The effect of synthesis route on the photocatalytic performance of Ag-TiO₂ using rhodamine b dyes, pesticides, and pharmaceutical waste as model pollutants

Emmanuel Nyankson 1, Nathaniel Yeboah 1, Samuel Ocrah Jnr 1, Sammy Onaja 1, Thomas Mensah 2 and Johnson K Efavi 1,∗

1 Department of Materials Science and Engineering, University of Ghana, LG 77, Accra-Ghana
2 Department of Chemistry, University of Ghana, LG 56, Accra-Ghana
∗ Author to whom any correspondence should be addressed.

E-mail: jkefavi@ug.edu.gh

Keywords: TiO₂-Ag, photodeposition, microwave assisted synthesis, photocatalysis, pharmaceutical waste and pesticides

Abstract
The use of noble metal loading such as Ag to improve the photocatalytic performance of TiO₂ has been well studied. Though different synthesis methods have been used to synthesize Ag-TiO₂ nano-composite, the effect of the different synthesis routes on the photocatalytic performance has not been studied and compared. This study focusses not only on the enhancement of photocatalytic performance by the addition of Ag, but also on the influence of the synthesis process on photocatalytic performance. Two different routes: photodeposition (PD) and formaldehyde assisted microwave (MW) synthesis of Ag-TiO₂ nano-composite and their photocatalytic performance were evaluated using model pollutants. The Ag-TiO₂ were synthesized using different wt% (0.5, 1.0, 1.5 and 2.0 wt%) of Ag. The synthesized Ag-TiO₂ were characterized with x-ray diffractometer, scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) and UV–vis spectrophotometry. The Ag-TiO₂ photocatalyst showed superior photocatalytic performance towards rhodamine b dye as compared to raw TiO₂. 0.5 wt% Ag-TiO₂-PD recorded the highest rate constant and degradation percent among the composites synthesized using photodeposition (PD) method. On the other hand, 1.0 wt% Ag-TiO₂-MW performed better among the composites synthesized using microwave and formaldehyde assisted synthesis. The potential of these best performing composites; 0.5 wt% Ag-TiO₂ and 1.0 wt% Ag-TiO₂ to photocatalytically degrade pharmaceutical (Naproxen Sodium and Flurbiprofen) and pesticide (Atrazine and Pyrimethanil) pollutants were examined. These composites degraded the pollutants exceptionally well with 0.5 wt% Ag-TiO₂-PD outperforming the 1.0 wt% Ag-TiO₂-MW. 1H NMR and 13C NMR analysis revealed that the synthesized Ag-TiO₂ were effective in degrading the model pollutants.

1. Introduction

Water is necessary for the sustainability of life, as well as for food production, economic development, and overall well-being. Even though there are other renewable resources it will be difficult to replace water due to its numerous applications [1]. Industries near waterbodies discharge untreated effluents into rivers and streams near them. Some of these industries include textiles, pharmaceuticals and agro-based industries [2].

Dyes and pigments are widely used in notable industries for leather tanning, paper production, food technology, agricultural research, light-harvesting arrays, photoelectrochemical cells, and hair coloring. A significant amount of these harmful substances is discharged into the environment via industrial effluents. These compounds discharged into the environment are extremely toxic and carcinogenic in nature, making it a major concern [3]. The high stability of these organic molecules with aromatic molecular structures are complicated and not biodegradation [4].
Pharmaceutical waste and agro-based waste are other forms of pollution that need to be tackled in time in other to reduce their effects on humans, plants, and other organisms. As the world population keeps increasing, the use of pharmaceutical products and agro products such as weedicides and pesticides in an effort to provide for the health and food needs of humans is expected to increase along with their harmful by products.

Several methods have been employed for wastewater treatment. These include chemical precipitation, coagulation/flocculation, froth flotation, adsorption/filtration, ion exchange, solvent extraction, electrochemistry and biological methods such as bioreactors, biological activated sludge and microbiological treatments. The biological methods require too much of attention and therefore difficult to practice on a large scale. The physical and chemical methods are too expensive and less efficient in terms of reagent consumption making their application on a large scale uneconomical. It is therefore necessary to find a method that is less expensive, efficient and environmentally friendly to deal with the increasing water contamination and other forms of pollution.

The potential of photocatalytic reactions to replace these conventional processes is particularly promising. For example photocatalytic reactions have been investigated for the production of hydrogen gas [5], dye degradation and oil-water emulsion separation [6], air purification or CO₂ photo-reduction and for pharmaceutical and agro-based waste treatment. Photocatalytic reactions have a high oxidation and reduction potential which allows for complete degradation of organic pollutants [7].

Titanium dioxide (TiO₂), is a well-researched metal oxide with photocatalytic properties in the presence of UV-light. TiO₂ has been vindicated to be the most suitable photocatalyst due to its strong photocatalytic activity, photosensitivity, chemical stability, abundance, low-cost and nontoxicity [8]. Despite the advantages TiO₂ possesses, its applicability to photocatalysis have been limited mainly due to its large band gap (3.0 eV and 3.2 eV, respectively, for the rutile and anatase phases) which restricts its absorptivity to the Ultra-violet (UV) region of the electromagnetic spectrum. The overall photocatalytic effectiveness of TiO₂ is lowered since UV accounts for ~5% of the electromagnetic spectrum. Also, fast backward reaction (electron-hole recombination) reduces the lifespan of photogenerated electron-hole pairs and hence the overall photocatalytic activity.

