Impact of Solubilising Matrices for $TiCl_4$ on the Formation of TiO_2 Nanoparticles

M.M. Ngandjou Douanla, S.K.O. Ntwampe, L.C. Razanamahandry, E. Malenga, E. Fosso-Kankeu and K. Fölck

***Abstract* — Several nanoparticles (Cu_2O, SnO, ZnO) have been intensively studied and applied in wastewater treatment research, with TiO_2 gaining popularity because of its stability, affordability, large band gap, recyclability and its efficiency in photocatalysis. This study reports on the influence of solubilising matrices on TiO_2 nanoparticle synthesis. A Wet Chemical Method was used to synthesis TiO_2 nanoparticles by solubilising $TiCl_4$ in three types of solvents: water, toluene and methylene chloride. Physical, chemical and optical properties of the TiO_2 nanoparticles obtained from these various solubilising agents were characterised by XRD, UV-Vis, FTIR and SEM. Results were compared for each solvent with TiO_2 nanoparticles solubilised in water having the best properties.**

***Keywords*—**Titanium Chloride, Titanium Oxide, Nanomaterials, Wet Chemical Method

I. Introduction

Several research fields address the issue of hazardous compounds in wastewater treatment with nanotechnology being one of the well understood, promising and innovative technologies which can be applied for the degradation of biological and chemical pollutants in wastewater treatment processes. Nanotechnology relies on the application of nanoparticles with most not naturally occurring in the environment. They are often synthesised via biological (plants, agro-waste) or chemical (chemical salts) techniques. Up to date, chemical methods are specifically applied for TiO_2 and a large number of other nanoparticle have been developed using methods such as chemical precipitation [1-3]; sol gel [4-6], hydrothermal [7-10], solvo-thermal [11, 12], combustion [13, 14], chemical vapour deposition (CVD) [15], electrochemical synthesis [16, 17] and fungus-mediated [18, 19], synthesis/methods. Amongst these, the Wet Chemical Method is known to be effective as chemical precipitation is applied with low chemical consumption, in a cost effective manner with better product quality outcomes.

TiO_2 appears in three forms in nature, i.e. anatase, rutile and brookite. Anatase is predominantly used in solar cells and its ease of conductivity allows electrons to move freely. Anatase can also be easily doped with certain chemicals to increase its conductivity with both anatase and rutile being know to have a band gap of 3.0 and 3.2 eV, respectively [20] which is suitable for photocatalytic degradation of pollutants. TiO_2 has a low absorption coefficient, a high refractive index, high surface area and a great photocatalytic activity with a high ion–exchange capacity where holes and electrons are produced for redox reactions to oxidise organic pollutant to non-toxic constituents such as CO_2 and water in wastewater treatment plants. Therefore, TiO_2 could be used in various applications such as photocatalysis for self-cleaning glasses [21, 22], photocatalysis for the remediation of naturally occurring organic matter [23], wastewater decontamination [24-26], environmental purification [27], interfacial charge carrier transfer, and the removal of organic pollutants such as cyanide [28].

Wet Chemical Methods have been intensively adopted and performed to synthesise nanoparticles but with the growth of hazardous compound in nature, researchers are more concerned with finding a green and environmental benign approach for TiO_2 synthesis. The Wet Chemical Method relies on the use of low solvent consumption, ease of performance and cost effectiveness. All the reagents involved are used in liquid form. More often, ammonium hydroxide is mixed with $TiCl_4$ or $TiOCl_2$ in aqueous solutions [29]. Many of the previous studies used ammonium hydroxide and ethanol [30] as solvents for $TiCl_4$. According to our knowledge, no study has presented the effect of solubilising agents for $TiCl_4$ on TiO_2 nanoparticles synthesis. Therefore, this paper reports on the influence of solubilising matrices on TiO_2 nanoparticle synthesis, in particular water, methylene chloride and toluene.

Manuscript received October 01st, 2018. The authors would like to acknowledge the financial assistance of the South Africa National Research Foundation (NRF).

