



Effect of Formation of $\text{Ag}_2\text{Ti}_4\text{O}_9$ Phase on Photocatalytic Activity of Ag-TiO_2 Nanocomposite

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ABSTRACT

Ag-TiO_2 nanocomposite with the optimum concentration of 1wt% was produced by a sol-gel process using Rhodamine B for the catalytic activity. The initial samples were prepared by heat treatment at various temperatures (266, 338, 390, 485, 600 and 700°C) with a holding time of 2 h. DTA and XRD of these samples led to choosing the temperature of 530°C as the heat treatment temperature. Then some samples were heat treated at this temperature for various times (0.5, 1, 2, 4, and 6 h). The samples heat treated for 2 h at 266 and 338°C exhibited better degradation efficiency. The 530°C-1 hr sample exhibited the best degradation performance even in comparison with the commercial nano TiO_2 purchased from Degussa. To the best of our knowledge, we report (for the first time) the formation of $\text{Ag}_2\text{Ti}_4\text{O}_9$ phase at ambient temperature. This silver titanate phase gives rise to a better degradation efficiency compared to anatase. Characterization of Ag-TiO_2 samples was done by DTA, XRD, PL and SEM.

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1. INTRODUCTION

Application of visible light in degradation process of pollutants is becoming increasingly common. Much research has been devoted to the type of the additive element and its effect on pollutant degradation, the efficiency of the nano composite in decomposition of pollutants under visible light, and the materials cost [1]. Photocatalytic behavior in a material is a function of particle size, surface area, and uniformity in the particle morphology. Small-size particles of titanium dioxide crystals facilitate the direct transfer of electrons from the valance to conduction band, thus increasing the electron-hole generation [2]. Various studies have shown the advantages of anatase crystals, such as the larger band gap of anatase favoring redox reactions, faster electron hole pair (EHP) recombination on the surface of rutile particles, and larger surface area of anatase powders due to decreased particle size [3]. It is commonly accepted that the anatase crystal structure is the most photoactive phase of TiO_2 and that the rutile

content is usually eliminated or significantly reduced. It is possible, however, that an interaction between highly optimized anatase and rutile particles may provide a synergistic photocatalytic effect due to increased efficiency in charge separation, using a sensitization method where photo excited electrons are transferred from the conduction band of an anatase particle to the lower energy conduction band of a rutile particle [4-6]. The transformation of anatase to rutile increased with a boost of calcination temperatures [7]. Doping TiO_2 with small quantities of some elements, e.g. transition elements and lanthanides is another way of trapping charge carriers. This would result in increased photocatalytic efficiency [8-12]. Wide-spread medical applications of Ag and antibacterial properties of TiO_2 has stimulated a great deal of research and development in order to combine the properties of both materials in products such as coatings of medical equipment, food covers, air conditioning fillers, etc. Ag absorbs electrons which are generated in the TiO_2 lattice, thus gives holes a longer time for the degradation of organic molecules. Silver shifts the absorption edge of TiO_2 towards visible light. The present work reports the effects of temperature and time

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of heat treatment on controlling the photocatalytic efficiency and phase transformation of TiO₂ nano particles synthesized by a modified sol-gel technique. The photocatalytic activity of the modified catalyst was compared to pure TiO₂ (P-25 Degussa) for degradation of Rhodamine B.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of Photocatalysts Commercial titanium isopropoxide (Merck 821895) and silver nitrate were used as the Ti and Ag sources for producing the Ag-TiO₂ photocatalyst. Isopropanol (Merck 109694) was used as an organic solvent. Hydrochloric acid (6 mL of HCl Merck 100317) was used as catalyst agent and to adjust the pH of the solution. The water used in this experiment was double distilled and deionized water (Merck 115333). Degussa has produced a commercial catalyst named Degussa P-25 TiO₂ that is commonly used as an “ideal” photocatalyst and as a reference for research laboratories worldwide. Degussa P-25 TiO₂ is created in powder form by flame hydrolysis of TiCl₄ at temperatures in excess of 1200°C. The finished product is more than 99.5% pure TiO₂. The anatase to rutile ratio is approximately 70:30 with a mean surface area of 50 m²/g and average particle size of 21 nm [13, 14]. Rhodamine B (Figure 1) (supplied by Merck) was the colorant dopant used to assist degradation tests. Water used for preparing the solutions was double-distilled.