Several techniques have been employed to overcome these challenges and these include dye sensitization and addition of non-metal ions [6], coupled semiconductor system [9], coating with transition metals [10] and noble metal loading [11, 12]. While all of these techniques have been reported to greatly increase the photocatalytic efficiency of TiO₂, the use of noble metal-TiO₂ photocatalyst instead of the conventional TiO₂ has gained a lot of attention over recent years [13]. Loading the surface of TiO₂ photocatalyst with noble metals not only extends its absorptivity into the visible region but greatly reduces the rate of photogenerated holes and electrons recombination.

Silver is the most promising of all the noble metals because of its high efficiency, inexpensive cost compared to other noble metals, antibacterial properties, and strong oxygen adsorption reactivity. The Ag particles when deposited on the surface of TiO₂ has two major effects: (a) first Ag particles can trap photogenerated electrons while leaving holes for pollutant degradation reactions to occur effectively, and (b) because of localized Surface Plasmon Resonance, Ag particles can absorb visible light, extending their wavelength response to the visible region and allowing new applications such as antibacterial textiles, engineering materials, medical devices, food preparation surfaces, air conditioning filters, and coated sanitary wares [14].

Due to these effects Ag coating/doping has on the photocatalytic activity of TiO₂, several efforts have been made to synthesize Ag coated/doped TiO₂ composites using different synthesis methods. Some have even gone further to investigate the relationship between the amount of Ag particles deposited on the TiO₂ surface and the photocatalytic activity of TiO₂. For example, it has been reported that increasing the amount of silver nanoparticles increases the photocatalytic activity of TiO₂ to a threshold value where this effect begins to decrease [15].

According to Gong et al combining plasmonic noble metals (such as Au and Ag) with photocatalysts is an effective strategy for reducing charge carrier recombination by utilizing the plasmonic effect to increase visible light absorption and trapping photogenerated electrons [3]. While several works have broaden the understanding of how Ag doping impacts the photo-activity of TiO₂, little or no attention has been given to the effect of synthesis route or method on the photocatalytic activity of Ag-TiO₂ photocatalyst. Most of the conventional method of synthesizing Ag-TiO₂ photocatalysts requires high temperature treatment and long synthesis time. This results in the aggregation of the samples and particles with less dispersion of Ag nanoparticles on the surface of Ag [16]. To address this issue, the authors decided to focus on photodeposition and microwave- and formaldehyde-assisted synthesis routes for the production of Ag-TiO₂ photocatalysts. The application of both photodeposition and microwave assisted synthesis routes for Ag-TiO₂ synthesis results in uniform dispersion of the cocatalysts on the TiO₂ enhancing the photocatalytic performance. In addition, both methods are simple, less time consuming, does not require high temperature treatments and the particle size and morphology can easily be manipulated [16–18].
An understanding of how the activity of TiO$_2$ as a photocatalyst is influenced by the choice of synthesis methods such as photodeposition and microwave and formaldehyde assisted synthesis will not only assess the strengths and weaknesses of each synthesis route but will also help to determine which direction future research effort should be geared towards. This will move a long way to reduce resource usage and hasten the application of the Ag-TiO$_2$ nano-composite since emphasis will now be applied to the synthesis routes which give the most output in terms of photocatalysis and other applications.

In this paper, Ag-TiO$_2$ composites were synthesized using photodeposition (PD) and microwave and formaldehyde assisted synthesis (MW) methods. The potential of the composites synthesized from each method to photocatalytically degrade pollutants were examined using rhodamine b dye, naproxen sodium, flurbiprofen, atrazine and pyrimethanil as model pollutants.

2. Experimental procedure

2.1. Materials
Absolute ethanol (98%), Formaldehyde (99.7%), Titanium oxide (99.5% trace metal basis), Silver nitrate (99%), Naproxen sodium (98%), Flurbiprofen (pharmaceutical standard), Pyrimethanil (analytical standards) and Atrazine (analytical standard) were obtained from Sigma Aldrich, UK.

2.2. Synthesis of Ag-TiO$_2$ photocatalyst
Two different synthesis routes including microwave and formaldehyde assisted synthesis, and photodeposition were used to synthesize the Ag-TiO$_2$ photocatalyst.

2.2.1. Formaldehyde assisted microwave synthesis
In a typical synthesis, 1.5 g of TiO$_2$ powder was dispersed in 200 mL deionized water and continuously stirred on a magnetic stirrer for 30 min. A calculated amount of AgNO$_3$ was added to the dispersed TiO$_2$ to obtain different weight percentages of Ag on TiO$_2$. Based on the result of a previous work by Nyankson et al [19], 8 ml of formaldehyde was added to the resulting solution of the dispersed TiO$_2$ and microwaved for 6 min. The microwaved solution was allowed to cool and centrifuged at 6000 rpm for 10 min. The supernatant was poured off and the particles dried at 85 °C for 2 h. The particles obtained from the formaldehyde assisted microwave synthesis route were labelled as ‘x’ wt% Ag-TiO$_2$-MW, where ‘x’ represents the wt% of Ag. The formaldehyde assisted microwave synthesis route is presented in figure 1(a).

