

Enhanced Activity of Metal Doped Titanium Dioxide in Photo catalytic Ozonation

Achisa C Mecha, Maurice S Onyango, Ochieng' Aoyi, and Maggie NB Momba

Abstract—Surface modification of synthesized titanium dioxide (TiO₂) particles was done by metal doping using the sol gel method. Silver, copper and iron were used as dopants. The morphology, composition, crystalline structure, and band gap energy were characterized using Scanning Electron Microscopy, Energy Dispersive X-ray spectroscopy, X-Ray Diffraction, Fourier Transform Infrared spectroscopy, and UV Diffuse Reflectance Spectroscopy. The effects of dopants on the morphologies, structure, and photo catalytic effectiveness of the catalysts were investigated. The results showed that the metal dopants were successfully introduced to the TiO₂ particles and reduced the band gap. The photo catalytic activity of the catalysts was evaluated by the removal of phenol in aqueous solution using Ultra Violet radiation coupled with ozonation. Complete degradation of phenol was obtained for the metal doped TiO₂ compared to the undoped TiO₂ and reaction time was reduced by 64 % using photo catalytic ozonation.

Keywords—metal doping, phenol, photo catalytic ozonation, titanium dioxide.

1. INTRODUCTION

PHENOL and its derivatives are highly poisonous contaminants mainly found in wastewater. Even low contamination at few ppm level of phenol is considered as highly toxic. These compounds have high toxicity for micro-organisms, high chemical oxygen demand and poor biodegradability. There have been a lot of studies on the removal of phenol from wastewater and most of the techniques employed require sophisticated equipment and chemicals, and also multiple treatment stages for removal of intermediate products [1].

Conventional wastewater treatment processes are often not effective against such recalcitrant contaminants. This necessitates the use of advanced oxidation processes (AOPs), such as photo catalysis and ozonation, which are able to mineralize the contaminants to the harmless products (carbon dioxide and water) [2].

The use of semiconductor photo catalysis for environmental remediation and pollutant destruction has been studied mainly employing the use of titanium dioxide (TiO₂). This is mainly because the conduction band electron and valence band hole of TiO₂ can reduce O₂ and oxidize H₂O/OH⁻, respectively, through one-electron transfer pathway. The major limitation of TiO₂ which hampers its large scale application is that the band gap of photo catalytically more active titania phase (anatase) is 3.2 eV, which requires UV irradiation ($\lambda \leq 387$ nm) [3] and hence it is not active under visible light. Therefore, great effort has been made in exploring ways of enabling it to be a visible-light-driven catalyst [4]. Among the numerous approaches employed to achieve this, metal elements doping is one of the effective ways of extending the spectral response of the titanium dioxide to visible-light region by providing defect states in the band gap [5] and ultimately making use of the abundant solar energy. The sol-gel method is one of the most widely used for preparing TiO₂ nanoparticles, due to its advantages, such as high homogeneity, low processing temperature, stability and versatility of processing, low cost, easy preparation and industrial viability [6]. Furthermore, the incorporation of an active metal in the sol during the gelation stage allows the metal to have a direct interaction with support, therefore the material possess special catalytic properties [7]. Ozonation is a more powerful and fast oxidation process used to degrade recalcitrant contaminants compared to photo catalytic processes which are often slow. By combining ozonation and photo catalysis the reaction time can be substantially decreased and effectiveness improved due to synergistic effect of the two processes. This study explores the coupling of metal doped photo catalysis and ozonation in the removal of phenol from water. Metal doping resulted in complete phenol removal while coupling with ozone reduced the reaction time by 64 %.

II. MATERIALS AND METHODS

A. Materials

Reagent grade chemicals were used as purchased without further purification. Titanium (III) chloride, ammonia, silver, copper and iron nitrates and phenol were obtained from Merck Chemicals (Pty) Ltd.

