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Photocatalytic and Antibacterial Activity of Ag-doped TiO_2 Nanoparticles

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Abstract

The powders of TiO_2 and TiO_2 doped with Ag were prepared by sol-gel method. The prepared powders were calined at the temperature of 400°C for 2 h with the heating rate of 10°C/min. The microstructures of the fabricated powders were characterized by SEM, XRD and EDX techniques, and the results show that all samples were the agglomeration and reveal only the anatase phase. The photocatalytic activities of the powders were also tested via the degradation of methylene blue (MB) solution under UV irradiation. Finally, antibacterial activity efficiency was evaluated by the inactivation of *E.coli.* It was observed that higher Ag concentration gives better photocatalytic and antibacterial activity. With the highest dopant concentration investigated in this experiment (TiO_2-5Ag condition) the powders show photocatalytic and antibacterial activities of 52.30 and 95.14%, respectively.

Keywords: TiO_2, Ag-doped, Photocatalytic activity, Antibacterial activity, Sol-gel

1. Introduction

In recent years, semiconductor photocatalyst has been a subject of considerable interest. Titanium dioxide (TiO_2) activated by near ultraviolet (UV) light is probably by far the most widely studied photocatalyst for its water and air purification capabilities. Nanometer semiconductor TiO_2 powders have excellent properties of photocatalytic degradation. The glass with TiO_2 powders have good performance of antibacterial, disinfections, antifogging and self-cleaning, etc. So it can be widely used in building, car, bathroom, public latrine and so on (1).

Nowadays, many studies have been devoted to further improve the photocatalytic and antibacterial properties of TiO_2 powders or thin films, and the investigations suggest that those properties can be enhanced by doping with transition metal such as Fe^{3+} (2), N (3), Cu (4), and Ag (5-6) which has also been investigated widely aiming at extending photocatalytic and antibacterial activities into the UV region.

Many methods are used to prepare TiO_2 powders. The sol-gel method is one of the most commonly employed methods due to high purity materials can be synthesized at low temperatures (7-8).

In this work, powders of TiO_2 and Ag-doped TiO_2 were prepared by sol-gel method. Based on our previous studies, the amount of Ag in the range of 0 to 5 mol% of TiO_2 is carried on. The effects of the Ag doping into TiO_2 powders on the microstructure photocatalytic and antibacterial activity were investigated.

2. Experimental and Details

2.1 Raw materials

Titanium (IV) isoproxide (TTIP) and silver nitrate ($AgNO_3$) were used as raw materials. Ethanol (C_2H_5OH) was used as a solvent.

2.2 Powders preparation

TiO_2 and TiO_2 doped with Ag (TiO_2-Ag) powders were prepared via sol-gel method. Firstly, $AgNO_3$ was introduced to maintain the mole ratio of Ag in the TiO_2 at 0, 1, 3 and 5 mol% of TiO_2 and TTIP with fixed volume at 10 ml were mixed into 150 ml of C_2H_5OH and the mixture was then vigorously stirred at room temperature for 15 min. The pH of the mixed solution was adjusted to about 3 - 4 by adding 3 ml of 2 M HNO_3. Finally, it was vigorously stirred at room temperature for 45 min, dried at 100°C for 24 h and calcined at 400°C for 2 h with a heating rate of 10°C/min.

2.3 Powders characterizations

The morphology and particle size of the fabricated powders were characterized by Scanning Electron Microscope (SEM-Quanta 400). The phase composition was characterized using an X-ray diffractometer (XRD) (Phillips X'pert MPD, Cu-K). The crystallite size was calculated by the Scherer equation, Eq. 1, (9).

$$D = 0.9\lambda/\beta \cos\theta B \qquad (1)$$

where D is the average crystallite size, λ is the wavelength of the Cu Kα line (0.15406), θ is the Bragg angle and β is the full-width at half-maximum (FWHM) in radians.

2.4 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 and TiO_2-Ag powders and kept in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. After photo-treatment for a certain time, the concentration of 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 in order to observe the photocatalytic degradation and the percentage degradation of the MB molecules (%DMB) was calculated by Eq. 2, (10).

$$\%DMB = 100(C_0-C)/C_0 \qquad (2)$$

where 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.