2.2.2. Photodeposition synthesis
Synthesis of Ag-TiO$_2$ photocatalyst by photodeposition was carried out by dispersing 1.5 g of TiO$_2$ powder into 200 ml of deionized water (solution A). Varying concentrations of silver nitrate (AgNO$_3$) was added as precursor for Ag to obtain calculated weight percent of 0.5, 1.0, 1.5 and 2 wt% of Ag in 50 ml of absolute ethanol (solution B). Solution A and solution B were mixed and vigorously stirred in the dark for 1 h. The resulting solution was exposed to UV irradiation for 2 h to induce reduction of Ag onto TiO$_2$ surface. The solution was centrifuged, and the slurry dried in the oven for 2 h at 85 °C. The particles obtained from the photodeposition synthesis route were labelled as ‘x’ wt% Ag-TiO$_2$-PD, where ‘x’ represents the wt% of Ag. The photodeposition synthesis route is presented in figure 1(b).
2.3. Characterization of Ag-TiO₂

Identification of the crystal phases and estimation of the crystallite sizes of each of the TiO₂ and Ag-TiO₂ was done using Empyrean x-ray Diffraction system. The analysis was done using a diffractometer operated at room temperature with Cu Kα radiation source (λ = 0.15418 nm) at 40 kV and 30 mA. The data were recorded in the 2θ range of 20° to 70° in steps of 0.2°.

The microstructure, surface morphologies and elemental composition of TiO₂ and Ag-TiO₂ samples were examined using SEM-EDX. The SEM micrographs were obtained using a Philips XL 30 electron microscope operating at 20 kV.

The structure of the TiO₂ and Ag-TiO₂ was examined using a U Raman™ with 532 frequency stabilized laser and a high sensitivity linear array detector.

Fourier-transform infra-red (FTIR) spectroscopy method was used to detect the structure of molecules using molecular characteristic infrared radiation absorption capable of determining bond mechanism in the TiO₂ and Ag-TiO₂ composite.

2.4. Evaluation of photocatalytic activity

The photocatalytic activity of TiO₂ and Ag-TiO₂ samples were assessed using Rhodamine B dye, Naproxen sodium, Flurbiprofen, Atrazine and Pyrimethanil as a model pollutant. The experiments were performed in a self-constructed glass reactor. UV light was used as source of ultraviolet light. For degradation experiments, 100 mg of the photocatalyst was added to 100 ml of the model pollutants in a beaker under stirring. The resulting solution was kept in the dark without irradiation for 30 min to equilibrate adsorption/desorption of pollutant molecules unto TiO₂’s surface. The mixture was placed on an orbital shaker and irradiated with UV light to induce photo-degradation. The wavelength coverage of the UV light was from 400–700 nm. To quantify the photocatalytic activity, 2 ml of the irradiated pollutant solution was withdrawn into Eppendorf tubes for UV–vis analysis. This was repeated after every specified time intervals. The entire procedure was repeated for each of the TiO₂ and Ag-TiO₂ photocatalysts.

3. Results and discussion

XRD was conducted on raw TiO₂, Ag-TiO₂-PD and Ag-TiO₂-MW samples and the results presented in figure 2. The XRD patterns were used to characterize the structure of the already prepared catalysts. X-ray diffraction studies indicated that the synthesized materials have TiO₂ anatase phase (figure 2(a)). The prominent peaks in the TiO₂, Ag-TiO₂-PD and Ag-TiO₂-MW occurred at 2θ of 25.27°, 27.43°, 37.89°, 48.12°, 54.03°, 55.21°, 62.7°, 70.11°, 75.31° and corresponds to (101), (112), (111), (105), (211), (204), (116), (220) and (215) lattice planes of anatase TiO₂, respectively. The spectra of the Ag doped samples were similar to that obtained from the raw TiO₂ indicating that the silver was not detected by the x-ray instrument. This is attributed to the sensitivity of the x-ray diffraction and its inability to detect constituents with concentration less than 5 wt%. Also there is no significant
shifts in the diffraction peaks recorded for all the samples and this confirms that no TiO$_2$-nAg$_x$O solid solution was formed. Using the Scherrer equation, the crystallite sizes of the TiO$_2$, 1.5 wt% Ag-TiO$_2$-PD and 1.5 wt% Ag-TiO$_2$-MW were calculated to be 21.9 nm, 22.7 nm and 23.2 nm, respectively. The crystallite sizes and peak intensities of the samples varied. This variation can be attributed to the different morphological changes during synthesis.

Raman Spectroscopy of the pure TiO$_2$ and Ag-TiO$_2$ is presented in figure 3. The following distinct peaks were observed in the Raman spectra of the pure TiO$_2$: 196 cm$^{-1}$, 395 cm$^{-1}$, 514 cm$^{-1}$ and 638 cm$^{-1}$ representing the $E_{g, B}$, $A_{1g}$ and $E_{1g}$ Raman modes of anatase TiO$_2$, respectively. In addition, an intense Raman peak at 146 cm$^{-1}$ representing the optical Raman mode of TiO$_2$ was observed $^{[20]}$. Similar peaks were observed in the Raman spectra of the Ag-TiO$_2$-MW and Ag-TiO$_2$-PD. However, these peaks were at slightly different wavenumbers. For example, in the Ag-TiO$_2$-MW and Ag-TiO$_2$-PD samples, the $E_g$ Raman mode of anatase TiO$_2$ was observed at 201 cm$^{-1}$ instead of 196 cm$^{-1}$ as observed in the pure anatase TiO$_2$. Similar
observation was seen in the A1g and E1g Raman modes. Though a distinct Ag Raman peak was not observed, the shift in the Raman modes observed in the Ag-TiO2-MW and the Ag-TiO2-PD may be attributed to the interaction between the Ag and the TiO2. The UV–visible spectra of the samples from each synthesis route are shown in figure 3(b). The spectra of raw TiO2 shows absorption in the wavelength range of 300 nm to 400 nm which is characteristic of absorption in ultraviolet region of the electromagnetic spectrum. The maximum absorption wavelength range of Ag-TiO2-PD and Ag-TiO2-MW was similar to that of the pristine TiO2.