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B. Synthesis of photo catalysts

The TiO₂ was synthesized using the method of Di Paola *et al* [8] with modifications. Ti (III) chloride solution was placed into a volumetric flask. Appropriate aqueous solution of concentrated ammonia and distilled water were mixed and then added drop wise to the titanium precursor solution under vigorous magnetic stirring at room temperature. The appropriate amount of silver, copper and iron was added to make 2 wt. % dopant. The mixture was stirred for 20 h, during which the colour of the dispersion gradually turned to white. The suspension was washed using deionized water and then centrifuged to remove the NH₄Cl side product. The precipitate was then dried at 100 °C for 10 h. The powder was crushed and calcined in a furnace at 500 °C for 4 h. Calcination temperature of 500 °C selected to ensure formation of anatase which has good photo catalytic ability rather than rutile. After calcination, the samples were cooled down to room temperature in a desiccator before use.

C. Characterization of photo catalysts

In heterogeneous catalysis, the reaction occurs at the surface of the catalyst. Catalytic surfaces hence need to be characterized with reference to their physical properties. The prepared TiO₂ nanoparticles were characterized for structural, morphological and chemical properties. A JEOL JSM 7600F field emission scanning electron microscope (FESEM) was used for microstructural analysis on the surface of photo catalysts. In addition, an energy dispersive X-ray (EDX) analyser was interfaced to the column to perform semi-quantitative chemical analysis and to obtain information on the doping metals distribution on the TiO₂ surface. The crystalline phase was determined using powder X-ray diffraction XRD. The XRD patterns were obtained at room temperature with a Bruker Analytical X-Ray systems diffractometer using Ni-filtered CuK α radiation. High-purity silicon powder (99.9999%) was used as an internal standard to account for instrumental line broadening effect during crystal size estimation. A Shimadzu UV-2450 UV-vis spectrophotometer equipped with an integrated sphere was used to record the diffuse reflectance spectra (DRS) and absorbance data of photo catalyst samples. The base line correction was performed using a calibrated reference sample of barium sulphate. The reflectance spectra of the metal doped loaded samples were analysed under ambient conditions in the wavelength range of 200-800 nm. The chemical composition of the synthesized photo catalysts was determined by FTIR. The infrared reflection spectra of the TiO₂ nano powder pressed into pellets was measured at room temperature using a Thermo Scientific FTIR spectrometer in the spectral range between 400 and 4000

D. Photo catalytic activity

Photo catalytic experiments were carried out in cylindrical quartz reactor of 1 L capacity. A magnetic stirrer was used to ensure proper mixing of feed solution and to keep the reaction mixture in suspension and prevent the TiO₂ particles from settling. A compressor was used to provide air to the ozone generator in order to supply ozone to the reactor. All experiments were conducted at room temperature. In a typical process, 0.5 g/L of TiO₂ was mixed with water containing phenol of a specific concentration and well mixed in the holding tank. The mixture was fed into the reactor using a peristaltic pump. Prior to irradiation, the feed was magnetically stirred in the dark for 30 min to ensure the establishment of adsorption/desorption equilibrium. The irradiation was carried out using a 150 W low-pressure UV lamp surrounded by quartz thimble cooled by a water jacket. At specific reaction times, samples were collected in triplicates, filtered and centrifuged and stored in amber bottles.

III. RESULTS AND DISCUSSION

1. Band gap energy

Band gap energy calculated using the equation:

$$E = h\nu = \frac{hc}{\lambda} \quad (1)$$

Where, E= band gap energy (eV)

λ = cut off absorption wavelength (nm)

h = Planck's constant (6,626 x 10⁻³⁴ Js)

c = the speed of light (3,0 x 10⁸ ms⁻¹).

