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Effect of Synthesis Method and Amount of Silver on Physicochemical Properties and Photocatalytic Activity of Ag Doped TiO_2 Nanoparticles

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***Abstract*:** *Ag doped TiO_2 (AgT) nanoparticles have been synthesized by solvothermal method (S) and impregnation method (I) with different amount of silver dopant. In order to study the effect of synthesis method and amount of silver on physical and chemical properties of AgT nanoparticles, X-ray diffraction (QXRD), field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDS) and UV-visible absorption spectrophotometer (UV-vis) were used to characterize the obtained nanoparticles. The results showed that solvothermal method provided smaller crystallite size, higher surface area and lower band gap energy of photo catalyst than that of impregnation method. The photocatalytic efficiency was evaluated by photo degradation of methylene blue under LED light irradiation. The 10%AgT synthesized from solvothermal method exhibited the highest photocatalytic efficiency (96.59%) due to its great physicochemical properties of TiO_2 such as small crystallite size, anatase form, high surface area, low band gap energy and the synergistic effect of Ag and TiO_2.*

Keywords: *photocatalysis, Ag doping, titaniumdioxide, solvothermal, crystallinity*

1. Introduction

Photocatalyst is one of smart materials that has received a great attention due to their wide applications for air purification [1, 2], water treatment [3], bacterial removal [4, 5] and other applications in environmental cleaning [6-8]. The fundamental process of photocatalysis is carried out by light irradiation through the semiconductor. Among semiconductors, titanium dioxide (TiO_2) is the most widely used. This is because TiO_2 exhibits high photosensitivity and strong photocatalytic reaction with non-toxic nature, low cost, and environmental friendly [9, 10].

Nevertheless, the photocatalysis of TiO_2 is limited by its large band gap energy of TiO_2 (about 3.2 eV). Accordingly, it is active only under UV light irradiation and rapid recombination between electron-hole pairs of TiO_2 can be occurred. These limits cause low photocatalytic reactivity of TiO_2 when it is applied under visible light [11].

Silver (Ag) metal doping on TiO_2 has been recommended in many researches [12-14] for improving the photoactivity of TiO_2 [5]. Ag deposited on TiO_2 has positive effects on the photoactivity in terms of narrowing band gap energy of TiO_2 by the surface plasmon resonance of Ag, resulting in extend range of the visible light absorption [15] and prevention of recombination between electron-hole pair [10]. In this work, we studied the effect of two different synthesis methods (solvothermal and impregnation) and Ag loading on the photocatalytic activity of doped TiO_2. Moreover, the crystal structure, optical properties and morphology of Ag doped TiO_2 nanoparticles were examined. The photocatalytic activities of Ag doped TiO_2 were examined by the degradation of methylene blue (MB) under visible light illumination compared with bare TiO_2.

2. Materials and Methods

2.1. Materials

All chemical reagents used for the synthesis of the modified TiO_2 nanoparticles were analytical grade without further purification. Titanium (IV) butoxide ($Ti(OC_4H_9)_4$, ⩾ 97%) was purchased from Fluka. Silver nitrate ($AgNO_3$, 99%), Ethanol (C_2H_5OH, 99.8%) and Nitric acid (HNO_3, 65%) were purchased from Merck. Commercial TiO_2 with anatase form was purchased from chemical village co.,ltd., China. Methylene blue (MB, ⩾ 96%) was purchased from Unilab and used for photocatalytic experiment. Deionizer water was used in all experiments.

2.2. Ag Doped Tio_2 Preparation by Solvothermal Method

Ag doped TiO_2 (AgT) were prepared by solvothermal method. Firstly, Ti solution was prepared by dissolving 34 mL of $Ti(OC_4H_9)_4$ in 90 mL of ethanol. After stirring for 15 min, 1.26 mL of HNO3 and 3.6 mL of distilled water were dropped into Ti solution, respectively. Secondly, Ag solution (5, 10 and 15%mol of Ag) was prepared by dissolving in 20 mL of ethanol. Finally, Ag solution was slowly added into Ti solution with magnetic stirring for 3 h. The obtained AgT sol was transferred into a teflon-lined stainless steel autoclave during 3 h at 250 ◦C. After washing by ethanol and distilled water, the obtained precipitate was dried at 100 ^{o}C for 24 h and calcined at 550 ◦C for 3 h. The as-synthesized AgT nanoparticles were obtained.