2.5 Antibacterial activity test

Antibacterial activity of TiO_2-Ag powders against the bacteria *Escherichia coli* (*E.coli*) was studied and compared to the TiO_2 powder. Aliquots of 100 ml *E.coli* conidial suspension (10^5 CFU/ml) were mixed with 0.05 g of powder. The mixture was then exposed to either UV irradiation (eleven 50 W of black light lamps) for 0, 15, 30, 45 and 60 min. Then, 0.1 ml of mixture suspension was sampled and spread on Macconkey Agar plate and incubated at 37°C for 24 h. After incubation, the number of viable colonies of *E.coli* on each Macconkey Agar plate was observed (2) and disinfection efficiency of each test was calculated in comparison to that of the control. Percentage bacterial reduction (%BR) or *E.coli* kill percentage was calculated according to the following equation, Eq. 3, (11).

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

where N_0 and N are the average number of live bacterial cells per milliliter in the flask of the control and thin films finishing agent or treated fabrics, respectively.

3. Results and Discussion

3.1 Powders characterizations

The surface morphology was observed with SEM. Figure 1 shows surface morphologies of TiO_2 and TiO_2-Ag powders. It was seen that for all powders, the agglomeration was observed and the particle size decreases with increasing Ag doping.

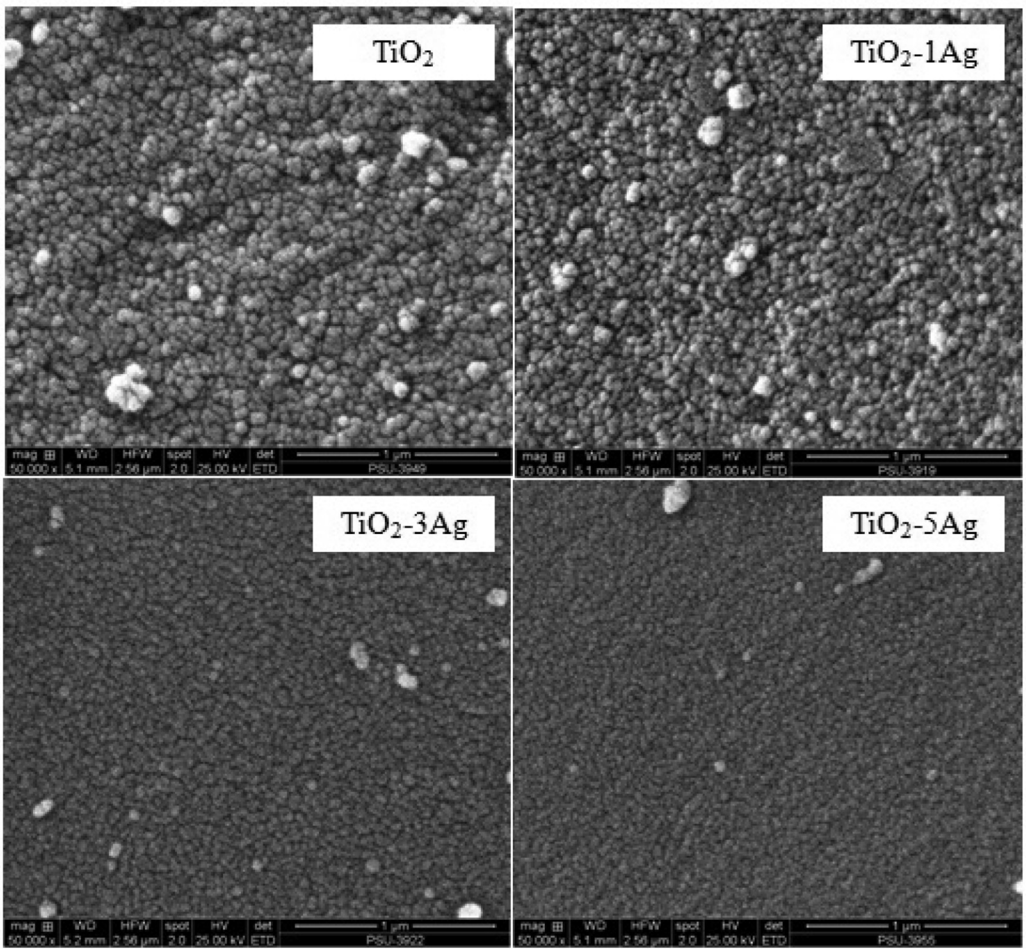

Figure 1. SEM surface morphology images of TiO_2 and TiO_2-Ag powders (magnification 50,000X)