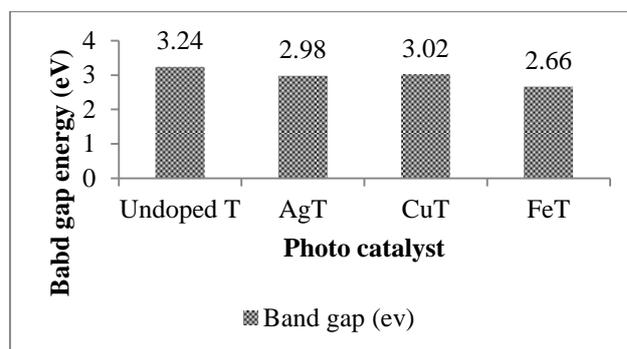


Fig.1 Band gap energy of the photo catalysts

Colour change from white to brownish yellow/red indicates the photo catalysts can absorb light over a wide range even the visible spectrum [3], [9]. The colour change was more dominant in the Fe doped sample which had the highest band gap reduction.

2. XRD spectra

The crystal structure and phase composition of the photo catalysts were determined by XRD and are shown in Fig. 2.

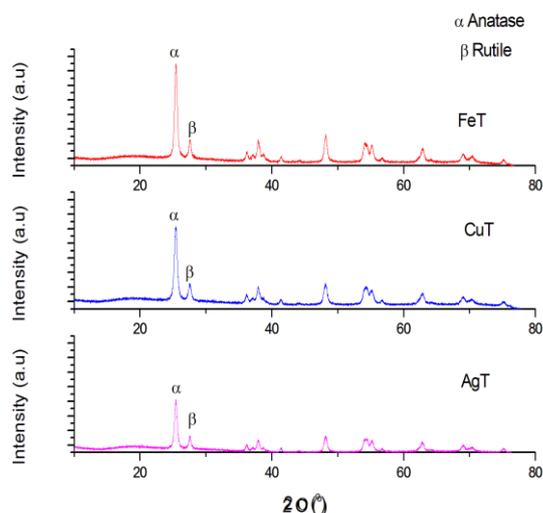


Fig.2 XRD spectra of synthesized photo catalysts

The photo catalysts showed crystalline nature with 2 θ peaks for anatase and rutile. Rutile (JCPDS 21–1276) and Anatase (JCPDS 21–1272) were identified in all samples as mixed phases. The anatase orientation corresponding to the plane (101) and rutile (110) were observed in all the samples in agreement with the literature [10], [11]. The absence of peaks of the doping metals as well as their oxides indicates efficient dispersion of nanoparticles and absence of metal ions [12], [13].

The average crystallite size, D (nm) was determined using the Scherrer's equation,

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

Where, D =average anatase grain sizes, k =Scherrer constant (0,9), λ =wavelength of radiation, β is the difference between the full width of the diffraction line at one half of the maximum intensity for the sample and the standard, and θ corresponds to the peak position, the average anatase grain size of TiO_2 powders were determined from the broadening of the anatase (101) peak and rutile leak (110).

The crystallite size D , for anatase component was calculated to be 17 nm for Ag doped, 23 nm for Cu doped and 18 nm for Fe doped. The corresponding crystallite sizes for rutile were 31 nm, 23 nm and 21 nm respectively. Commercial anatase (undoped TiO_2) had a crystallite size of 35 nm. Thus the synthesized photo catalysts had smaller particle sizes and theoretically should have a large surface area for photo catalysis.

Since the photo catalysts were mixed phases of anatase and rutile, the phase composition was calculated using the Spur – Meyer's equation,

$$W_A = \frac{100}{[1+1,26(IR/IA)]} \quad (3)$$

It was determined that anatase was dominant in all samples, being 54% in AgTiO_2 , 70% in CuTiO_2 , and 67% in FeTiO_2 .

3. SEM/EDX

The morphology and chemical composition are shown in Fig. 3.

