Photocatalytic Degradation of Chlorazole Black E Dye using Silver Doped Titanium Dioxide

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ABSTRACT

The photocatalytic degradation of Chlorazole black E using various concentration of the silver doped titanium dioxide (TiO_2) under UV light was evaluated. Also, the effect of various parameters such as irradiation time, metal loading and substrate concentration on photodegradation was observed. The incorporation of the silver in the titanium dioxide enhance the morphology and surface properties suitable for operation within the visible region. The catalyst was synthesized by wet impregnation of silver onto titanium dioxide followed by calcination. Chlorazole black E dye was used to assess the rate of photodegradation. The percentage conversion respectively under UV light after 80min in UV light. The degradation efficiency was found to be efficient in 1% Ag-TiO_2

Keywords: Ag-TiO_2, Chlorazole black E, Degradation, Photocatalytic, UV light

INTRODUCTION

Dye pollutants produced from textile industries are becoming a major source of environmental contamination. Among the different types of dyes used in textile industries, 60-70% are azo compounds. These dyes have chromophore of N=N unit in their molecular structure and are lost in water during dyeing operation. These soluble azo dyes when incorporated into the body are split into corresponding aromatic amines which can cause cancer in human. Various physical and chemical processes involves in photocatalytic degradation such as coagulation, adsorption on activated charcoal, reverse osmosis are not destructive, but only transfer the dye from one phase to another.

TiO_2 is known to have large band gap energy, due to its large band gap of 3.2eV. All photo driven applications of TiO_2require ultraviolet light for excitation. It is therefore, critical to make

TiO_2absorb light in the visible range in order to facilitate its direct applications into fields such as photovoltaics and visible light photocatalysis. In addition, the photocatalytic efficiency of TiO_2 is low due to the high rate of electron-hole recombination. To overcome these limitations, many techniques such as chemical synthesis and ion implantation have been developed to extend the photocatalytic response of TiO_2 to the visible light range and to reduce electron-hole recombination [1]. A noble metal is commonly defined as a metal that can resist oxidation, even at high temperatures. Noble metals include rhenium, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold. Of these, the most commonly used in combination with TiO_2 are gold and silver. As noble metals are resistant to oxidation, they are thought to act as an electron sink, promoting the movement of reactive electrons away from the TiO_2 molecule onto the surface of the noble metal [2]. The noble metal surface then acts as a site where redox reactions occur, thus preventing charge recombination within the TiO_2 and increasing its photocatalytic reactivity.

In many studies, silver has been deposited onto TiO_2, primarily because it is more cost effective than gold and platinum, it also improve the photocatalytic activity of TiO_2 at nanoscale3]. Silver is a chemical element with symbol Ag, and atomic number 47. Silver is a soft, white, lustrous transition element that possesses the highest electrical conductivity, thermal conductivity and reflectivity of any metal [4]. The main objective of doping is to induce a bathochromic shift i.e. a decrease of the band-gap [5]. Silver- doped TiO_2 (Ag-TiO_2) has been one of the extensively studied doped TiO_2 photocatalysts due to its wider applications in environmental remediation, antimicrobial activity, catalytic oxidation reactions, etc [2].

Based on previous research and literature review [5,6] no efficient and cost-effective methods have been employed for the treatment of these dye pollutants. The photocatalytic process using TiO_2 semiconductor particles under UV light illumination has being shown to be potentially advantageous and applicable in the treatment of wastewater pollutant when compared to other traditional, physical, chemical and biological processes which leads to secondary pollutants [1, 6].

The aim of this investigation was to use sol immobilization method to synthesize Ag-$TiO_2$with enhance morphology and surface properties on TiO_2 whose photocatalytic degradation activity was evaluated on chlorazole black E dye.

MATERIALS AND METHOD

Preparation of the photocatalyst (Ag-TiO$_2$)

The catalyst was synthesized based on the method of catalyst preparation described by [7]. 1% Ag-TiO$_2$ was prepared by adding 14.763g of TiO$_2$ and 0.15g AgNO$_3$ into 100ml distilled water. It was stirred for 1hr on a magnetic stirrer after which it was oven dried at 150°c for 24hrs and calcined in a muffle furnace at 600°c for 2hrs. The same process was repeated for the 3% Ag-TiO$_2$, and 5%Ag-TiO$_2$