From the XRD study as shown in Figure 2, it was found that TiO_2 and TiO_2-Ag powders reveal only the anatase phase. Ag-compound phase can't be verified in these XRD peaks due to a very small amount of Ag doping. The anatase peaks were observed about at 25.50°, 37.59°, 48.01°, and 54.16° (2), and all samples have the crystallite sizes of anatase phases in the range of 20.7 to 23.6 nm. The presence of Ag and Ti in the TiO_2-Ag powders was determined by EDX spectra and the result is shown in Figure 3, confirming the presence of the Ti and Ag composition in the powders.

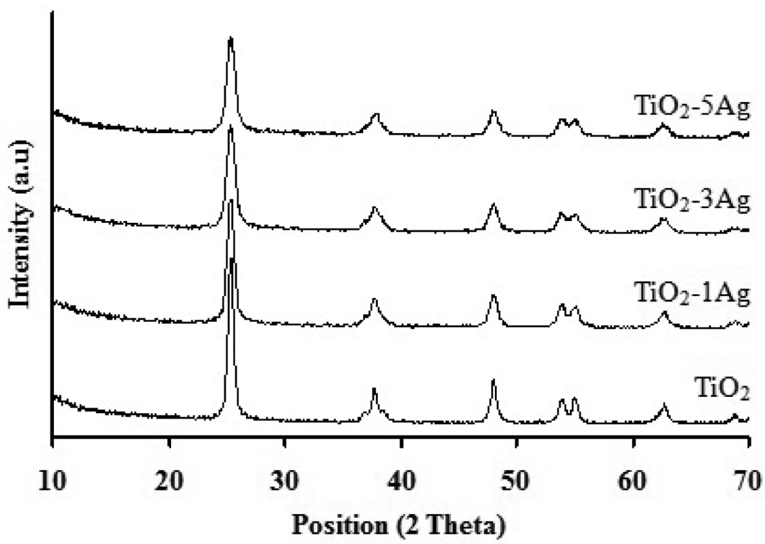

Figure 2. XRD patterns of TiO_2 and TiO_2-Ag powders

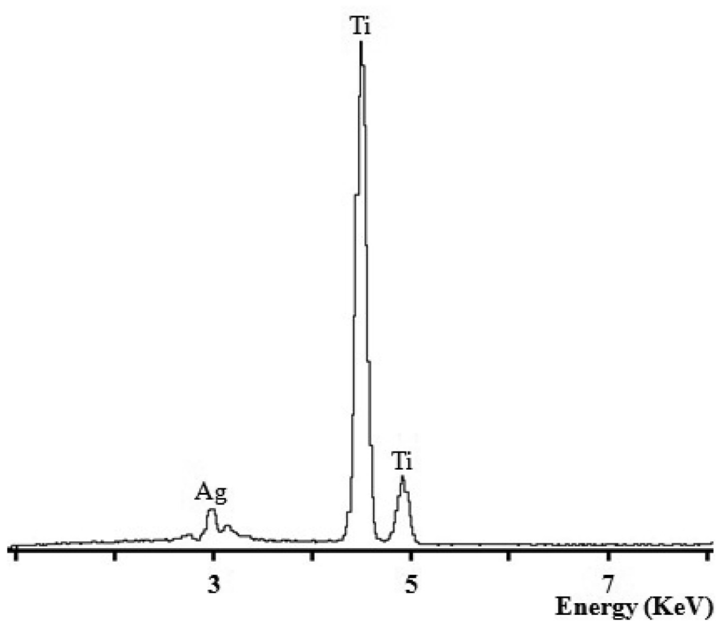

Figure 3. EDX spectra of TiO_2-5Ag powders

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using TiO_2 and TiO_2-Ag powders under UV irradiation is shown in Figure 4. It was apparent that Ag added in TiO_2 has significantly effect on photocatalytic reaction under UV irradiation, with the photocatalytic activity increases with increasing Ag doping. The MB degradation percentage of TiO_2 and TiO_2-Ag powders under UV irradiation is shown in Table 1. It was found that MB degradation percentage of TiO_2 and TiO_2-Ag powders under UV irradiation for 6 h are 43.89, 46.66, 48.60 and 52.30% for 0, 1, 3 and 5 mol% of Ag doping, respectively. It was found that TiO_2-5Ag powders show the best photocatalytic activity.