Ag-TiO₂ nano composite was prepared using sol-gel technique. The molar ratio of H₂O/precursor (R_w) was 7 and pH was set at 2. Optimum concentration of Ag/Ti was 1% mol. Firstly, 25 mL of titanium isopropoxide was dissolved in 40 mL of dry isopropanol. Then 20 mL of isopropanol, 7 mL of deionized water, and 3.79 g silver nitrate were added to the above solution. The obtained mixture was further stirred for 20 min at room temperature until a thick transparent gel was obtained. Then the gel was dried in oven at 80°C for 12 h. The resulting solid gel was ground to a fine powder and subsequently heat-treated to study the structure, morphology and phase transformations.

2.2. Characterization of Photocatalysts The precipitated crystalline phases were identified using X-ray diffractometer (Seisert 3003TT, 2000, Germany).

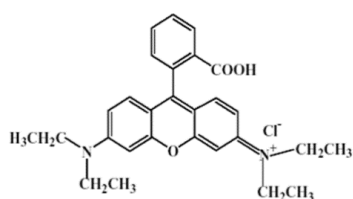


Figure 1. The molecular structure of Rhodamine B dye

DTA was recorded under air atmosphere using a spectrometer (Perkin Elmer instrument, pyris Diamond TG/DTA). The Scanning Electron Microscopy was carried out by FE-SEM Hitachi S416. Luminescence Spectroscopy (Luminescence Spectrometry LS-5 Perkin Elmer) and a static degradation test using a photo reactor was employed to characterize the samples.

2.3. Photocatalytic Activity Evaluation The photocatalytic activity of synthesized nano particles were tested by degrading Rhodamine B dye solution in a batch reactor (350 mL Pyrex glass beaker with a magnetic stirrer). The volume of Rhodamine B aqueous solution was 250 mL with an initial concentration of 50 ppm. The solution was continuously stirred at 500 rpm in all experiments. A total of 0.15 mg of catalyst was used for all experiments. Initially the reactor was kept in the dark for 45 min to establish adsorption equilibrium. Following this, the reactor was irradiated with visible light using three 90W lamps (Philips). A 5 mL sample was taken at different intervals for 250 min (a total of 5 samples). Before concentration measurement, all the samples were centrifuged for 20 min at 2000 rpm to remove the suspended nano particles. The concentration of Rhodamine B in the samples was determined by a UV-vis spectrophotometer (Chromophor, Vario 2600 model absorption at 554 nm, and standard calibration curve). Spectrometer acquired between 190 nm and 1100 nm at a resolution of 2 nm and a scan speed of 240 nm/min. The time-concentration data of Rhodamine B in the solution was then used to determine the degradation kinetics.

3. RESULTS AND DISCUSSION

3.1. DTA And XRD Analysis With respect to the DTA results presented in Figure 2, it was decided to investigate the effect of 2h heat treatment at 6 different temperatures, i.e. 266, 338, 390, 485, 600 and 700°C for holding time of 2 h; the heating rate was 10°C/min. Then the samples were analyzed by XRD. The results (Figure 3) indicated that Ag₂Ti₄O₉ phase formed in all samples. However, by increasing temperature, the intensities of the Ag₂Ti₄O₉ peaks were weakened while the anatase and rutile peaks started to appear at 370 and 510°C, respectively. This is an indication that the exothermic peaks in the DTA graphs around 370°C, and 510°C correspond to the formation of anatase and rutile phases, respectively. Therefore, the temperature 530°C (just above the rutile formation temperature) was chosen as just about the right temperature to yield a suitable anatase/rutile ratio, e.g. 70/30. Then, a set of new samples were prepared and heat treated at 530°C but at 5 different times (0.5, 1, 2, 4, and 6 h). The XRD results for this set of samples indicate the formation of Ag₂Ti₄O₉ as well as anatase and rutile phases (Figure 4).

