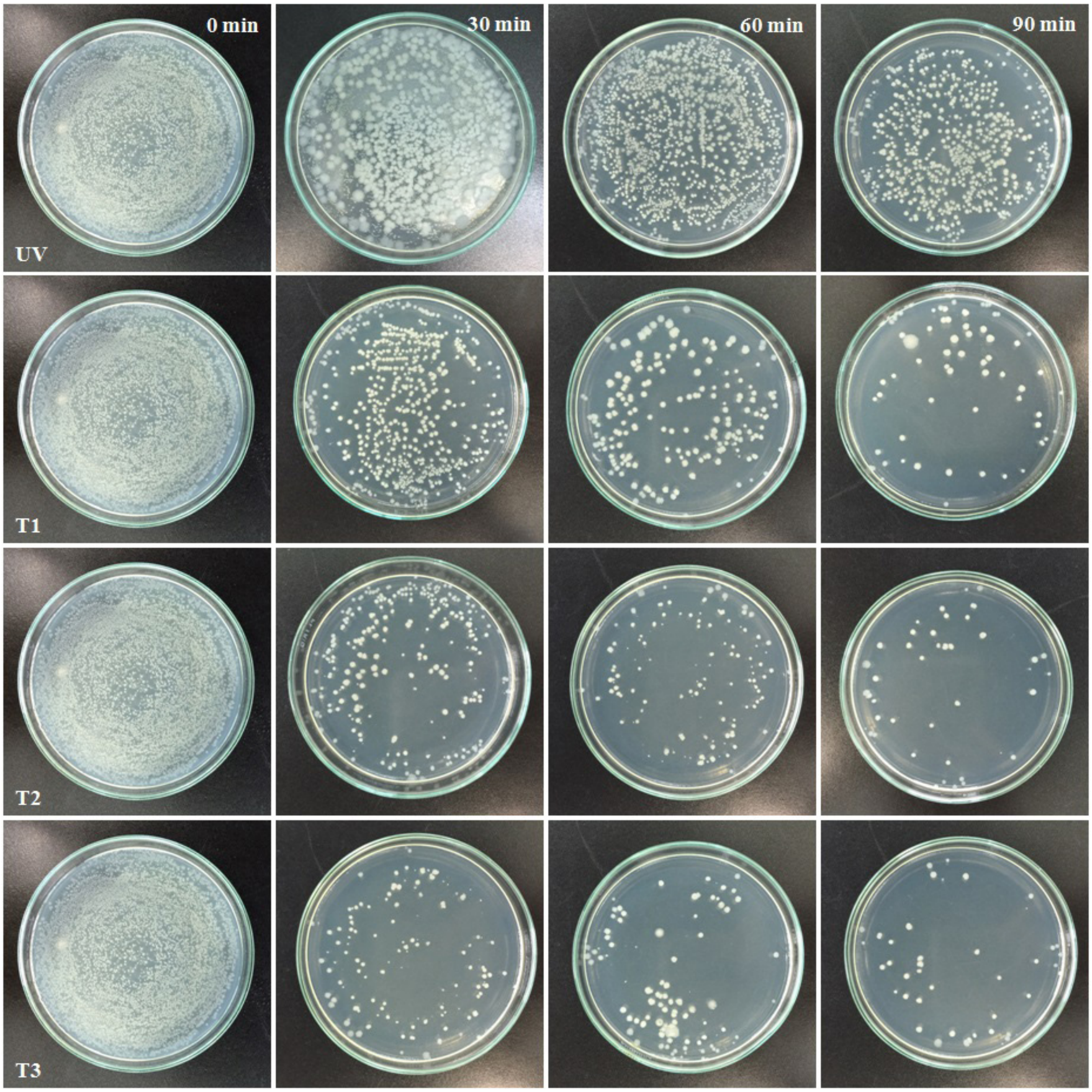

Figure 7. Photo of viable *S. aureus* colonies under UV irradiation of TiO_2 powder refluxed at 180 W for 1, 2 and 3 h under UV irradiation compared with control condition (UV case)

4. Conclusion

In this work, TiO_2 powder was fabricated via microwave-assisted sol-gel method which the powder was refluxed at 180 W for 1-3 h and dried at 180 W for 1 h by a conventional microwave oven. The effects of refluxed time on microstructure, photocatalytic and antibacterial activities were investigated and concluded as followings,

1. Nanocrystalline anatase TiO_2 particles with spherical shape were obtained and their crystallite sizes decreased considerably with increasing refluxed time.

2. Photocatalytic and antibacterial activities of the synthesized powder were greatly enhanced when longer refluxed time

was applied, and thus the TiO_2 powder refluxed for 3 h offered the highest photocatalytic and antibacterial activities under UV irradiation with MB degradation percentage of 68.66% and *S. aureus* kill percentage of 91.67%.

3. The presence of anatase TiO_2 was believed to be responsible for such a high efficiency in the photocatalytic and antibacterial activities under UV light.

5. Acknowledgements

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6. Reference

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