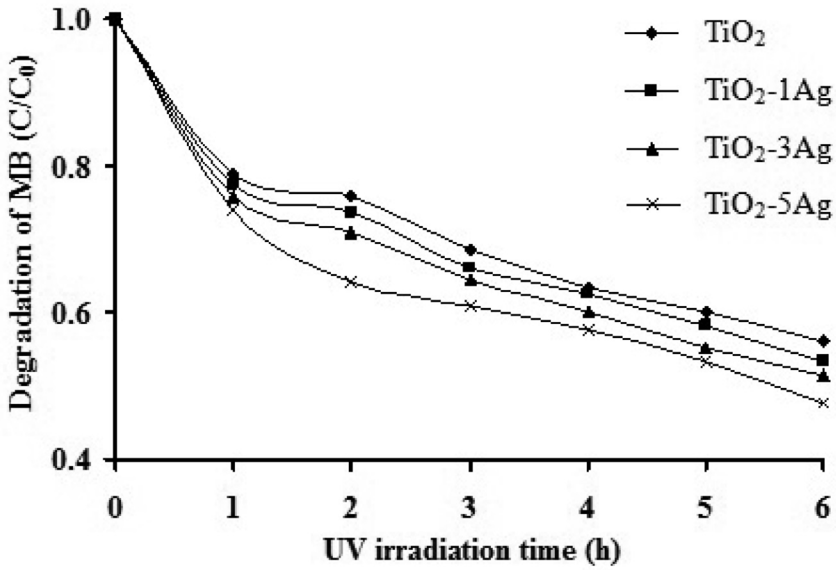

Figure 4. The photocatalytic activity of TiO_2 and TiO_2-Ag powders under UV irradiation

Table 1. The MB degradation percentage of TiO_2 and TiO_2-Ag powders under UV irradiation

Sample	UV irradiation time (h)						
	0	1	2	3	4	5	6
TiO_2	0.00	21.24	24.09	31.33	36.75	39.83	43.89
TiO_2-1Ag	0.00	22.56	26.37	33.88	37.55	41.94	46.66
TiO_2-3Ag	0.00	24.09	28.94	35.57	39.97	44.81	48.60
TiO_2-5Ag	0.00	26.09	35.96	39.08	42.31	36.67	52.30

3.3 Antibacterial activity

Figure 5 displays the *E.coli* survival rate (N/N_0) after testing with UV illumination on TiO_2 and TiO_2-Ag powders. The result shows that the *E.coli* survivals decrease with UV irradiation time. It also indicates that the TiO_2 doped with 5% Ag powders exhibit higher antibacterial activity compared to TiO_2 and TiO_2 doped with 1 and 3% Ag powders, respectively. The *E.coli* kill percentage of TiO_2 and TiO_2-Ag powders under UV irradiation is shown in Table 2. It is found that the *E.coli* kill percentage of TiO_2 and TiO_2-Ag powders under UV irradiation for 1 h are 51.43, 62.86, 84.00 and 95.14% for TiO_2 and TiO_2 doped with 1, 3 and 5% Ag powders, respectively. In this research, Researchers have studied the influence of UV disinfection affecting *E.coli* (case no TiO_2 and TiO_2-Ag powders) from testing found the *E.coli* kill percentage infection was very low. The percent mortality was only 5% under UV irradiation for 1 h, so the factors that affect the *E.coli* kill percentage infection for this research came from the influence of Ag mixed into the TiO_2. The photo of viable bacterial colonies (red spots) on fabricated TiO_2, TiO_2-Ag powders and the control treated with UV for 1 h are illustrated in Figure 6.