M.M. Ngandjou Douanla is with Bioresource Engineering Research Group (*BioERG*), Faculty of Applied Sciences, Department of Biotechnology, Cape Peninsula University of Technology, Cape Town, South Africa.

S.K.O. Ntwampe is the founder of Bioresource Engineering Research Group (*BioERG*), Faculty of Applied Science Department of Biotechnology, Cape Peninsula University of Technology, Cape Town, South Africa.

L.C. Razanamahandry is with the UNESCO UNISA Africa Chair in Nanoscience's/Nanotechnology Laboratories (U2AC2N), College of Graduate Studies, University of South Africa (UNISA), Muckleneuk Ridge, P.O. Box 392, Pretoria, South Africa and with Nanosciences African network (NANOAFNET), Materials Research Group (MRG), iThemba LABS-National Research Foundation (NRF), 1 Old Faure Road, 7129, P.O. Box 722, Somerset West, Western Cape Province, Cape Town, South Africa.

E. Malenga is with the Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, North-West University, Private Bag X1290, Potchefstroom, 2520, South Africa.

E. Fosso-Kankeu is with the Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, North-West University, Private Bag X1290, Potchefstroom, 2520, South Africa.

K. Fölck is the founder and CEO of the juicebox Pty Ltd renamed Cape Town cold drink company Pty Ltd.

II. Materials And Methods

A. TiO_2 Synthesis

All the reagents used in the study were of analytical grade. All the TiO_2 nanoparticles derived from the use of $TiCl_4$ in different solvents were synthesized under the same conditions using the Wet Chemical Method. $TiCl_4$ solutions (1M) in toluene, water and methylene chloride were purchased from Sigma Aldrich (Germany). Ammonium hydroxide (32%) was used to precipitate the nanoparticles in the solutions.

$TiCl_4$ (2 mL) was added drop-wise in a 100 mL beaker containing ammonium hydroxide solution, under vigorous stirring for 10 min until an amorphous white precipitate was obtained. The synthesis was done at 60°C in a water bath. The samples were dried in an oven at 80°C to transform the amorphous phase to a solid phase. The dry particles were transferred in tubes and washed several time with warm distilled water to remove the excess $TiCl_4$. All the samples were collected by centrifugation subsequent to acetone supplementation to dry the sample before they were transferred in crucibles for annealing at 350^{o}C for 6 h. The annealed powders were thereafter characterised using XRD, SEM-EDS, FTIR and UV-Vis spectrometry techniques.

B. TiO_2 Characterisations

XRD and SEM were used to investigate the TiO_2 physical properties, i.e. the TiO_2 nanoparticles crystallisation and its surface topographic, respectively. The average size (D) of the annealed TiO_2 nanoparticles was estimated by using the Debye-Schereer's equation:

$$D = 0.9\lambda /(ß \times \cos \Theta) \quad (1)$$

Where:

λ: is the wavelength of the copper anode radiation that used during the XRD analysis, with a value 1.5406 Å,

ß: is the full width half maximum (FWHM) of the peak, in radians, and

Ɵ: is the Bragg's angle; in degrees.

Chemical properties, such as elemental composition and chemical bonding of the annealed TiO_2 nanoparticles were identified by EDS and FTIR, respectively.

Furthermore, optical properties were studied by running an UV-Vis within a spectra range of 200 to 800 nm.

III. Results And Discussion

The solvents used for $TiCl_4$ solubilisation, have all been shown to be effective as suitable solvents for the synthesis of TiO_2 nanoparticles. The UV-VIS analyses have shown the presence of TiO_2 nanoparticles as shown in Figure 1. The TiO_2 nanoparticles' UV-VIS absorption spectra was determined to fit within the invisible UV range of sunlight, i.e. between 100-400 nm [31]. The TiO_2 nanoparticles could absorb the UV of sunlight for various applications including for dermal applications [32].

TiO_2 nanoparticles had an adsorbance peak at 280nm for UV–VIS spectroscopy studies. The same adsorption wavelength observed herein was reported by various researchers [33, 34]. However, the adsorption peak was higher for TiO_2 synthesised by solubilised $TiCl_4$ in water than when using methylene chloride and toluene.