The band gaps of the photocatalysts were calculated using the tauc equation and the plots are shown in figures 3(c)–(e). The band gap of raw TiO2 is higher than that of Ag-TiO2-PD and Ag-TiO2-MW photocatalyst as expected. Some researchers have argued that adding Ag to TiO2 improves its photocatalytic activity by extending the absorption into the visible region [16]. The calculated band gap of the Ag-TiO2-MW samples were smaller than that of the Ag-TiO2-PD samples. This is also in agreement with published data which suggests that, the band gap of Ag-TiO2 synthesized by microwave assisted synthesis is generally lower than that of Ag-TiO2 synthesized from other methods [16]. Table 1 summarizes the optical band gaps for the different photocatalysts synthesized using the photodeposition and microwave assisted synthesis routes.

The morphology and the elemental composition of the Ag-TiO2-PD and Ag-TiO2-MW were examined using SEM-EDX and the results presented in figure 4. The SEM images revealed that the particles were spherical in shape with some degree of agglomeration. There was no difference in the morphology and shape of the Ag-TiO2-PD and Ag-TiO2-MW. This suggest that the synthesis route did not affect the morphology and texture of the nanomaterials.

Energy dispersive x-ray spectroscopy of the samples revealed the presence of Ag in both samples. As already discussed, XRD and Raman spectroscopy could not detect the presence of Ag in both samples. The detection of Ag in both samples through EDX is not surprising since EDX is a surface sensitive characterization technique while XRD is a bulk sensitive characterization technique [19]. It should be stated that, despite the theoretical wt% of Ag used in the synthesis was 0.5 wt%, the EDX detected 0.1 wt% Ag and 0.07 wt% Ag in the 0.5 wt% Ag-TiO2-PD and 0.5 wt% Ag-TiO2-MW samples, respectively. This suggests that, though a solution of the same silver concentrations were used in the synthesis, different amounts of the Ag were deposited on the TiO2 for each of the synthesis routes adopted.

The FTIR spectra was done to assess the surface functional groups and chemical bonding in the composite. Figure 5 shows the FTIR spectra of TiO2 and the different weight percent composition of Ag-TiO2 composite formed. The peaks at 581, 667 and 1404 cm\(^{-1}\) are assigned to the lattice vibration of TiO2 (Ti–O–Ti stretching). Peaks at 1549 and 3343 cm\(^{-1}\) are OH bending and stretching modes indicating the surface adsorbed OH groups or water molecules. Upon addition of 0.5 wt% and 1 wt% of Ag to the TiO2, it can be noticed that the lattice vibration of TiO2 observed at 1404 cm\(^{-1}\) has been diminished or lost it intensity which shows an interaction between the Ag with the TiO2 nanoparticle and also the peaks at 1549 has been shifted to 1639 and 1634 cm\(^{-1}\) for both 0.5 and 1 wt% respectively and it can be seen that the peak at 3343 has widen compared to that of the pure TiO2. The peak at 2954 cm\(^{-1}\) in the pure TiO2 is assigned to C–H stretching vibration of alkane bonding groups.

The potential application of the synthesized Ag-TiO2 in degrading water-soluble dye was examined using rhodamine b as a model pollutant. The degradation efficiency and the pseudo first order rate constants were calculated and presented in figures 6 and 7. The degradation efficiency and the pseudo first order rate constant were dependent on the presence of Ag, the wt% of the Ag and the synthesis route. Generally, when the degradation percentage and pseudo first order rate constants were compared, the Ag-TiO2 samples performed better than the pristine TiO2. For example, the degradation percent and pseudo first order rate constants were 81% and 0.06731 min\(^{-1}\), and 99% and 0.14432 min\(^{-1}\) for TiO2 and 0.5 wt% Ag-TiO2-PD. Upon solar irradiation of the Ag-TiO2, electron-hole pair are generated. The electrons in the valence band of TiO2 are excited to the conduction band. The improved photocatalytic activity after Ag loading can be ascribed to the fact that the Fermi level of Ag is lower than the conduction band energy level of TiO2. Due to the good electron

| Wt% of Ag | Photodeposition (PD) | Microwave (MW) |
|----------|----------------------|----------------|
|          | Bang Gap (eV)        | Bang Gap (eV)  |
| 0.5      | 2.65                 | 2.55           |
| 1.0      | 2.74                 | 2.47           |
| 1.5      | 2.75                 | 2.44           |
| 2.0      | 2.58                 | 2.37           |

Table 1. Summary of optical band gaps estimated from the Tauc Plot.
conductivity of Ag, the excited electrons are quickly transferred to the Ag \[7, 21\]. That is the Ag acts as electron acceptor reducing the electron-hole recombination phenomena usually observed in TiO$_2$. This allows the photogenerated holes and electrons to be utilized for the degradation of the water-soluble dye. Another contribution to the enhanced photocatalytic performance may be attributed to the surface plasmon-effect by Ag.
This results from the collective oscillation of surface electrons leading to the generation of magnetic field. This inner generated magnetic field also enhances the separation of the electrons and holes impeding the electron-hole recombination[22].