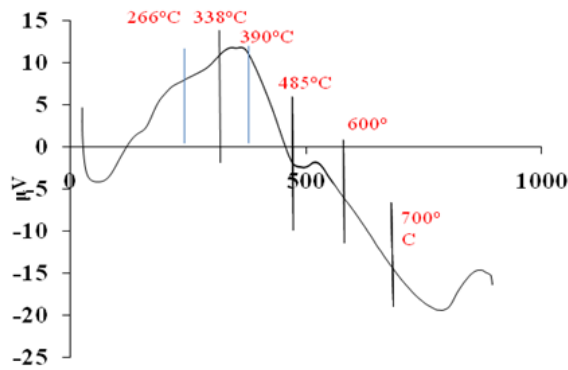


Figure 2. DTA analysis of samples at heating rate of 10 °C/min

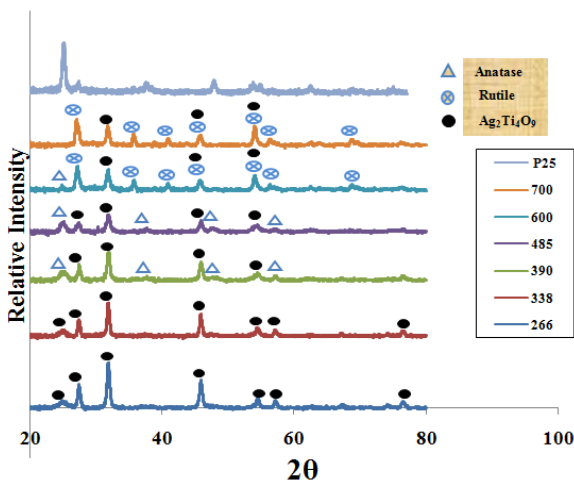


Figure 3. XRD patterns of samples heat treated at various temperatures for 2 h

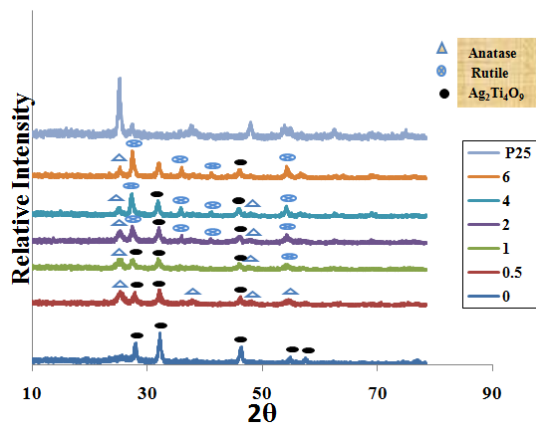


Figure 4. XRD patterns for heat treated samples at 530°C for various times

At the beginning of the heat treatment process (0 h) $\text{Ag}_2\text{Ti}_4\text{O}_9$ was the only phase present. However, peak

intensities for this phase decreased by increasing heat treatment time. The anatase phase formed at 0.5 and 1 h, while rutile phase formed by longer heat treatments, and its quantity increased at the expense of anatase as the heat treatment continued. Crystallite sizes for the anatase and rutile phases were estimated using peak broadening analysis and the Scherrer's equation; results are presented in Tables 1 and 2.

$$L = K\lambda/(\beta\cos\theta) \quad (1)$$

where β =FWHM, λ = wavelength, K =form factor: 0.89 for cubic and 0.94 for spherical crystallites, L =crystallite thickness, and θ =Bragg angle.

3. 2. SEM Analysis

Microstructures of the heat treated samples were examined by SEM (Figures 5 and 6).

It seems from the micrographs that by increasing the heat treatment temperature from 266 to 485°C, the microstructure becomes finer. However, this does not seem to happen for temperatures above 485°C. Micrographs of Figure 6 indicate that heat treatment up to 1 h produces a fine microstructure which is desirable for degradation efficiency of the photocatalyst.

TABLE 1. Results of crystallite size calculations for samples heat treated at various temperatures

Sample code	FWHM	Rutile (nm)	Anatase (nm)	Ag (nm)	FWHM
266	2.9176	-	-	13.7	2.9176
338	2.9314	-	-	15	2.9314
390	2.9523	-	5.8	12.7	2.9523
485	2.9245	-	6.8	11	2.9245
600	2.9176	10.2	-	15	2.9176
700	2.9107	11.7	-	12.7	2.9107
P25	3.1472	18.2	14	-	3.1472

TABLE 2. Results of crystallite size calculations for samples heat treated at various times

Sample code	Ag (nm)	Anatase (nm)	Rutile (nm)	FWHM
0	19.7	-	-	
0.5	16.5	8.1	-	2.9107
1	12.7	11.6	-	2.9245
2	13.7	9	12.6	2.9245
4	13.8	10.2	13.6	2.9245
6	15	16.3	14.9	2.9176
P25	-	14	18.2	3.1472

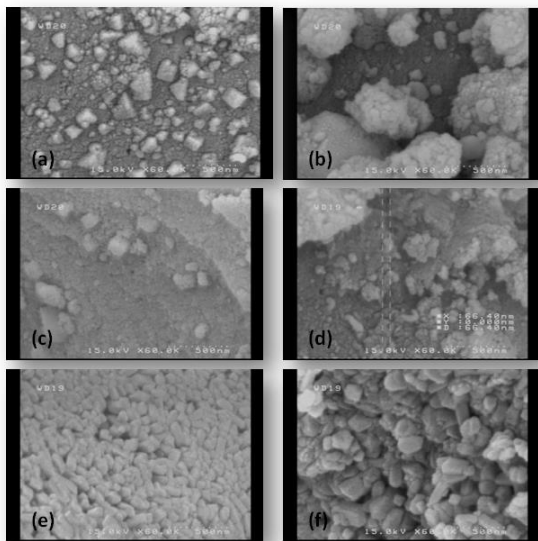


Figure 5. SEM micrographs of samples heat treated at (a) 266, (b) 338, (c) 390, (d) 485, (e) 600, and (f) 700°C