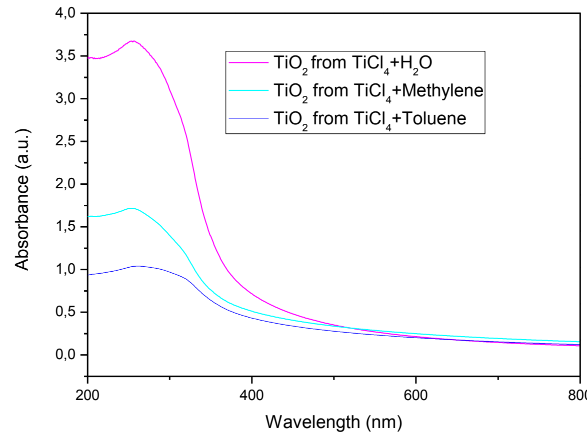


Fig. 1: UV-Vis absorbance of TiO_2 nanoparticles from various $TiCl_4$ solubilisations

Figure 2 shows the XRD patterns of each TiO_2 nanoparticle produced from various $TiCl_4$ solubilisations. The Muller's indices (hkl) was detected at 2Ɵ (degree) = 25.281; 37.801; 48.050; 53.891; 55.062; 62.690 and 75.032 for hkl = 101; 004; 200; 105; 211, 204 and 215, respectively. Similar peaks were obtained for all synthesised TiO_2. Based on the hkl indices, the atom position of each TiO_2 was determined to be have a body-centred tetragonal. The average size (D) of the nanoparticles was 12 nm; 7 nm and 10 nm for $TiCl_4$ solubilised in water, methylene chloride and toluene, respectively.

SEM images presented in Figure 3 shows that the TiO_2 nanoparticles were quite polydispersed in methylene chloride and toluene than in water, and their maximum size was 124 nm, 100 nm and 120 nm size, respectively. The chemical elemental composition of TiO_2 nanoparticles obtained by EDS is shown in Figure 4, which elucidated that the particles had C, O and Ti : C and O chemical elements, which are indicative of oxidation reactions with which the TiO_2 nanoparticles were derived [35].

FTIR spectroscopy analyses are shown in Figure 5, illustrating peak bands at 3327.65 cm^{-1}, 1635.33 cm^{-1} and 605.53 cm^{-1} for $TiCl_4$ solubilised in methylene chloride and toluene and 3207.61 cm^{-1}, 2350.40 cm^{-1}, 2030.61 cm^{-1}, 1622.16 cm^{-1} and 659.63 cm^{-1} for $TiCl_4$ solubilised in water. Characteristic bands indicated at 1635.33 cm^{-1} and 1622.16 cm^{-1} represent saturated hydrocarbons, i.e. the C=C link. Bands 3327.65 cm^{-1} and 3207.61 cm^{-1} indicated the O-H, with the peaks at 2350.40 cm^{-1}, 2030.61 cm^{-1} corresponding to the C-O stretching alcohols from methylene chloride and toluene. All bands were generated by the chemical and elemental interaction forms of water, methylene chloride and toluene. The presence of TiO_2 nanoparticles was indicated by the peak 605.53 cm^{-1} and 659.63 cm^{-1} for $TiCl_4$ in water and for $TiCl_4$ in methylene chloride and toluene, respectively.