Catalyst characterization

Characterization of the synthesized photocatalyst was done using the following techniques. The powder X-Ray Diffractogram was obtained using Philips X'Pert3 Analytical diffractometer (UK) using Cu Kα radiation with λ=0.15406 nm. The crystalline structure and external morphology of the catalyst was viewed using Quanta Scanning Electron Microscope FEI Quanta 250,USA. The measurement of transmission electron microscopy (TEM) was carried out on a FEI Tecnai^{TM} F20 Transmission electron microscopes (TEM), USA at 200kV. The optical characterization of the photocatalyst was carried out using Diffuse Reflectance UV–vis spectrophotometer equipped with a Harrick Praying Mantis TM diffuse reflection accessory used for solid samples (Perkin Elmer Lambda 6505), USA in the wavelength range from 250 to 800 nm with scanning speed of 300nm/min. The ultraviolet visible diffuse reflectance spectra (UV-vis DRS) of the as-synthesized samples were recorded on a UVX Radiometer (UVP Inc., Upland CA, USA, equipped with a UVX-36 long wave sensor equipped with an integrating sphere and using BaSO$_4$ as the reference. The thermogravimetric analysis was performed using Mettler-Toledo TGA/DSC I STAR, USA instrument with heating rate of 20°C/min in nitrogen (N$_2$) atmosphere. FT-IR analysis of the fresh and used catalyst was measured after the photocatalysis process.

Photocatalytic Degradation of Chlorazole E Dye

The photocatalysis was performed using a photoreactor as reported by Yilleng et al [1]. 0.20g of the catalyst was suspended in 100ml aqueous solution of 2.0 x 10^{-5}moldm^{-3} of the dye with continuous stirring using a magnetic stirrer. 10 ml of the sample was taken at 20 min interval and filtered using PTFE micro syringe to remove the catalysts and the absorbance was measured at 385nm using Jenway UV/Vis spectrophotometer (UK).

RESULT AND DISCUSSION

FTIR measurement

The FTIR spectra of pure 1% Ag-TiO$_2$ is shown in Figure 1. Based on the results obtained the following deductions were inferred from the spectra at various frequencies. A broad brand observed at 3402.54cm^{-1} is related to O-H bending vibrations and is attributed to adsorbed water molecules and hydroxyl ion. It also corresponds to the O-H stretching vibration and is attributed to the interaction between the hydroxyl groups of the titanium dioxide. The vibrations observed from 900cm^{-1} to 400cm^{-1} is attributed to Ti-O stretching vibrations and Ti-O-Ti lattice. On comparing the fresh and used samples the following observations were made. A vibration is observed 3410.26cm^{-1} and 1172.76cm^{-1} which corresponds to O-H due to phenol and C-N due to aromatic amines broken from chlorazole black E respectively. The vibration at 1033.88cm^{-1} is observed due to aromatic C-H groups broken down from the dye molecule during the photocatalytic process. The 1627.97cm^{-1} is due to primary amine N-H group formed as an intermediate during irradiation.
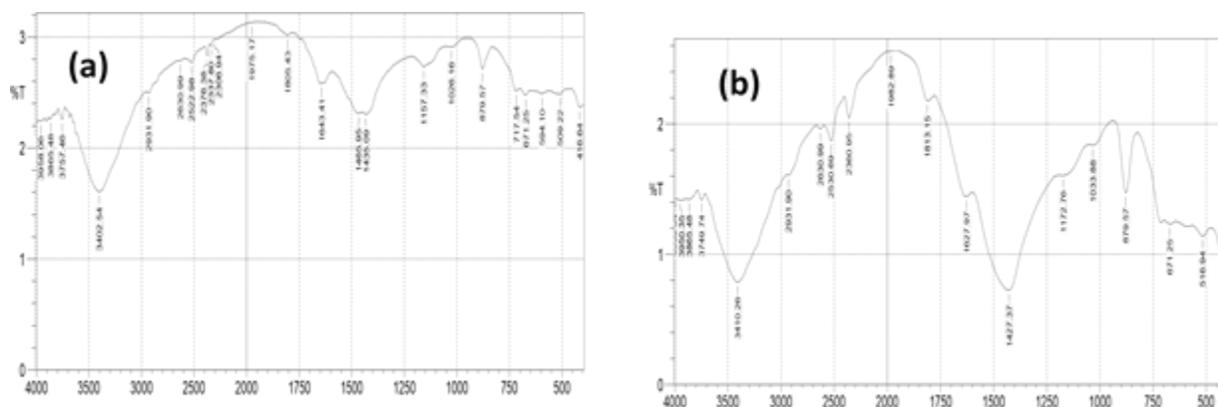

Fig. 1: FTIR spectra of 1%Ag-TiO$_2$: (a) Fresh, (b) Used

XRD measurement

The Ag-TiO$_2$ materials show a high degree of crystallinity with the existence of anatase and rutile phase after calcination at 600ºC. As shown on Figure 2, peaks due to silver were not observed on the samples due to the sizes of the silver particles in the TiO$_2$ suggesting that silver particles are homogeneously dispersed on the TiO$_2$ matrix. Doping with silver does not disturb the crystal structure of anatase TiO$_2$ indicating that the silver dopants are merely placed on the

surface on crystal without being covalently anchored into the crystal lattice. This was supported by the TEM result.