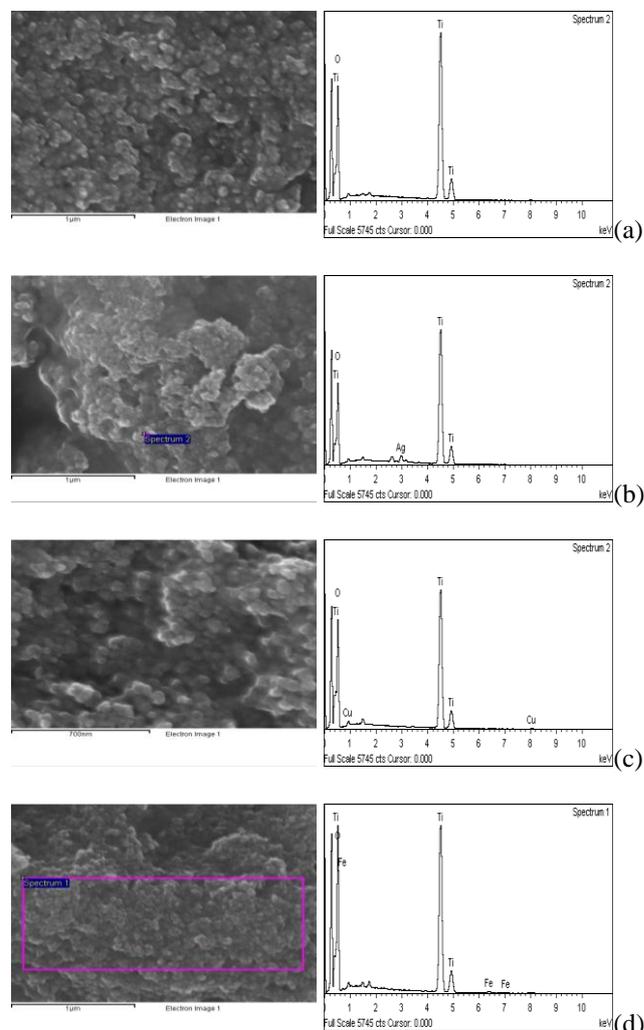


Fig.3a-d. SEM images of photo catalysts together with the corresponding EDX showing the presence of doping metals (Undoped, Ag, Cu and Fe)

Energy dispersive X-ray spectrometry (EDX) analysis of TiO_2 nanoparticles showed peaks for titanium (Ti), oxygen and the doping metals. No trace of any other impurities could be seen.

4. FTIR

The IR spectra of the photo catalysts is shown in Fig. 4.

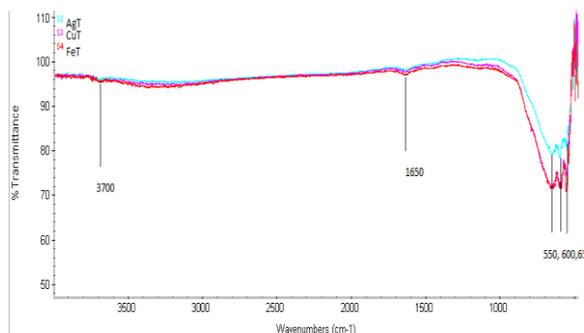


Fig.4 IR spectra of synthesized photo catalysts

The peaks at 550- 650 cm^{-1} represent O–Ti–O stretching bonds, thus TiO_2 was formed. The band centred at 1650 cm^{-1} is the characteristic of surface-adsorbed water and hydroxyl groups showing O-H bending and vibration. The peak at 3700 cm^{-1} represents stretching of hydroxyl (O-H) [14]. Generally, the synthesized photo catalysts had similar curves indicating the effectiveness of the sol gel method and that doping with metals did not result in the formation of other compounds.

5. Treatment of 100 ppm phenol using individual processes

The phenol concentration in aqueous phase exponentially decreased with irradiation time and ozonation. There was negligible phenol degradation in the dark phase of photo catalysis whereas UV alone did not achieve complete phenol removal in 7 hours. UV with undoped TiO_2 (UVT) performed better than UV alone but also did not achieve complete degradation. However, complete phenol degradation was observed for all the metal doped TiO_2 . Thus complete phenol degradation was due to semiconductor photo catalysis and it was dependent on the different catalysts.

