Photocatalytic and UV-VIS Optical Properties of Titanium-Silver Doped Composite Synthesized by Hydrothermal Method

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ABSTRACT

Titanium (TiO₂) has been studied and proved to be the most ideal photocatalyst due to several aspects such as high photoactivity, thermal and chemical stability, relatively inexpensive and non-toxicity. As the problem statement, the photoactivity and optical stability are the crucial aspects to synthesize an ideal photocatalyst. These aspects can be improved through the synthesize method to enhance its nanocrystal crystallinity. The purpose of this research is to synthesize the high crystalline silver-titanium (AgTiO₂) nanoparticles and study its photoactivity and optical properties. The Ag-TiO₂ was synthesized through the modification of caustic hydrothermal method and molten salt doping process to dope the silver nitrate (AgNO₃) as a dopant agent. The photoactivity performance of high grade TiO₂ and high crystallinity Ag-TiO₂ were examine via a Methylene Blue Degradation (MBD) testing under both visible light and UV light. The optical properties were measured through the Surface Area BET (SBET) and UV-Vis-NIR spectrophotometer (UV-Vis). The UV-Vis results show that the 0.01%-Ag-TiO₂ sample has a lowest band gap with 2.6eV compared to the commercial TiO₂ (P25) and other samples. The SBET analysis shows that, the biggest surface area was formed in 0.05%-Ag-TiO₂ followed by 0.01%-Ag-TiO₂, un-doped TiO₂ and 0.03%-Ag-TiO₂. For the MBD-testing, the high crystalline Ag-TiO₂ was performed a better photoactivity compared to the high grade TiO₂. The 0.05%-Ag-TiO₂ has the best crystallinity and morphology growth compared to 0.01%-Ag-TiO₂ and 0.03%-Ag-TiO₂ doping samples. The results obtained proves that, the presence of silver dopants was successfully improved the nanocrystal crystallinity of Ag-TiO₂ and influenced its photoactivity performance.

Keywords:
Titanium; silver nitrate; methylene blue degradation; surface area BET; UV-VisNIR spectrophotometer

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1. Introduction

Titanium (TiO₂) has been studied and proved to be the most ideal photocatalyst due to several aspects such as high photoactivity, thermal and chemical stability, relatively inexpensive and non-toxicity. Titanium Dioxide (TiO₂) photocatalyst is the metal oxide which is most widely being studied in classical photocatalyst. The photocatalytic properties of TiO₂ are attributed to the production of photogenerated electrons in the conduction band (CB) and holes in the valence band (VB), which can

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only absorb short wavelength light, which falls in the UV region (10-400 nm) due to the relatively large band gap (3.0-3.2 eV) of TiO$_2$ [1,2]. The TiO$_2$ extraction from the synthetic rutile in Malaysia via a modified hydrothermal synthesis method had been done by previous researcher [3]. The extracted TiO$_2$ from the synthetic rutile were dope with silver via a molten salt doping process has been considered as an efficient method to produce a high industrial potential Ag-TiO$_2$ material in future. The introduction of green synthesis method which requires a low equipment cost and simple experimental steps are the novel theories in this research study.

The photoactivity and optical stability are the crucial aspects to synthesize an ideal photocatalyst. A common issue with most of the photocatalytic materials is that the fast charge recombination and limited spectral response have hindered their potential in commercial applications [4]. Therefore, to design a highly efficient photocatalysts, the band gap energy of the photocatalyst has been an utmost concerned. The alignment of the crystal phase, band structures, and interfacial contact of the contacted materials are essential for the successful construction of photocatalyst [5]. Therefore, the purpose of this research is to synthesize the high crystalline silver-titanium (Ag-TiO$_2$) nanoparticles and study its photoactivity and optical properties.

The photoactivity performance of high grade TiO$_2$ and high crystallinity Ag-TiO$_2$ were examine via a Methylene Blue Degradation (MBD) testing under both visible light and UV light. The optical properties were measured through the Surface Area BET ($S_{BET}$) and UV-Vis-NIR spectrophotometer (UV-Vis). The Brunauer, Emmet and Teller (BET) technique using a gas adsorption analysis to measure the surface area of samples. The band gap can be determined from the UV-Vis results. The lower the band gap, the better absorption edge and electron transitions from the VB to the CB which lead to a better photoactivity performance [6]. The results obtained proves that, the presence of silver dopants was successfully improved the nanocrystal crystallinity of Ag-TiO$_2$ and influenced its photoactivity performance.