Each crystal size of the sample is calculated using the full width at half maximum (FWHM) diffraction peak using Scherrer's equation:

$$D = \frac{K\lambda}{\beta cos\theta} \ldots\ldots\ldots\ldots\ldots (1)$$

Where D is the average crystal size of the sample, λ the X-ray wavelength (1.54056 Å), β the full-width at half maximum (FWHM) of the diffraction peak (radian), K is a coefficient (0.89) and θ is the diffraction angle at the peak maximum.
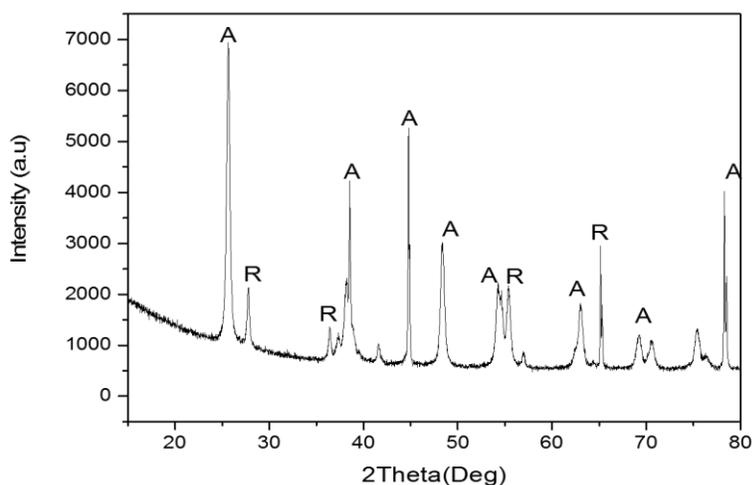

Fig. 2: XRD pattern of 1%Ag-TiO$_2$

SEM and TEM measurement

The morphology of the 1%Ag-TiO$_2$ particles measured by SEM is given in Figure3a. Noticeably, the sample was mainly composed of 8~13 nm spherical particles and presented the porous structures, which was a little larger than the value determined by XRD analysis. The SEM images ofAg-TiO$_2$ are shown in Fig. 3. They depict that doping silver metal into TiO$_2$ does not leave any change in the regularity of the catalyst surface. It reveals that the distribution of silver on the surface of titanium dioxide is not uniform and the Ag-TiO$_2$ catalyst contains irregular shaped particles which may be due to the aggregation of tiny crystals. However, it cannot be

ignored that some silver particles are too small to be observed at certain resolution of the microscope. Meanwhile, TEM images of the 1%Ag-TiO$_2$ sample were also conducted and shown in Fig.3b. It could be observed that the sample consisted of a great deal of small nano-particles and the crystallite size was about 6 nm in diameter, which supported the crystallite sizes calculated from the XRD patterns.
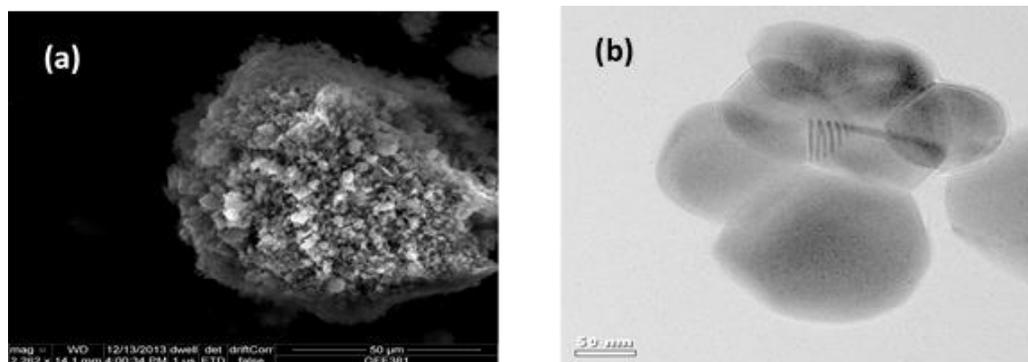