Another observation is that the degradation percentage and pseudo first order rate constant differ with the different wt% of Ag loaded (figures 6 and 7). For Ag-TiO2-PD, the degradation and rate constants were 99 and 0.14432, 90 and 0.08545, 93 and 0.08776; and 94% and 0.08999 min$^{-1}$, for 0.5 wt% Ag-TiO2-PD, 1.0 wt% Ag-TiO2-PD, 1.5 wt% Ag-TiO2-PD and 2.0 wt% Ag-TiO2-PD, respectively. That is for the photodeposition synthesis route, the sample with 0.5 wt% Ag recorded the highest degradation percent and pseudo first order rate constant.

On the other hand, the following degradation percent and pseudo first order rate constant were obtained for 0.5 wt% Ag-TiO2-MW, 1.0 wt% Ag-TiO2-MW and 1.5 wt% Ag-TiO2-MW, respectively; 91 and 0.08079, 99 and 0.13759, 91 and 0.06991, and 92% and 0.07926 min$^{-1}$, respectively. That is for the formaldehyde assisted microwave synthesis, the sample with 1.0 wt% Ag performed better.

Increasing the Ag wt% beyond the threshold resulted in a decrease in the photocatalytic activity. Yu et al reported that increase in the Ag wt% resulted in growth in Ag particle size and agglomeration and the size of the Ag plays a critical role in the plasmon mediated reduction of the electron hole recombination [22]. This may explain why the photocatalytic performance differ with different wt% of the Ag. The results also depicted that different synthesis route resulted in different theoretical optimal amount of Ag loaded onto TiO2 and hence different photocatalytic performance. A recent review paper published by Chakhtouna et al reported that the difference in photocatalytic activity of Ag-TiO2 photocatalysts synthesised by different route can be attributed to the oxidation state of Ag on TiO2, particle size, the wt% of Ag loading in the photocatalysts and thermal treatment during the photocatalysts preparation [23]. In both cases, the Ag is expected to be in the oxidation state of 0. For the photodeposition method, irradiating a mixture of TiO2 nanoparticles and AgNO3 aqueous solution resulted in the reduction of the Ag$^{+}$ to Ag0 and their subsequent deposition of well-defined Ag0 on the TiO2 surface. Studies have shown that photodeposition method results in the formation of metallic cocatalysts.

Figure 6. Photocatalytic Degradation of Rhodamine B Dye by (a) 0.5 wt% Ag-TiO2-MW, (b) 1.0 wt% Ag-TiO2-MW, (c) 0.5 wt% Ag-TiO2-PD and (d) 1.0 wt% Ag-TiO2-PD.
while other methods result in a cocatalysts with different oxidation states[24]. On the other hand, the presence of formaldehyde in the microwave assisted synthesis is expected to aid in the reduction of the Ag$^{+}$ to Ag$^{0}$[7].

The optimal photocatalytic performance for the Ag-TiO$_2$ synthesized through the photodeposition method was 0.5 wt% while that of the formaldehyde assisted microwave method was 1.0 wt%. It should be noted that the optimal photocatalytic performance was 99% degradation removal efficiency for both synthesis routes though their pseudo first order rate constants were different, that is 0.13759 and 0.14432 min$^{-1}$ for microwave assisted synthesis and photodeposition routes, respectively. The slight difference in the pseudo first order rate constant can be attributed to the slight variation in the crystallite size of the samples synthesized using different routes.

For the samples synthesized using the photodeposition method, it was observed that increase in the wt% of Ag loaded resulted in a decrease in the photocatalytic activity with 0.5 wt% Ag recording the highest photocatalytic activity. This is in agreement with an already published work by Behnajady et al[18]. The effectiveness of the photocatalysis process is influenced by the size of the Ag cocatalyst. Smaller Ag particle size increases the interfacial contact between the Ag and the TiO$_2$. This enhances charge transfer and reduces the electron-hole recombination[25]. Bhardwaj et al has reported that, the average diameter of Ag increases with increasing wt% of Ag loaded[26]. This reduces the total surface area and the active sites available for effective photocatalysis. This explains why for the photodeposition method, the photocatalytic activity reduced with increasing wt% of Ag loaded.