2. Methodology

2.1 Materials

A high crystalline silver doped titanium dioxide (Ag-TiO$_2$) nanoparticle is mainly involving three stages processes which are a caustic hydrothermal method, doping via a molten salt method and samples characterization including the photoactivity testing. The main equipment to run this research work are ultrasonic, high temperature furnace, hot plate with magnetic stirrer, centrifuge, and heating/drying oven. The starting material been used to prepare the high crystalline Ag-TiO$_2$ nanoparticles are synthetic rutile waste, Ammonium Hydroxide (NaOH), Sulfuric acid (H$_2$SO$_4$), deionized water, ethyl alcohol and Silver Nitrate (AgNO$_3$).

2.2 Preparation of Titanium-silver doped Composite by Hydrothermal Method

2.2.1 Fusion process using a high temperature furnace

The low-grade synthetic rutile as shown in Figure 1 were fused in the Sodium Hydroxide (NaOH). The mixture was then labelled as the sodium titanate mixture ($Na_2TiO_3$) as shown in Figure 2. The $Na_2TiO_3$ then placing in the high temperature furnace and heated at the 550$^\circ$C temperature for 3 hours. Figure 3 shows the fusion products was washed overnight before undergo filtration process. Finally, the collected precipitate sample were dried in an oven at 80$^\circ$C temperature for 4 hours before the leaching process.
Fig. 1. Synthetic Rutile Waste

Fig. 2. Fusion products: Synthetic Rutile Waste mixed with NaOH

Fig. 3. Washed fusion products overnight

The conversion of synthetic rutile waste to Na$_2$TiO$_3$ compound via fusion process can be represented as equation (1) below. The Ti-O-Ti bond of the synthetic rutile waste will be break then fuses with the Na-OH bond. This led to the Ti-O-Na and Ti-OH bonds production. The formation of these new bonds helps to release the impurities that embedded among themselves and simultaneously decrease the particle size by producing a smaller matrix of Ti-O bonds.

$$TiO_2 + 2NaOH \rightarrow Na_2TiO_3 + H_2O \quad (1)$$

2.2.2 Leaching and calcination process using Autoclave

The sodium titanate mixture (Na$_2$TiO$_3$) was mix with sulfuric acid. The samples were heated simultaneously in a digital hot plate with 500rpm speed of magnetic stirrer at the various synthesis condition as shown in Figure 4. The obtained leached acidic mixture was washed to remove the dispersed impurity in Na$_2$TiO$_3$ and Sulphur as shown in Figure 5. The sample were filtered and dried in an oven before being crushed into a fine powder as shown in Figure 6 and 7 respectively. The calcination process using a high temperature furnace at 600°C temperature for 2 hours was shown in Figure 8 below.
Fig. 4. The mixtures were heated using a digital hot plate with magnetic stirrer at fixed 500rpm

Fig. 5. The leached acidic mixture were washed

Fig. 6. The sample in the solution form then filtered by using a filter pump to collect the precipitate sample

Fig. 7. The precipitate sample after dried in an oven and ready to be crush and ground into a fine powder

Fig. 8. Calcination process using a high temperature furnace

The silver nitrate (AgNO₃) was mix with the un-calcine TiO₂ via a molten salt method as shown in Figure 9. The silver doped mixture was then placed in the high temperature furnace at 600°C temperature for 5 hours. Next, the silver doped samples were washed with the distilled water and left overnight before undergoing the filtration process as in Figure 10. The collected fine powder is labelled as high crystalline Ag-TiO₂ sample and ready for optical characterization and photoactivity testing.
2.3 Optical Properties and Photocatalytic Activity

There are 4 samples were prepared in this experiment. The name of samples is based on the percentage of silver being doped in extracted TiO$_2$. The name of samples is un-doped TiO$_2$, 1Ag-TiO$_2$, 3Ag-TiO$_2$ and 5Ag-TiO$_2$. The number 1, 3 and 5 are represents the percentage; 0.01%, 0.03% and 0.05% of silver being doped in the TiO$_2$. The 4 samples then characterize via Surface Area BET ($S_{BET}$), UV-Vis-NIR spectrophotometer (UV-Vis) and Methylene Blue Degradation (MBD) testing under both visible light and UV light.