Fig.3: (a) TEM (b) SEM. images of N-TiO$_2$ sample

TGA measurements

The TGA curve obtained for 1%Ag-TiO$_2$ in Figure 4, shows the weight loss in two steps. In the first step the main weight loss is between 60 and 86°C which corresponds to the removal of volatiles solvents like n-hexane, methanol and 1-butanol that were used in the preparation of the catalyst. The second step is a weight loss between 124 to 302°C which is due to adsorbed water, other organics or could be assigned to high temperature used in the catalyst preparation or might probably be assigned to loss accompanied with collapse of inter-agglomerate and escape of trace moiety during the phase transformation from anatase to rutile [8]. This is also in agreement with the results obtained from the XRD analysis. The weight loss within the spectrum has a percentage loss of 5.8389% and 4.7231% for first and second step respectively, and is a proof that it has higher percentage of volatile substance than less volatiles one.
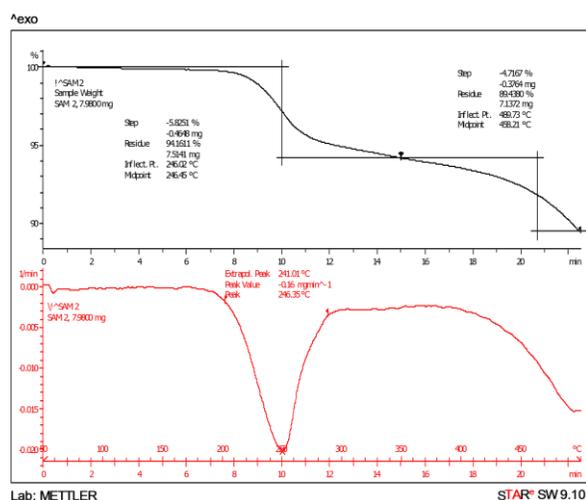
Fig. 4: TGA spectra of 1%wtN-TiO$_2$

Diffuse reflectance UV-Vis measurement

Fig. 5. Show the diffuse reflectance UV-Vis spectra of the 1%Ag-TiO$_2$.The spectra evidently showed a significant shift of the absorption peak toward the visible regions of the solar spectrum. Ag-TiO$_2$ nanomaterials exhibited a maximum wavelength at around 410 nm with a band invariably suggesting an increase of the photocatalytic activity efficiency within the visible range. It also showed increase of the absorption values in the UV region as observed. Moreover, absorption bands at 410 nm may be also attributed to Ag clusters of about 10 nm.   These findings suggest that the applied sol-gel hydrothermal induces a modification of TiO$_2$ structure. This change might represent the bulk change inside the oxide, or rather a modification on the surface. Also, the decrease in the energy edge on Ag-TiO$_2$ composites as compared to pure TiO$_2$ where there is a forbidden band called the band gap. This separates the Valence band from the Conduction band. The band gap energy, of TiO$_2$ (anatase) is 3.2 eV, which corresponds to photons with a wave length of 388 nm [9].
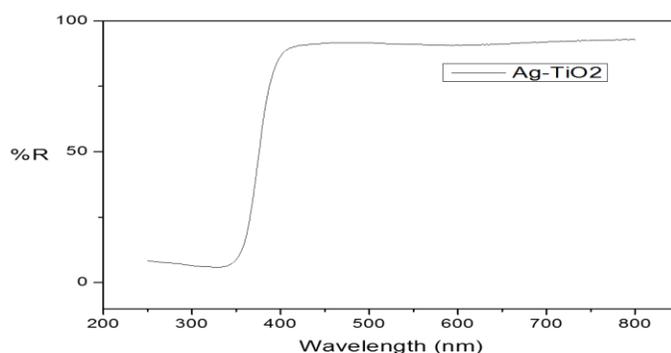
Fig. 5: Diffuse reflectance UV-Vis spectra

Photocatalytic degradation efficiency of chlorazole Black E dye by 1%wtAg-TiO$_2$