The photocatalytic activity of the formaldehyde assisted microwave synthesis of Ag-TiO$_2$ nanoparticles was higher than that of TiO$_2$ and at certain wt% of Ag loaded, performed better than Ag-TiO$_2$-PD. With the exception of 1.0 wt% Ag-TiO$_2$-MW, the photocatalytic activity of Ag-TiO$_2$-MW prepared with different weight percent of Ag was lower than that of Ag-TiO$_2$-PD. Hart et al has reported that microwave heat treatment promotes the transformation of anatase phase to rutile phase[27]. The photocatalytic activity of the anatase phase is much better than the rutile phase. This is because, the anatase phase promotes the electron transfer from TiO$_2$ to adsorbed pollutants and has a longer charge carrier life[28]. Promoting the conversion of anatase phase to rutile phase in TiO$_2$ will therefore have a negative impact on the photocatalytic activity. As the wt% of Ag on Ag-TiO$_2$-MW was increased from 0.5 wt% to 1.0 wt%, the photocatalytic activity increased and this can be attributed to a better dispersity of the Ag on TiO$_2$ surface[16]. As the wt% of Ag is increased, the degradation percentage and the pseudo first order rate constants decreased. Increase in wt% of Ag loaded resulted in

---

**Figure 7.** Rate constant and degradation percent of (a) TiO$_2$ and 0.5 wt% Ag-TiO$_2$, (b) TiO$_2$ and 1.0 wt% Ag-TiO$_2$, (c) TiO$_2$ and 1.5 wt% Ag-TiO$_2$ and (d) TiO$_2$ and 2.0 wt% Ag-TiO$_2$. 

---
excessive covering of the TiO₂ surface leading to a decrease in the available active sites, decrease in photogenerated charge carriers and subsequently, a decrease in the photocatalytic activity [29].

The performance of 0.5 wt% Ag-TiO₂-PD and 1.0 wt% Ag-TiO₂-MW as a photocatalyst was also examined using pharmaceutical waste (Naproxen sodium and Flurbiprofen) and pesticides (Atrazine and pyrimethanil). The UV vis of the photodegradation of these pollutants and the degradation percentage and pseudo first order rate constants are presented in figures 8–10, respectively. Generally, the degradation of the pesticides and pharmaceuticals by 0.5 wt% Ag-TiO₂-PD was more efficient than 1.0 wt% Ag-TiO₂-MW as can be seen in figures 8–10. Basically because, low content of Ag deposits smaller Ag Nps on TiO₂ surfaces and thereby having a higher surface to volume ratio which in turn means, shorter migratory paths and thereby limiting the likelihood of produced electrons and holes from the bulk recombination before reaching the surface. At high quantities of Ag doping, on the other hand, leads to the Ag ions to become recombination centers. As the Ag doping concentrations grow, the electric field may easily separate e⁻–h⁺ couples inside this area, resulting in a thinner space charge layer where e⁻–h⁺ pairs can be separated before recombination [30]. Therefore, increase in Ag content reduces the space charge layer which makes the light penetration depth to exceed the width of space charge layer resulting of lack of a driving force to separate them increasing the rate of recombination [30].

The degradation of Naproxen sodium by Ag-TiO₂-PD and Ag-TiO₂-MW occurred within 10 min while that of Flurbiprofen occurred in 60 min. From figure 10, the degradation percent of Naproxen sodium by Ag-TiO₂-PD and Ag-TiO₂-MW was ~80% and 74%, respectively. However, the degradation of the pesticides by Ag-TiO₂-PD and Ag-TiO₂-MW was not as pronounced as observed in the degradation of the pharmaceuticals. For example, for Atrazine and pyrimethanil, the highest degradation percent recorded were 48% and 56%, respectively. These were recorded by Ag-TiO₂-PD.

It was observed that, as the atrazine solution was subjected to photocatalysis, the intensity of the atrazine peak reduced slightly and was accompanied by the appearance of a different peak between 250–275 nm. This may be attributed to the formation of an intermediate photodegradation by-product. It is obvious that, the pharmaceuticals photodegraded much better than the pesticides.

The photodegraded flurbiprofen and pyrimethanil samples were subjected to NMR analysis to help us examine the degradation mechanism and possibly identify the degradation by-products.
1H NMR and 13C NMR were used to analyse the pure and degraded pyrimethanil and flurbiprofen. The 1H NMR and 13C NMR of the pure and degraded pyrimethanil are presented in figure 10 below. From figure 11(a), all the 13 Proton contained in the pyrimethanil were identified from the 1H NMR spectrum with their chemical shifts being in the expected region of the spectrum. Structurally pyrimethanil consist of 6 aromatic protons found in the two aromatic rings, six aliphatic proton which is are located on the methyl carbons and 1 acidic proton which is almost disappearing due to the possibility of exchanging with deuterium. The two methyl protons are very similar. From the structure, pyrimethanil is fully aromatized with two methyl groups meta connected to a pyrimidine ring. The chemical shifts obtained from the 13 CNMR (figure 11(b)) suggest that the compound is made of two aromatic rings evidenced by their chemical shifts further authenticating the correctness of the structure. The assignments were made technically with number of carbons and the poor relaxations of quaternary carbons and the benefits of methine carbons by their corresponding protons. In summary the pyrimethanil is made up 12 carbons with 10 sp² hybridized carbons and 2 sp³ hybridized carbons. Pyrimethanil is an alkaloid with the molecular formular C₁₂H₁₃N₃.

Figure 11(c), which represent the 1H NMR data for the degraded Pyrimethanil confirmed that indeed the pyrimethanil has degraded. In comparing the data from the degraded sample (figure 11(c)) to the original data (figure 11(a)), there has been disappearance of most of the major peaks in the proton spectrum. The highly intense peak observed for aliphatic protons which occurred at 2.34 ppm has disappeared with some dwarf peaks seen in the spectrum. Those weak peaks observed around the region can be assigned to some methyl residues which are products of the degradation. Also, there is a tremendous change in the aromatic region suggesting the disintegration of the pyrimethanil. Some traces of peaks seen indicate the fact that no reaction goes into 100 percent completion. There is a poorly resolved aromatic peak which signifies mono substitution of benzene which is also a possible product of the degradation. On the other hand, the 13 CNMR data shows that there is an aromatic fragment as seen below (figure 12) from the proposed degradation mechanism due to the high stability of the benzamine or the positively charged benzene or the benzyl radical.