By analyzing the diffuse reflectance of UV-Vis’s spectroscopy, we can further study the interaction between Ag and TiO$_2$ in high crystalline sample, Ag-TiO$_2$. The wavelength (nm) in the absorption edge above can be used to indicate the elemental band gap absorption of TiO$_2$ resulting from the electron transition from the VB to the CB [7, 8]. The higher the wavelength (nm) in the absorption edge, means the lower the elemental band gap absorption which leads to the better photoactivity performance. That is because, it proves that the electron at the VB do not need to absorb a high energy from the UV light to excite and escape to the CB. According to Mills et al., [9] and Pelaez et al., [10], the sufficient decreased band gap energy of the TiO$_2$ photocatalyst can help to absorb the visible light range energy and might be possible to utilise the solar spectrum up to 40% instead of less than 1% only before the band gap alteration. Due to Suwarnkar et al., [11], the decreased band gap of Ag-TiO$_2$ (2.98eV) from pure TiO$_2$ (3.20eV) has led to improve its photoactivity. Therefore, we measure the band gap of our high grade TiO$_2$ and high crystalline Ag-TiO$_2$ then study their affect to photoactivity.

The surface area of sample can be determined from the BET analyzation, the bigger the surface area, the better the photoactivity can occur. According to Chen et al., [13], the relatively small particle size with a diameter 5 - 50nm is the main reason of its limited photoactivity reaction. The small particle size of TiO$_2$ is offering a high surface area and more active sites, but in contrast, it will cause the rapidly aggregation which will decrease the effective surface area and photocatalytic efficiency [12]. The low effective surface of TiO$_2$ photocatalyst will cause a poor absorptive power [13] which lead to the low photoactivity.

3. Results
3.1 UV-VIS and $S_{BET}$ Analysis for Optical Properties

Figure 11 shows the UV-Vis diffuse reflectance spectra for 3 samples: commercial TiO$_2$ (P25), un-doped TiO$_2$ and 1Ag-TiO$_2$. The result significantly shows that, the wavelength in absorption edge for the spectra of commercial TiO$_2$ (P25), un-doped TiO$_2$ and 1Ag-TiO$_2$ are 310nm, 280nm and 290nm,
respectively. Notably that the synthesized 1Ag-TiO₂ were shifted to the higher wavelength in the absorption edge compared to the un-doped TiO₂ sample.

Figure 11. UV-Vis diffuse reflectance spectra of P25, un-doped TiO₂ and 1Ag-TiO₂ sample.

Figure 12 shows a Kubelka-Munk function plot of commercial TiO₂ (P25), un-doped TiO₂, 1Ag-TiO₂, 3Ag-TiO₂ and 5Ag-TiO₂. By using this Kubelka-Munk function plot, it can determine the optical bandgap for all samples. We can see the approximated band gap of the P25, un-doped TiO₂, 1Ag-TiO₂ and 5Ag-TiO₂ are 3.4eV, 3.2eV, 3.1eV and 3.1eV, respectively. The results are almost similar with the Ag-TiO₂ band gap size which reported by Mahdi et al., [14] with 3.23eV. It can be concluded that the doped samples have a better band gap size compared to the un-doped TiO₂ and P25. A lower band gap led to the better absorption edge and lead to a better electron transitions from the VB to the CB for a better photoactivity performance. This hypothesis was confirmed by the MBD testing at the end of this experimental work.

Figure 13 shows the BET analysis for all samples, un-doped TiO₂, 1Ag-TiO₂, 3Ag-TiO₂ and 5Ag-TiO₂. The results clearly shows that the sample 5Ag-TiO₂ have the biggest surface area with 19.883 mm²/g and then followed by 1Ag-TiO₂, un-doped TiO₂ and 3Ag-TiO₂ samples with 11.57m²/g, 10.259m²/g and 9.06m²/g respectively. The results successfully improved the surface area of synthetic rutile (raw material) as reported by [15] with only 3.9m²/g.