2.3. Ag Doped Tio_2 Preparation by Impregnation Method

Firstly, 8 g of commercial TiO_2 anatase was dissolved in 100 mL of distilled water and then an appropriate amount of dopant was added to Ti suspension under stirring. Next, the slurry was stirred continuously for 3 h before drying in an air oven at 110◦C for 24 h. Finally, the dried solids were crushed to fine powder with an agate mortar before calcination at 550◦C for 3 h. The sample ID of all the obtained nanoparticles synthesized by solvothermal method and impregnation method were given in Table I.

2.4. Characterization

The structural and morphological characterizations of all synthesized photocatalysts were carried out by the quantitative X-ray diffraction (QXRD) using a Cu Kα radiation source (λ = 1.54 Å) operated at 50 kV and 50 mA, field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray (EDX) analyzer operating at 15 kv. The absorption edge wavelengths were recorded by UV-vis Near Infrared Spectrometer within the range 300-700 nm (Perkin Elmer, Lambda 950) and the surface area of the nanoparticles was analyzed by BET method.

2.5. Photoactivity Test

The photocatalytic activity of synthesized nanoparticles was evaluated by the decolorization of methylene blue (MB) solution under LED light irradiation. The experiment was carried out in a closed wooden box with dimensions of 30 x 40 x 60 nm. A LED lamp (16 W, General Electric) was equipped at the top center of a closed wooden box and parallel with a photoreaction in a beaker with distance of 15 cm from the bottom of a beaker. The experiment was divided into two steps. Firstly, 1 g of the synthesized TiO_2 nanoparticles dispersed in 100 mL of 1x10-5 M of MB solution was kept under dark condition for 3 h in order to obtain the adsorption-desorption equilibrium between catalyst and MB solution. Secondly, the reactor with new MB solution was then irradiated with LED light lamp for 6 h. Every 30 min, 5 mL of MB solution was taken out and centrifuged at 6,000 rpm for 10 min to separate the nanoparticles. The decolorization of the centrifuged MB solution was measured by UV-vis spectrophotometry at the maximum wavelength of 664 nm. The degradation efficiency of MB was calculated by using formula (1).

$$\text{Degradation efficiency (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad (1)$$

Where C_0 is initial concentration of MB and C_t is a concentration of MB at a measuring time (t)

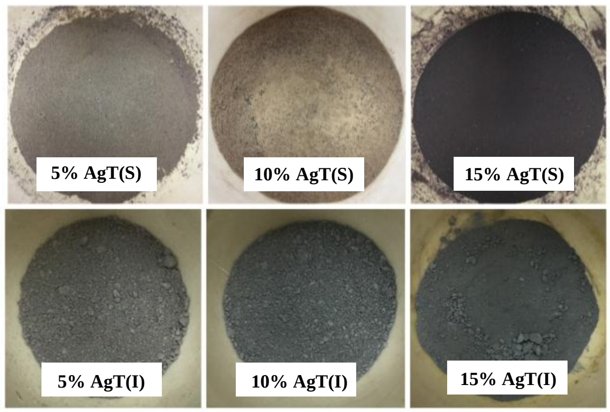

Fig. 1: The Obtained AgT(S) and AgT(I) nanoparticles via different synthesis method and different Ag loading

TABLE I: Physical properties of Ag doped TiO_2 nanoparticles

Sample ID[a]	Crystal phase[b] (%)	Band gap (eV)	Crystal size (nm)
T (S)	A:100	3.35	28.36
T (I)	A:100	3.40	39.76
5% AgT (S)	A:100	2.90	24.66
10% AgT (S)	A:100	2.50	20.55
15% AgT (S)	A:54; R:46	2.26	21.27
5% AgT (I)	A:100	3.26	55.98
10% AgT (I)	A:100	3.26	54.54
15% AgT (I)	A:100	3.20	51.26

[a]T, S, and I denote titaniumdioxide, solvothermal method and impregnation method, respectively.
[b]A and R denote anatase and rutile phase, respectively.