The data obtained from 1H NMR and 13C NMR of the pure and photodegraded Flurbiprofen are presented in figure 13. Flurbiprofen is made up two aromatic rings which are monosubstituted and trisubstituted and is
Figure 10. Degradation Percent and Rate Constant for (a) Flurbiprofen, (b) Naproxen Sodium, (c) Atrazine and (d) Pyrimethanil by 0.5 wt% Ag\textsubscript{2}O\textsubscript{2}-PD and 1.0 wt% Ag\textsubscript{2}O\textsubscript{2}-MW.

Figure 11. (a) $^1$H NMR of pure pyrimethanil, (b) $^{13}$C NMR of pure pyrimethanil, (c) $^1$H NMR of photodegraded pyrimethanil, (d) $^{13}$C NMR of photodegraded pyrimethanil.
used to treat the symptoms of Rheumatoid Arthritis and Osteoarthritis. Structurally, it contains eight aromatic protons, four aliphatic and one acidic proton which is subject to exchange with deuterium in deuterated systems. This absence of the carboxylate proton in the spectrum (figure 13(a)) is a classic example. The molecular formula is \( \text{C}_{15}\text{H}_{13}\text{FO}_2 \). The 13 C NMR data (figure 13(b)) revealed that the structure of flurbiprofen contains 13 SP\(^2\) and 2 SP\(^3\) hybridised carbons. The spectrum and the corresponding chemical shifts further
confirm the structure and the level of purity of the sample used in the analysis. The characteristic peaks are the aromatic carbons with the carbonyl carbon from the carboxylic acid functionality.

The 1H NMR data (figure 13(c)) of the photodegraded flurbiprofen revealed the disappearance of majority of the peaks from the data suggesting that the compound has broken down successfully. Some traces of peaks seen indicate the fact no reaction goes into 100 percent completion. There is a poorly resolved aromatic peak which signifies mono substitution of benzene which is also a possible product of the degradation. The 13C NMR data (figure 13(d)) further confirmed the degradation of the compound. The carboxyl group will be the first fragment to be degraded because CO₂ gas is one of the very good leaving groups in organic chemistry reactions.

A Closer inspection of the structure of flurbiprofen led to the proposed fragmentation of flurbiprofen (presented in figure 14). The total disappearance of almost all the peaks in the carbon NMR spectrum suggest that the fragments obtained in the degradation were not stable. However, the benzene radical is quite stable. There is a weak peak seen in the aromatic region of the carbon spectrum with a chemical shift of 128.05 ppm and this can be related to the benzene radical stabilized by resonance.

4. Conclusion

The findings from this study revealed that, the photocatalytic performance of Ag-TiO₂ in the degradation of water soluble dyes, pharmaceutical wastes and pesticides are dependent on the synthesized route adopted. In addition, though a solution of the same Ag concentrations were used during the synthesis, the amount of Ag detected in the different samples from EDX were different suggesting that the amount of Ag deposited is dependent on the synthesis route used. For each of the synthesis routes adopted, the estimated band gap was smaller than that of the pure TiO₂. The degradation performance of the Ag-TiO₂-PD and Ag-TiO₂-MW towards
rhodamine B dye was dependent on the wt% of Ag with the best performing samples being 0.5 wt% Ag-TiO2-PD and 1.0 wt% Ag-TiO2-MW. For all the pharmaceutical and pesticides pollutants examined, the 0.5 wt% Ag-TiO2-PD was more effective than 1.0 wt% Ag-TiO2-MW. From the 1H NMR and 13C NMR data of the degraded pyrimethanil, it was observed that the degradation was not 100% complete and some methyl residues and benzyl radicals were identified as possible degradation products. In addition, from the 1H NMR and 13C NMR data of the degraded flurbiprofen, the carboxyl group was suggested to be the first to have been degraded. In addition, the degradation products were not stable except for benzyl radical. The results from the study revealed that, synthesis route influences the photocatalytic performance of Ag-TiO2.

Acknowledgments

This project was funded by the University of Ghana BANGA-Africa programme with funding from the Carnegie Corporation of New York.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Johnson K Efavi @ https://orcid.org/0000-0002-9809-533X