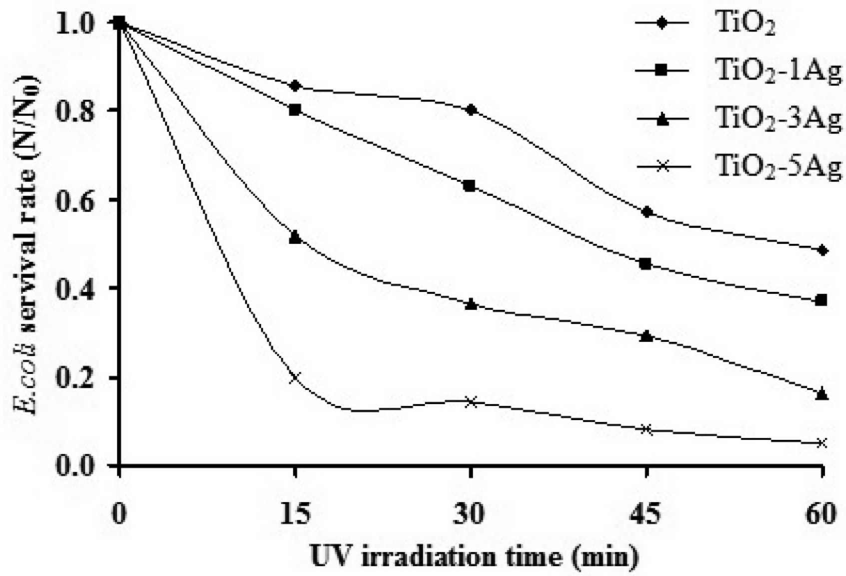

Figure 5. The antibacterial activity of TiO_2 and TiO_2-Ag powders under UV irradiation

Table 2. The *E.coli* kills rate percentage of TiO_2 and TiO_2-Ag powders under UV irradiation

Sample	UV irradiation time (min)				
	0	15	30	45	60
TiO_2	0.00	14.29	20.00	42.86	51.43
TiO_2-1Ag	0.00	20.00	37.14	54.29	62.86
TiO_2-3Ag	0.00	48.00	63.71	70.86	84.00
TiO_2-5Ag	0.00	80.00	85.71	92.71	95.14

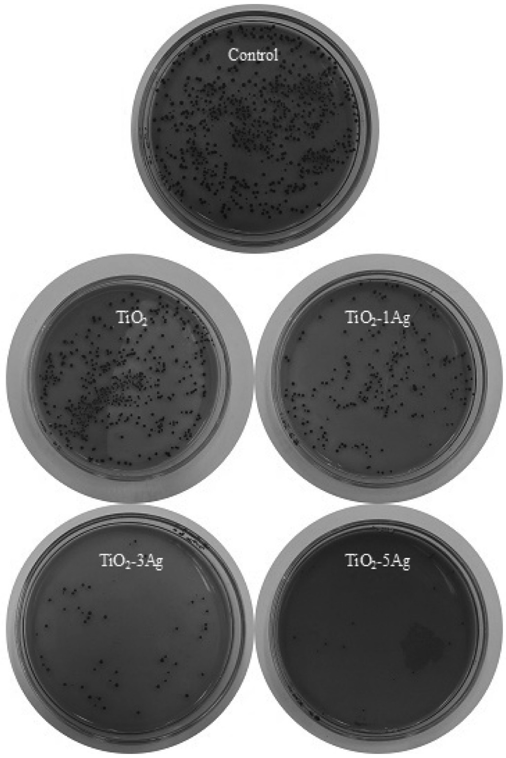

Figure 6. Photo of viable *E.coli* colonies during 1 h UV irradiation of TiO_2 and TiO_2-Ag powders compared with control condition

4. Conclusion

In this work, TiO_2 and TiO_2 doped with Ag powders were fabricated by sol-gel method. The effect of Ag doping into TiO_2 powders on microstructure, photocatalytic and antibacterial activity were investigated and concluded as followings,

1. TiO_2 and TiO_2-Ag powders reveal only the anatase phase and surface morphologies was found that for all powders, the agglomeration was observed and the particle size decreases with increasing Ag doping.

2. The photocatalytic and antibacterial activities of TiO_2-Ag powders increases with Ag doping concentration and thus, TiO_2 doped with 5% Ag powders exhibits higher photocatalytic and antibacterial activities under UV irradiation with MB degradation percentage of 52.30% and *E.coli* kill percentage of 95.14%.

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6. References

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