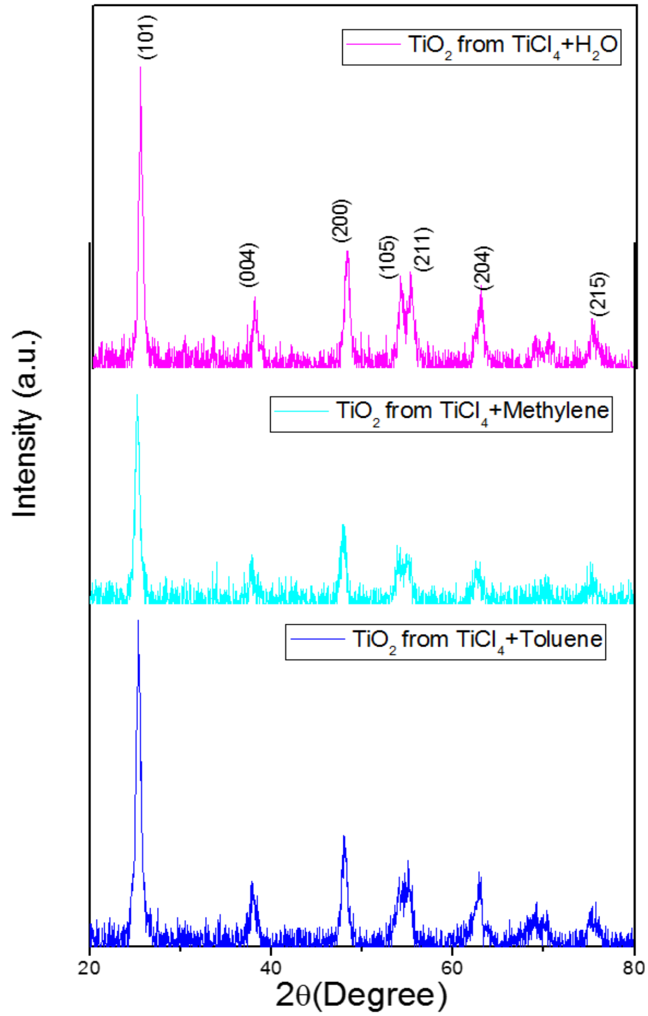


Fig. 2: XRD patterns of TiO_2 nanoparticles from various $TiCl_4$ solubilisations