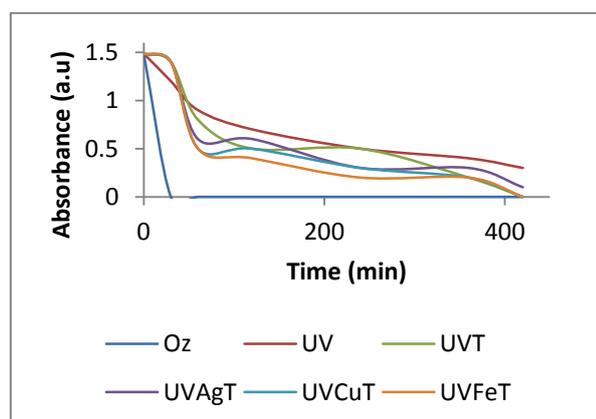


Fig.5 Removal of 100 ppm phenol using individual processes

Ozone was extremely fast as expected and achieved complete degradation of phenol in 30 minutes. However, intermediates were formed as observed by a major peak at 300 nm that persisted for more than 3 h. For photo catalysis

phenol degradation was complete in 7 h and no other peaks were detected, not even the one at 300 nm.

6. Treatment of 100 ppm phenol using combined processes (photo catalytic ozonation)

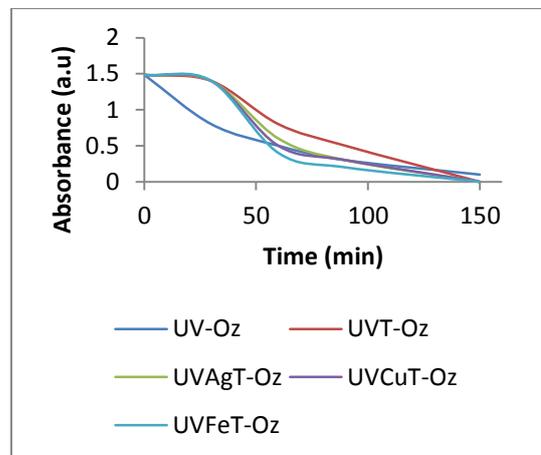


Fig.6 Treatment of 100 ppm phenol using combined processes (photo catalytic ozonation)

The time required for degradation of 100 ppm phenol was significantly reduced in photo catalytic ozonation from 7 h to 2.5 h (64 % reduction). Similarly, there was no peak at $\lambda = 300$ nm observed for the combined processes. In this case too, the photo catalysts performed better than photolysis (Uv-Oz) and achieved complete phenol removal in 2.5 h. Simultaneous photo catalytic ozonation results in the use of one reactor and hence saving on reactor cost and space especially in large scale operation.

IV. CONCLUSIONS

Silver, copper and iron were successfully incorporated in TiO_2 and reduced the band gap. This is beneficial in utilization of solar light. The study demonstrated the better performance of metal doped TiO_2 under UV light and future work will involve their use in visible light photo catalysis. Photo catalytic ozonation resulted in significant reduction in reaction time for complete degradation of phenol.

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REFERENCES

- [1] M. A. Gondal, M. N. Sayeed, Z. H. Yamani, and A. R. Al-Arfaj, "Efficient removal of phenol from water using Fe_2O_3 semiconductor catalyst under UV laser irradiation," *J. Environ. Sci. Health., Part A* vol. 44, pp. 515-521, 2009/03/02 2009.
- [2] T. Oyama, I. Yanagisawa, M. Takeuchi, T. Koike, N. Serpone, and H. Hidaka, "Remediation of simulated aquatic sites contaminated with recalcitrant substrates by TiO_2 /ozonation under natural sunlight," *Appl. Catal., B, Environ.*, vol. 91, pp. 242-246, 2009. <http://dx.doi.org/10.1016/j.apcatb.2009.05.031>
- [3] Z. Ambrus, N. Balázs, T. Alapi, G. Wittmann, P. Sipos, A. Dombi, et al., "Synthesis, structure and photocatalytic properties of Fe(III) -