3.2 The Photoactivity of High Grade TiO₂ and High Crystallinity Ag-TiO₂ Nanoparticles

The Methylene Blue Degradation (MBD) testing is to analyse the photoactivity of a high grade TiO₂ and high crystalline Ag-TiO₂ nanoparticles. The MBD testing for this project were using both Visible and UV light. Figure 14 shows the graph of MBD results under the visible light irradiation. All samples un-doped TiO₂, 1Ag-TiO₂, 3Ag-TiO₂ and 5Ag-TiO₂ were irradiated with initial concentrations, 1.5ppm of MB. Then, after 2 and a half hours, all samples perform a photodegradation process at varies percentage. The un-doped TiO₂ and 3Ag-TiO₂ samples were shows a 25% reduction of MB concentration, while the 1Ag-TiO₂ and 5Ag-TiO₂ samples were showing a 31% and 66% reduction, respectively.
Fig. 12. Kubelka-Munk function plot of P25, un-doped TiO$_2$, 1Ag-TiO$_2$, 3Ag-TiO$_2$ and 5Ag-TiO$_2$

![Kubelka-Munk function plot of P25, un-doped TiO$_2$, 1Ag-TiO$_2$, 3Ag-TiO$_2$ and 5Ag-TiO$_2$](image1)

Fig. 13. The $S_{BET}$ results of un-doped TiO$_2$, 1Ag-TiO$_2$, 3Ag-TiO$_2$ and 5Ag-TiO$_2$

![Surface Area BET (mm/g)](image2)

Figure 15 shows the graph of MBD results under the UV light irradiation. The initial concentrations of MB are 3ppm same for all 4 samples. After 24 hours of irradiation, all samples show a photodegradation process at varies percentage. The samples 3Ag-TiO$_2$ and un-doped TiO$_2$ shows a 37% and 50% reduction of MB concentration, respectively. The 1Ag-TiO$_2$ sample shows 68% reduction while the 5Ag-TiO$_2$ sample shows the best performance with 75% reduction.
The photocatalytic testing results in Figure 14 and 15 successfully prove that the presence of silver dopants could influence the photoactivity of the high grade TiO$_2$. That was occurred due to its affects to the crystal structure, which inevitably reduces the energy band gap and decelerate the electron-hole recombination rate. The results successfully improved the results reported by Mahdi et al., [3] which shows only 31% and 43% of degradation by anatase and rutile phase TiO$_2$, respectively after 2 hours irradiated under the visible light.

4. Conclusions

The optical stability and photoactivity are the crucial aspects to synthesize an ideal photocatalyst. The band gap energy of the photocatalyst has been an utmost concerned and affect its photoactivity performance. 4 samples with different doping ratios, un-doped TiO$_2$, 1Ag-TiO$_2$, 3Ag-TiO$_2$ and 5Ag-TiO$_2$ were successfully extracted and analysed in this experimental works. The UV-Vis results shows that the 1Ag-TiO$_2$ and 5Ag-TiO$_2$ samples has a lowest band gap with 3.1eV compared to the commercial TiO$_2$ (P25) and un-doped TiO$_2$. The lower band gap leads to the better photoactivity performance because the electron at the Valance Band of sample do not need to absorb high energy from the irradiation light to excite and escape to the Conduction Band. Besides that, the BET analysis shows that the sample 5Ag-TiO$_2$ have the biggest surface area with 19.883 mm$^2$/g compared to the others sample. The size of surface area also affects the performance of photoactivity. The electron in sample easily absorbs the energy from the irradiation light and perform
the photoactivity if it has a large surface area. The photoactivity performance were examine using the MBD testing. From the Photoactivity testing, it shows that doped Ag-TiO\textsubscript{2} was performed a better photoactivity compared to un-doped TiO\textsubscript{2} and the 5Ag-TiO\textsubscript{2} has the best performance for both Visible and UV light irradiations. As a conclusion, the presence of silver dopants was successfully improved the optical properties of Ag-TiO\textsubscript{2} and influenced its photoactivity performance. The green and environmentally friendly raw material, low equipment cost and simple and efficient experimental works are the most precious factors to commercialize this high crystallinity Ag-TiO\textsubscript{2} sample at a large scale production in future.

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