3. Results and Discussion

3.1. Physical and Structural Properties

Ag doped TiO_2 (AgT) nanoparticles with different amounts of Ag dopant (5%, 10% and 15% mol) were prepared by solvothermal method and impregnation method. The obtained nanoparticles of AgT were shown in Fig. 1. The results showed that the obtained AgT nanoparticles from solvothermal (AgT(S)) and impregnation methods (AgT(I)) had different colors varying from pale gray (low Ag loading) to dark brown (high Ag loading). The different color of Ag doped TiO_2 nanoparticles might be explained by the partial reduction of Ag from Ag^+ to Ag^0 during synthesis process [13]. As a result, the reduction of Ag caused the formation of Ag_2O and Ag^0 deposited on TiO_2 nanoparticles.

3.2. XRD Analysis

To investigate the change of the TiO_2 crystallinity affected by different Ag loading, the quantitative XRD patterns of as-synthesized nanoparticles were examined in the range of 20-80^o as shown in Fig. 2. The results showed that all AgT had observable anatase phase at 25° (101), except for 15% AgT(S) small rutile phase was observed at 27° (110). The phase transformation to rutile could occur at the higher temperature (>550 ^{o}C) when using the excessive amount of Ag metal in the solvothermal process [16-17]. AgT(S) and AgT(I) catalysts had additional peaks at 2θ value of 44.3° (111) which was attributed to the crystal planes of metallic silver. The content of Ag dopant and synthesis method have significant effects on the crystalline structure of doped TiO_2.

The crystallite size of nanoparticles can be estimated from the strongest peak of anatase following the Scherrer's equation. The XRD peaks of samples synthesized by solvothermal method were broader than the catalyst synthesized by impregnation method. This indicated that solvothermal gave smaller crystallite size than impregnation. This is in agreement with the averaged grain sizes of anatase as presented in Table I.

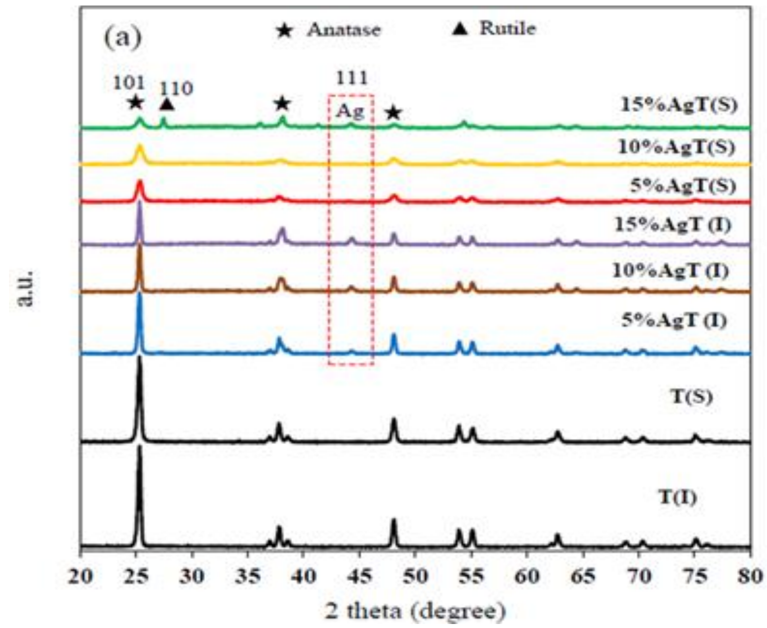

Fig. 2: XRD patterns of AgT(S) and AgT(I) nanoparticles via different amount of Ag loading (5%, 10% and 15% mol)