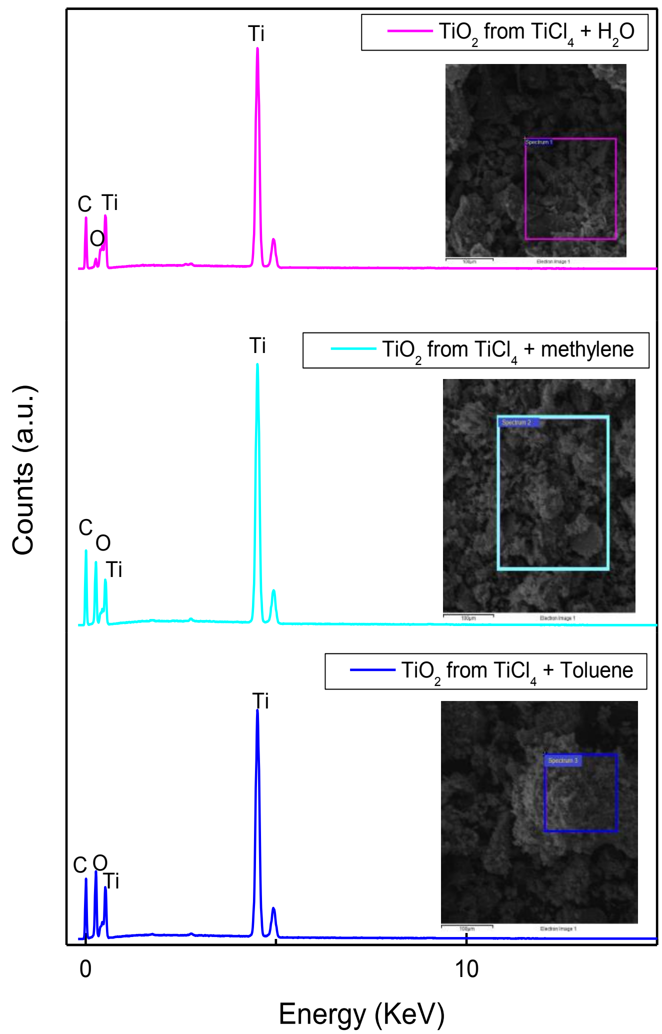


Fig. 4: EDS graphs of TiO_2 nanoparticles from various $TiCl_4$ solubilisations

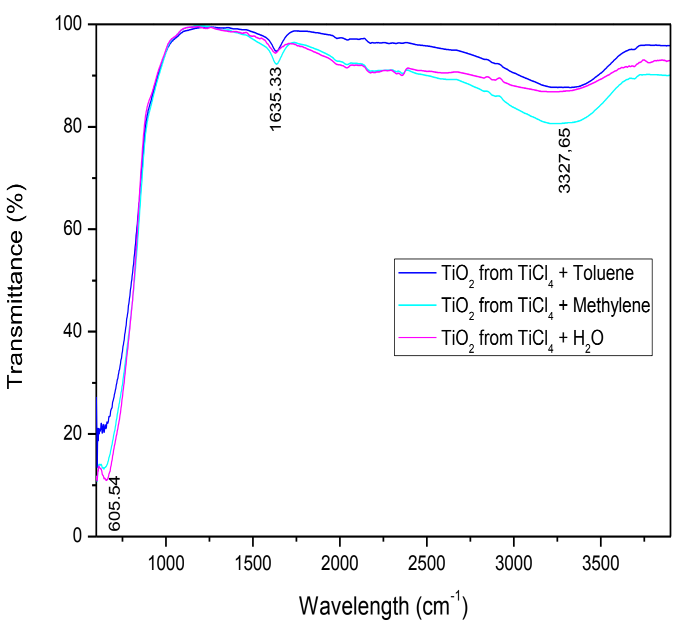
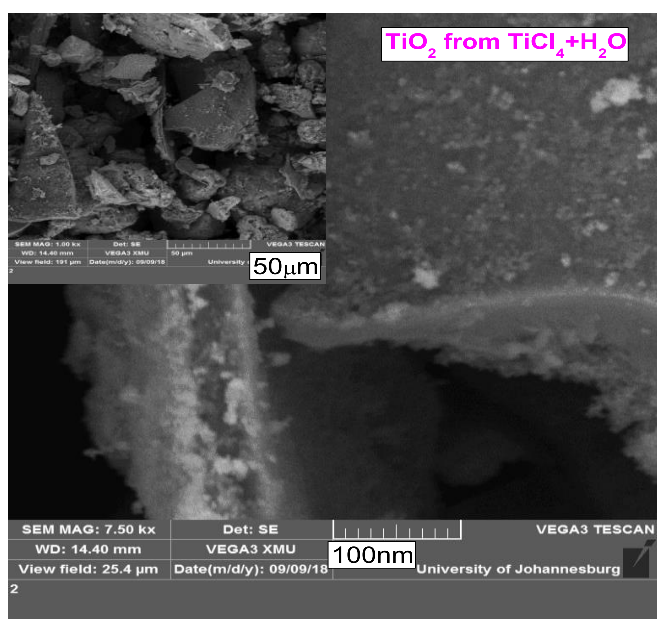
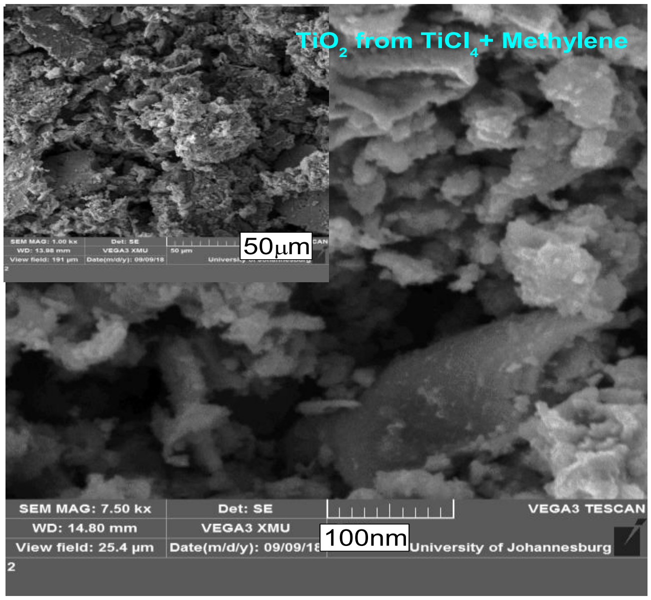