- doped TiO₂ prepared from TiCl₃," *Appl. Catal., B: Environ.*, vol. 81, pp. 27-37, 2008.
<http://dx.doi.org/10.1016/j.apcatb.2007.11.041>
- [4] L. Wan, J. Sheng, H. Chen, and Y. Xu, "Different recycle behavior of Cu²⁺ and Fe³⁺ ions for phenol photodegradation over TiO₂ and WO₃," *J. Hazard. Mater.*, vol. 262, pp. 114-120, 2013
<http://dx.doi.org/10.1016/j.jhazmat.2013.08.002>.
- [5] J. Yu, Q. Xiang, and M. Zhou, "Preparation, characterization and visible-light-driven photocatalytic activity of Fe-doped titania nanorods and first-principles study for electronic structures," *Appl. Catal., B: Environ.*, vol. 90, pp. 595-602, 2009
<http://dx.doi.org/10.1016/j.apcatb.2009.04.021>.
- [6] M. A. Behnajady, H. Eskandarloo, N. Modirshahla, and M. Shokri, "Investigation of the effect of sol-gel synthesis variables on structural and photocatalytic properties of TiO₂ nanoparticles," *Desal.* vol. 278 pp. 10-17, 2011
<http://dx.doi.org/10.1016/j.desal.2011.04.019>.
- [7] J. C. S. Wu and C.-H. Chen, "A visible-light response vanadium-doped titania nanocatalyst by sol-gel method," *J. Photochem. Photobiol. A: Chem.*, vol. 163, pp. 509-515, 2004
<http://dx.doi.org/10.1016/j.jphotochem.2004.02.007>.
- [8] A. Di Paola, E. García-López, G. Marci, C. Martín, L. Palmisano, V. Rives, et al., "Surface characterisation of metal ions loaded TiO₂ photocatalysts: structure-activity relationship," *Appl. Catal., B: Environ.*, vol. 48, pp. 223-233, 2004.
<http://dx.doi.org/10.1016/j.apcatb.2003.10.015>
- [9] Y. Yalçın, M. Kılıç, and Z. Çınar, "Fe³⁺-doped TiO₂: A combined experimental and computational approach to the evaluation of visible light activity," *Appl. Catal., B: Environ.*, vol. 99, pp. 469-477, 2010
<http://dx.doi.org/10.1016/j.apcatb.2010.05.013>.
- [10] R. Vijayalakshmi and V. Rajendran, "Synthesis and characterization of nano-TiO₂ via different methods," *Arch. Appl. Sci. Res.* vol. 4, pp. 1183-1190, 2012.
- [11] J. Xu, L. Li, Y. Yan, H. Wang, X. Wang, X. Fu, et al., "Synthesis and photoluminescence of well-dispersible anatase TiO₂ nanoparticles," *J. Colloid Interface Sci.*, vol. 318, pp. 29-34, 2/1/2008.
- [12] N. N. Binitha, Z. Yaakob, M. R. Reshmi, S. Sugunan, V. K. Ambili, and A. A. Zetty, "Preparation and characterization of nano silver-doped mesoporous titania photocatalysts for dye degradation," *Catal. Today*, vol. 147, Supplement, pp. S76-S80, 2009
<http://dx.doi.org/10.1016/j.cattod.2009.07.014>.
- [13] J. Zhu, F. Chen, J. Zhang, H. Chen, and M. Anpo, "Fe³⁺-TiO₂ photocatalysts prepared by combining sol-gel method with hydrothermal treatment and their characterization," *J. Photochem. Photobiol. A: Chem.*, vol. 180, pp. 196-204, 2006
<http://dx.doi.org/10.1016/j.jphotochem.2005.10.017>.
- [14] M. M. Ba-Abbad, A. A. H. Kadhum, A. B. Mohamad, M. S. Takriff, and K. Sopian, "Synthesis and Catalytic Activity of TiO₂ Nanoparticles for Photochemical Oxidation of Concentrated Chlorophenols under Direct Solar Radiation," *Int. J. Electrochem. Sci.*, vol. 7, pp. 4871 - 4888, 2012.