From the results shown in Figure 6 the percentage conversion after 80min of irradiation was 99.05%, 83.27% and 82.42% using 1%, 3% and 5% Ag-TiO$_2$ under UV light respectively. There was reduction in the photocatalytic activity according to the order: 1%>3%>5% Ag-TiO$_2$. This trend is dependent on the metal load on the TiO$_2$ photocatalyst. The higher the metal load on the TiO$_2$ photocatalyst the lower the photocatalytic activity due to the deactivation of active molecules by collision with ground state molecules, dominating the reaction.
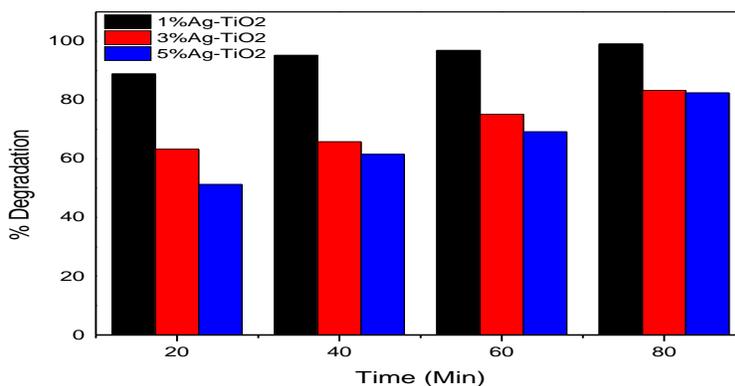

Fig. 6: Rate of photocatalytic degradation of chlorazole Black E dye using Ag-TiO$_2$ under UV-lightin percent

Kinetics of the photodegradation process

Fig. 7 shows plot of –lnC/Co of chlorazole black E dye against irradiation time for photocatalytic degradation using 1%wtAg-TiO$_2$, 3%wtAg-TiO$_2$, and 5%wtAg-TiO$_2$ photocatalyst in the reaction reactions. As it is clear from these Figures, removal of the dye concentration obeys a

linear pattern in this coordinate with good precision in both cases. This shows constancy in the rate constants of the reaction for each prepared photocatalyst in the degradation of chlorazole black E dye for the 80 minutes of irradiation with respect to first order equation. This means that the pseudo-first order kinetic of dye removal kinetic is acceptable for all photocatalytic processes [1]. Comparison of the lines average rate constant 0.078, 0.030 and 0.028 corresponding to 1%wtAg-TiO$_2$, 3%wtAg-TiO$_2$, and 5%wtAg-TiO$_2$photocatalysed reaction which is the apparent rate constant shows that 1%Ag-TiO$_2$>3%Ag-TiO$_2$ >5%Ag-TiO$_2$ catalysed reaction photoactivity follow the trend indicated in the photocatalytic degradation at the same conditions.

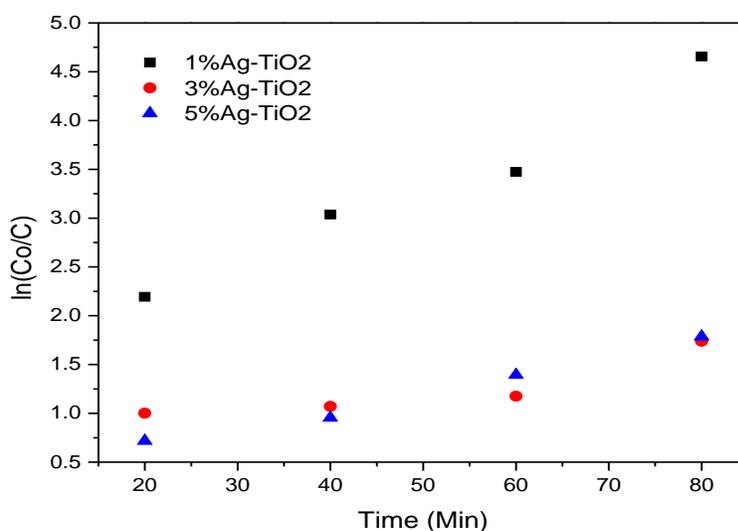Fig. 7: Rate of photocatalytic degradation of chlorazole Black E dye using Ag-TiO$_2$ under UV-light

CONCLUSION

The 1%wtAg-TiO$_2$ after characterization shows high potential at 430nm and 2.75eV wavelength and band gap energy toward visible light activity which constitutes the greater fraction of the solar radiation. The Ag-TiO$_2$ photocatalyst activity was evaluated in the treatment of organic industrial dyes by degrading chlorazole black T dyes which serve as a model dye. The percentage conversion for the rate of degradation of chlorazole black T was 99.05%, 83.27%, and 82.42% using 1%Ag-TiO$_2$, 3%Ag-TiO$_2$, 5%Ag-TiO$_2$ under ultraviolet light after 80 minutes of irradiation respectively. Generally, the degradation efficiency follows the following trend

1%Ag-TiO_2>3%Ag-TiO_2 >5%Ag-TiO_2.   Therefore, doping TiO_2 with silver shows higher activity toward degradation of chlorazole black T dye.

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