3.3. SEM Analysis

FESEM images illustrated in Fig. 3 clearly show that AgT(I) nanoparticles have uniform in spherical shape, particle size, and particles dispersion. The addition of Ag had no significant change in the morphology of AgT nanoparticles compared to bare TiO_2. The average particle sizes of AgT(I) from the FESEM images were approximately 100 nm, larger than that of AgT(S), which was only 50 nm. This is a similar trend with the crystallite sizes determined from the XRD patterns. The images of AgT(S) in Fig. 3(e-h) indicated the aggregation of a large number of small spherical particles. The aggregation is caused by the suppression of grain growth under high temperature and pressure inside an autoclave. As a result, small sized particles were formed and aggregated rapidly [18, 19]. The present of Ag on the TiO_2 surface was confirmed by EDX analysis as shown in Table II.

3.4. Optical Properties

The UV-vis absorption spectra of AgT and T nanoparticles were collected in the wavelength range of 200-800 nm. The calculated band-gap energy (Eg) values are shown in Table I. It reveals that Eg values of AgT(S) are dramatically decreased compared to bare T from 3.35 to 2.26 eV, whereas the Eg values of AgT(I) are slightly decreased from 3.40 to 3.20 eV, upon doping of Ag. The reduction of band-gap energy attributed to the surface plasmon resonance of Ag in the crystal structure phase [13, 20], which extended the light absorption to longer wavelengths. Thus, we can conclude that the deposition of Ag on TiO_2 successfully reduced the band gap energy, extended the light absorption to visible region [14, 15].

3.5. Photocatalytic Performance

The photocatalytic activity of pure T and AgT nanoparticles were evaluated by the photodegradation of MB solution under white LED light irradiation. The MB photodegradation of AgT nanoparticles were shown in Fig. 4. The result showed that the photocatalytic activities of all AgT nanoparticles under LED light were improved when compared to bare T due to their higher visible light absorption of TiO_2 upon Ag doping. The efficiency of the catalysts for MB photodegradation followed the order: AgT(S) (92-96%) > AgT(I) (73-83%) > T(S) (57%) >

T(I) (43%). The photocatalytic activity of nanoparticles synthesized by solvothermal method or AgT(S) was higher than nanoparticles synthesized by impregnation method (AgT(I)) due to their lower band gap energy and smaller crystallite size which result in the higher specific surface area. Among the synthesized photocatalysts, 10%AgT(S) had the highest photocatalytic activity followed by 15%AgT(S). The excess amount of Ag (15%mol) could prevent the light absorption of TiO_2 resulting in the interrupt photoactivity. Hence, these phenomena confirm that the solvothermal synthesis and the optimal of Ag amount significant effect on the enhancement photocatalytic performance under visible light irradiation.

TABLE II: Composition of AgT nanoparticles according to EDX Analysis

Samples	Ti (%wt)	O (%wt)	Ag (%wt)
5% AgT (S)	32.39	5.73	1.77
10% AgT (S)	57.51	37.15	5.34
15% AgT (S)	51.24	41.52	7.25
5% AgT (I)	70.51	28.59	0.82
10% AgT (I)	67.90	31.28	0.90
15% AgT (I)	71.16	27.25	1.59