References

[1] Simon M and Joshi H 2021 A review on green technologies for the rejuvenation of polluted surface water bodies: Field-scale feasibility, challenges, and future perspectives Journal of Environmental Chemical Engineering 9 105763
[2] Hanafi M F and Sapawe N 2020 A review on the water problem associated with organic pollutants derived from phenol, methyl orange, and remazol brilliant blue dyes Materials Today: Proceedings 31 A141–50
[3] Saeed M et al 2019 Azadirachta indica leaves extract assisted green synthesis of Ag-TiO2 for degradation of Methylene blue and Rhodamine B dyes in aqueous medium Green Processing and Synthesis. 8 659–66
[4] Mondal S 2008 Methods of dye removal from dye house effluent—an overview Environ. Eng. Sci. 25 383–96
[5] Chen Q et al 2018 A novel photocatalytic membrane decorated with RGO-Ag-TiO2 for dye degradation and oil–water emulsion separation Journal of Chemical Technology & Biotechnology. 93 761–75
[6] Nyankson E et al 2020 Microwave- and formaldehyde-assisted synthesis of Ag–Ag3PO4 with enhanced photocatalytic activity for the degradation of rhodamine B dye and crude oil fractions ACS Omega 5 13641–55
[7] Chen Y et al 2018 Green synthesis of Ag–TiO2 supported on porous glass with enhanced photocatalytic performance for oxidative desulfurization and removal of dyes under visible light ACS Sustainable Chemistry & Engineering. 6 13276–86
[8] Ko S 2014 Photochemical synthesis, characterization and enhanced visible light induced photocatalysis of Ag modified TiO2 nanocatalyst J. Nanosci. Nanotechnol. 14 6923–8
[9] Khan R and Kim T-J 2009 Preparation and application of visible-light-responsive Ni-doped and SnO2-coupled TiO2 nanocomposite photocatalysts J. Hazard. Mater. 163 1179–84
[10] Murakami N et al 2008 Switching redox site of photocatalytic reaction on titanium (IV) oxide particles modified with transition-metal ion controlled by irradiation wavelength Appl. Catal., A 348 148–52
[11] Rosaseer O et al 2010 Solar light photocatalytic hydrogen production from water pt and Au/TiO2 (anatase/rutile) photocatalysts: Influence of noble metal and porogen promotion J. Catal. 269 179–90
[12] Kim H and Lee K 2013 Photocatalytic Activity of TiO2 Nanotubes Doped with Ag Nanoparticles J. Nanosci. Nanotechnol. 13 5597–600
[13] Bhardwaj S et al 2019 Photodeposition time dependant growth, size and photoactivity of Ag and Cu deposited TiO2 nanocatalyst under solar irradiation Sol. Energy 194 618–27
[14] Alibert E et al 2015 Photocatalytic deposition of Ag nanoparticles on TiO2: Metal precursor effect on the structural and photoactivity properties Journal of Saudi Chemical Society. 19 563–73
[15] Coto M et al 2017 Tuning the properties of a black TiO2–Ag visible light photocatalyst produced by a rapid one-pot chemical reduction Materials Today Chemistry. 4 142–9
[16] Li X, Wang L and Lu X 2010 Preparation of silver-modified TiO2 via microwave-assisted method and its photocatalytic activity for toluene degradation J. Hazard. Mater. 177 639–47
[17] Tongon W, Chawengkiwianich C and Chiarakorn S 2014 Visible light responsive Ag/TiO2/MCM–41 nanocomposite films synthesized by a microwave assisted sol–gel technique Superlattices Microstruct. 69 108–21
[18] Behnajady M et al 2008 Enhancement of photocatalytic activity of TiO2 nanoparticles by silver doping: photodeposition versus liquid impregnation methods Global NEST Journal. 10 1–7
[19] Nyankson E et al 2020 Microwave- and formaldehyde-assisted synthesis of Ag–Ag3PO4 with enhanced photocatalytic activity for the degradation of rhodamine B Dye and crude oil fractions ACS Omega. 5 13641–55
[20] Ahmed F et al 2021 An experimental and theoretical study on the effect of silver nanoparticles concentration on the structural, morphological, optical, and electronic properties of TiO2 nanocrystals Crystals. 11 1488
[21] Yu B et al 2016 Photocatalytic reduction of CO2 over Ag/TiO2 nanocomposites prepared with a simple and rapid silver mirror method Nanoscale. 8 11870–4
[22] Liu Y et al 2012 One-pot pyridine-assisted synthesis of visible-light-driven photocatalyst Ag/Ag3PO4 Appl. Catalysis B 115 245–52
[23] Chakhtouna H et al 2021 Recent progress on Ag/TiO2 photocatalysts: photocatalytic and bactericidal behaviors Environmental Science and Pollution Research. 28 44638–66
[24] Jiang X et al 2015 Photocatalytic reforming of glycerol for H2 evolution on Pt/TiO2: fundamental understanding the effect of co-catalyst Pt and the Pt deposition route J. Mater. Chem. A 3 2271–82
[25] Zhang Z and Yates J T Jr 2012 Band bending in semiconductors: chemical and physical consequences at surfaces and interfaces Chem. Rev. 112 5520–51
[26] Bhardwaj S et al 2020 Influence of photodeposition time and loading amount of Ag co-catalyst on growth, distribution and photocatalytic properties of Ag@TiO2 nanocatalysts Opt. Mater. 106 109975
[27] Hart J N et al 2007 A comparison of microwave and conventional heat treatments of nanocrystalline TiO2 Sol. Energy Mater. Sol. Cells 91 6–16
[28] Luttrell T et al 2014 Why is anatase a better photocatalyst than rutile?-Model studies on epitaxial TiO2 films Sci. Rep. 4 1–8
[29] Xin B et al 2005 Effects of simultaneously doped and deposited Ag on the photocatalytic activity and surface states of TiO2 J. Phys. Chem. B 109 2805–9
[30] Phromma S, Wutikhun T, Kasamechonchung P, Sattayaporn S, Eksangsri T and Sapcharoenkun C 2022 Effects of Ag modified TiO2 on local structure investigated by XAFS and photocatalytic activity under visible light Mater. Res. Bull. 148 111668