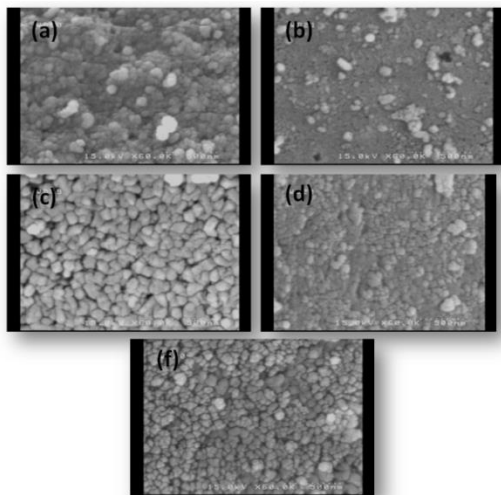


Figure 6. SEM micrographs of samples heat treated for (a) 0.5, (b) 1, (c) 2, (d) 4, and (e) 6 h

3. 3. The Photoluminescence Emmission Studies

Figures 7 and 8 show the results of luminescence test for the heat treated samples. The Photoluminescence emission (PL) is useful to disclose the efficiency of charge carrier trapping, immigration and transfer, and to understand the fate of electron-hole pairs in semiconductor particles [15]. It is known that the PL emission is the result of the recombination of excited electrons and holes; the lower PL intensity may indicate the lower recombination rate of electron-holes under light irradiation [16].

Results in Figure 7 show a relatively low-intensity luminescence for samples heat treated at 266 and 338°C. This is an indication of good electron-hole separation in the nano composite. Moreover, the lowest intensity in 1 h heat treated sample was observed in

Figure 8, implying that the charge carriers were separated more effectively, which reasonably led to a higher photocatalytic activity since the photo degradation reactions were evoked by these charge carriers. The 1 h heat treated sample is expected to have better degradation efficiency because of its finer microstructure as well as its phase composition (anatase and $Ag_2Ti_4O_9$).

3. 4. Photocatalytic Degradation Test

Results of degradation tests for sample heat treated for 2 h at various temperatures are shown in Figure 9. Also results for samples heat treated at 530°C for various times are shown in Figure 10. These results indicate that samples heat treated at 266 and 338°C exhibit better degradation properties against Rhodamine B pollutant. The two samples have similar composition and microstructure; therefore, they are expected to have similar degradation behaviors. It is known that silver particles deposited on the surface of titania can act as electron-hole separation centers [17].

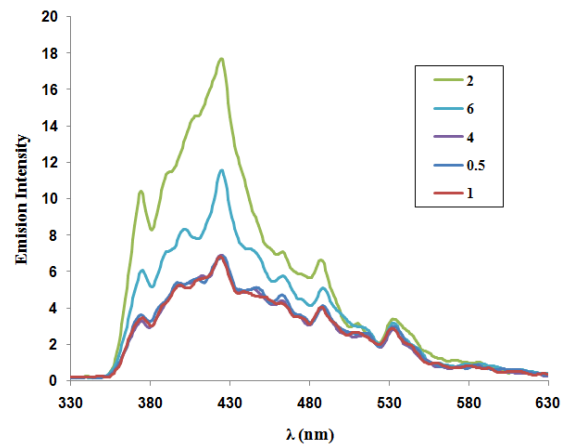


Figure 7. Luminescence results for samples heat treated at various temperatures for 2 h

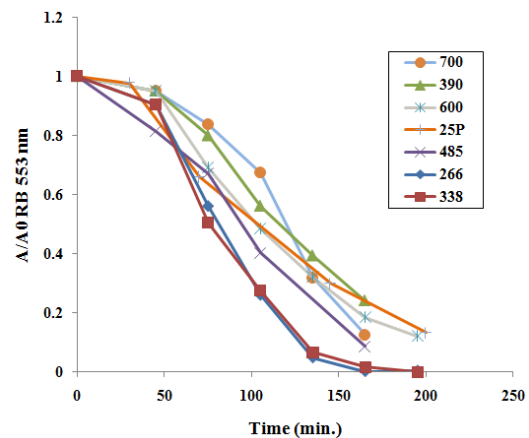


Figure 8. Luminescence results for samples heat treated at 530°C for various times