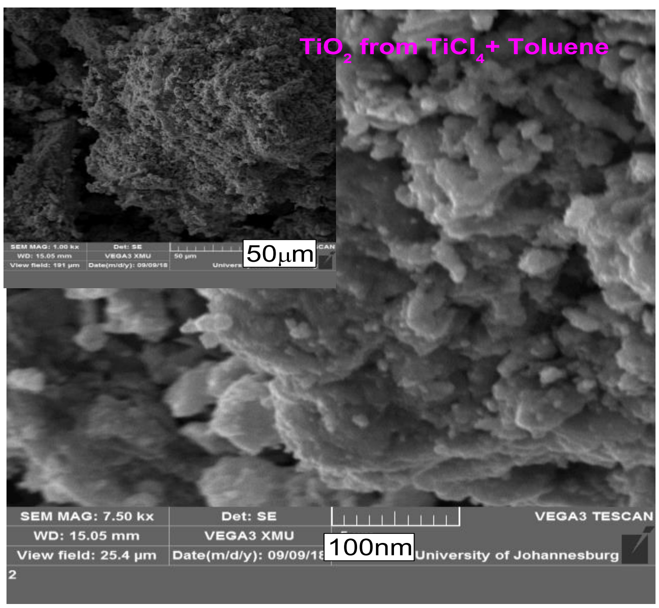
Fig. 3: FTIR Spectra of TiO_2 nanoparticles from various $TiCl_4$ solubilisations



A



B



C

Fig. 5: SEM images of TiO_2 nanoparticles from various $TiCl_4$ solubilisations, a) water b) methylene chloride and c) toluene

IV. Conclusion

In summary, TiO_2 was successfully synthesised by solubilising $TiCl_4$ in various solvents, such as water, methylene chlorine and toluene. All TiO_2 nanoparticles synthesised have a single phase anatase structure. However, $TiCl_4$ solubilised in water have shown to have had the best crystallisation. Therefore, water as a solvent is highly recommended to solubilise the matrix $TiCl_4$ to synthesis TiO_2 for photocalytic operations.

References

[1] G. Collazzo, S. Jahn, N. Carreño, and E. Foletto, "Temperature and reaction time effects on the structural properties of titanium dioxide nanopowders obtained via the hydrothermal method," *Brazilian Journal of Chemical Engineering*, vol. 28, no. 2, pp. 265-272, 2011. https://doi.org/10.1590/S0104-66322011000200011

[2] A. Jaggessar, A. Mathew, H. Wang, T. Tesfamichael, C. Yan, and P. K. Yarlagadda, "Mechanical, bactericidal and osteogenic behaviours of hydrothermally synthesised TiO_2 nanowire arrays," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 80, pp. 311-319, 2018. https://doi.org/10.1016/j.jmbbm.2018.02.011

[3] N. Syuhada, and B. Yuliarto, "Synthesis and Characterization Hierarchical Three-Dimensional TiO_2 Structure via Hydrothermal Method." p. 012052.

[4] B. K. Mutuma, G. N. Shao, W. D. Kim, and H. T. Kim, "Sol–gel synthesis of mesoporous anatase–brookite and anatase–brookite–rutile TiO_2 nanoparticles and their photocatalytic properties," *Journal of Colloid and Interface Science*, vol. 442, pp. 1-7, 2015. https://doi.org/10.1016/j.jcis.2014.11.060

[5] D. Pinjari, K. Prasad, P. Gogate, S. Mhaske, and A. Pandit, "Synthesis of titanium dioxide by ultrasound assisted sol–gel technique: effect of calcination and sonication time," *Ultrasonics sonochemistry*, vol. 23, pp. 185-191, 2015. https://doi.org/10.1016/j.ultsonch.2014.10.017

[6] V. Vetrivel, K. Rajendran, and V. Kalaiselvi, "Synthesis and characterization of pure titanium dioxide nanoparticles by sol-gel method," *Int. J. ChemTech Res*, vol. 7, pp. 1090-1097, 2015.