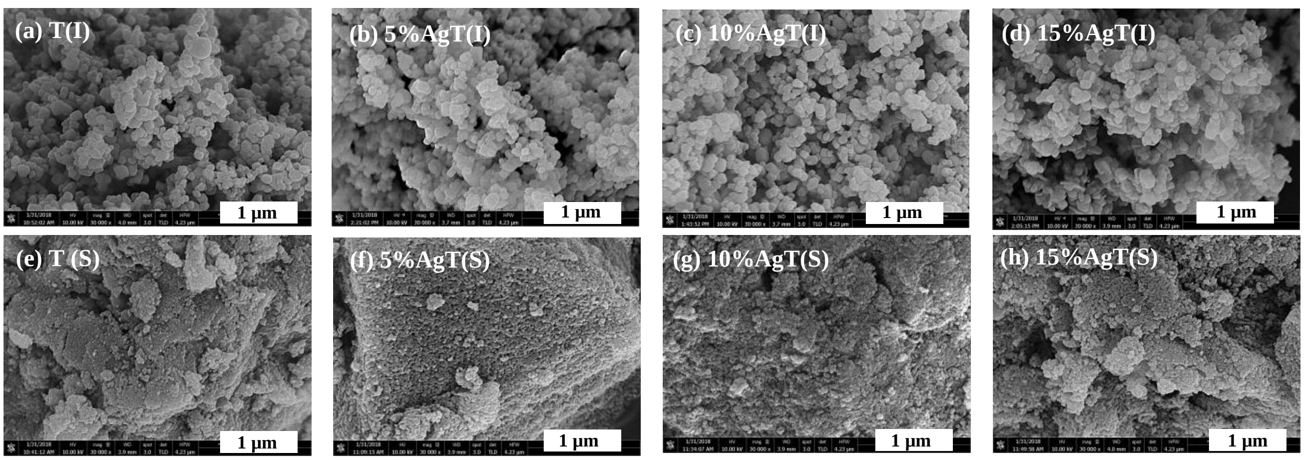

Fig.3: FESEM Images of the obtained T and AgT nanoparticles synthesized by Impregnation method and Solvothermal method

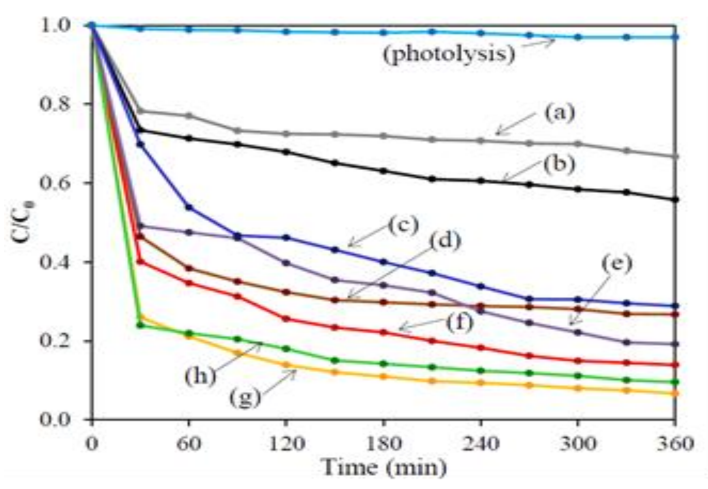

Fig. 4: The MB photodegradation under visible light irradiation by (a) T(I), (b) T(S), (c) 5%AgT(I), (d)10%AgT(I), (e) 15%AgT(I), (f) 5%AgT(S), (g) 10%AgT(S) and (h)15%AgT(S)

4. Conclusion

In summary, the synthesis of Ag doped TiO_2 photocatalysts with different amount of Ag (5%, 10% and 15% mol) using solvothermal method (AgT(S)) and impregnation method (AgT(I)) were carried out. The results show that the synthesis method and the amount of Ag play an important role in photocatalytic reactivity of TiO_2. AgT synthesized by solvothermal method with 10% Ag loading is a promising photocatalyst due to its small crystalline size, uniformly particles dispersion and large specific area. Overall photocatalytic performance of AgT under visible light irradiation can be improved by the synergistic effect between Ag and TiO_2. Ag doping on TiO_2 can facilitate the photoreaction by reducing band gap energy, extending wavelength absorption to visible light region and minimizing recombination of electron-hole. The highest MB photodegradation by 10%AgT (S) was increased to 96%.

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