The radius of Ag^+ ions (126 pm) is much larger than that of Ti^{4+} (68 pm) and so the Ag^+ ions introduced by the sol-gel process would not enter into the lattice of anatase phase. During calcination, these uniformly dispers resulting in silver deposition on the surface on calcination ed Ag^+ ions would gradually migrate from the volume of the TiO_2 to the surface by enhancing their crystallinity resulting in silver deposition on the surface on calcination [18]. Electron transfer from conduction band of TiO_2 to the metallic silver particles at the interface is possible, because the Fermi level of TiO_2 is higher than that of silver metal [19]. This results in the formation of Schottky barrier at the Ag-TiO_2 contact region, which improves the photocatalytic activity [20]. In addition, there may be residual Ag^+ ions within the material, acting as efficient electron traps; these may contribute to enhanced photocatalytic activity of these samples [21].

These results indicate that the sample heat treated for 1 h at 530°C exhibits superior degradation behavior compared to other samples including Degussa P25 (the reference specimen). Degussa P25 is prepared by electropyrolysis and has a porous structure containing 70% anatase and 30% rutile which means very good photocatalytic properties. But our findings in the present work suggest that the nanocomposite produced by sol-gel technique as described above exhibits a better photocatalytic characteristic. The fact that our nanocomposite exhibited a superior photocatalytic behaviour compared with a well-known commercial product might look surprising. But such performance should be justified if one consider these differences: 1- Degussa P25 is composed of anatase and rutile, while our sample (530°C , 1 h) is composed of anatase and $\text{Ag}_2\text{Ti}_4\text{O}_9$; 2- silver has a positive effect on photocatalytic efficiency by increasing the Schottky barriers, and thus delaying the recombination process; lower luminescence intensity of the sample suggests this; 3- a fine microstructure associated with our sample is another reason for its better photocatalytic performance [22]. More recently some interesting results have been reported on various applications of Ag-TiO_2 nanocomposites [23-26], which will help us with further investigations of Ag-TiO_2 systems in the future.

4. CONCLUSIONS

Ag-TiO_2 nano composite containing 1% Ag heat treated for 2 h at 266 and 338°C exhibited better degradation efficiency compared to other samples. But the sample heat treated for 1 h at 530°C possessed an exceptionally good degradation efficiency, even superior to commercial Degussa P25 specimen. Our results show that $\text{Ag}_2\text{Ti}_4\text{O}_9$ phase which is formed at room temperature, has higher degradation potential than the

anatase phase. Also, a fine microstructure, as was the case in our samples, leads to higher degradation efficiency by providing a vast surface area needed for photocatalytic activity.

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Effect of Formation of Ag₂Ti₄O₉ Phase on Photocatalytic Activity of Ag-TiO₂ Nanocomposite

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نانو کامپوزیت Ag-TiO₂ که با میزان ۱ درصد وزنی Ag رفتار کاتالیزوری بهینه‌ای را از خود نشان داد، توسط پروسه سل-ژل و بکارگیری رودامین تهیه شد. نمونه‌های اولیه توسط حرارت‌دهی در دماهای متفاوت (۲۶۶، ۳۳۸، ۳۹۰، ۴۸۵، ۶۰۰، و ۷۰۰ درجه سانتیگراد) با زمان ماندگاری ۲ ساعت تهیه شدند. با استفاده از DTA و XRD دمای ۵۳۰°C بعنوان دمای انجام عملیات حرارتی انتخاب شد. سپس تعدادی نمونه در این دما بمدت متفاوت (۱/۵، ۱، ۲، ۴، ۶ ساعت) تحت عملیات حرارتی قرار گرفتند. نمونه‌های تهیه شده در دمای ۲۶۶ و ۳۳۸°C با زمان ماندگاری ۲ ساعت راندمان تخریب بهتری را از خود نشان دادند. نمونه تهیه شده در دمای ۵۳۰°C بمدت ۱ ساعت بهترین کارایی تخریب را از خود نشان داد که حتی از نمونه تجاری TiO₂ نانو خریداری شده از شرکت Degussa بالاتر بود. ما با توجه به بررسی مراجع برای اولین بار تشکیل فاز Ag₂Ti₄O₉ را گزارش می‌دهیم. این فاز تیتانات نقره باعث بالا رفتن راندمان تخریب نسبت به فاز آاناتاس می‌گردد. مشخصه‌یابی نمونه‌های Ag-TiO₂ توسط DTA، XRD، PL و SEM انجام گردید.

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