[7] L. Cano-Casanova, A. Amorós-Pérez, M. Ouzzine, M. A. Lillo-Rodenas, and M. C. Román-Martínez, "One step hydrothermal synthesis of TiO_2 with variable HCl concentration: Detailed characterization and photocatalytic activity in propene oxidation," *Applied Catalysis B: Environmental*, vol. 220, pp. 645-653, 2018. https://doi.org/10.1016/j.apcatb.2017.08.060

[8] Y. Gao, L. Wang, A. Zhou, Z. Li, J. Chen, H. Bala, Q. Hu, and X. Cao, "Hydrothermal synthesis of TiO_2/Ti_3C_2 nanocomposites with enhanced photocatalytic activity," *Materials Letters*, vol. 150, pp. 62-64, 2015. https://doi.org/10.1016/j.matlet.2015.02.135

[9] N. Li, Y. Li, W. Li, S. Ji, and P. Jin, "One-step hydrothermal synthesis of TiO_2/MoO_3 core–shell nanomaterial: microstructure, growth mechanism, and improved photochromic property," *The Journal of Physical Chemistry C*, vol. 120, no. 6, pp. 3341-3349, 2016. https://doi.org/10.1021/acs.jpcc.5b10752

[10] H. Wu, J. Fan, E. Liu, X. Hu, Y. Ma, X. Fan, Y. Li, and C. Tang, "Facile hydrothermal synthesis of TiO_2 nanospindles-reduced graphene oxide composite with a enhanced photocatalytic activity," *Journal of alloys and compounds*, vol. 623, pp. 298-303, 2015. https://doi.org/10.1016/j.jallcom.2014.10.153

[11] M. Xie, L. Jing, J. Zhou, J. Lin, and H. Fu, "Synthesis of nanocrystalline anatase TiO_2 by one-pot two-phase separated hydrolysis-solvothermal processes and its high activity for photocatalytic degradation of rhodamine B," *Journal of Hazardous Materials*, vol. 176, no. 1-3, pp. 139-145, 2010. https://doi.org/10.1016/j.jhazmat.2009.11.008

[12] H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, H. M. Cheng, and G. Q. Lu, "Solvothermal synthesis and photoreactivity of anatase TiO_2 nanosheets with dominant {001} facets," *Journal of the American Chemical Society*, vol. 131, no. 11, pp. 4078-4083, 2009. https://doi.org/10.1021/ja808790p

[13] X. Ma, L. Xue, X. Li, M. Yang, and Y. Yan, "Controlling the crystalline phase of TiO_2 powders obtained by the solution combustion method and their photocatalysis activity," *Ceramics International*, vol. 41, no. 9, pp. 11927-11935, 2015. https://doi.org/10.1016/j.ceramint.2015.05.161

[14] S. Umale, V. Sudhakar, S. M. Sontakke, K. Krishnamoorthy, and A. B. Pandit, "Improved efficiency of DSSC using combustion synthesized TiO_2," *Materials Research Bulletin*, 2018.

[15] Y. Chimupala, P. Junploy, T. Hardcastle, A. Westwood, A. Scott, B. Johnson, and R. Brydson, "Universal synthesis method for mixed phase TiO_2 (B)/anatase TiO_2 thin films on substrates via a modified low pressure chemical vapour deposition (LPCVD) route," *Journal of Materials Chemistry A*, vol. 4, no. 15, pp. 5685-5699, 2016. https://doi.org/10.1039/C6TA01383J

[16] S. T. Döşlü, B. D. Mert, and B. Yazıcı, "The electrochemical synthesis and corrosion behaviour of TiO_2/poly (indole-co-aniline) multilayer coating: Experimental and theoretical approach," *Arabian Journal of Chemistry*, vol. 11, no. 1, pp. 1-13, 2018. https://doi.org/10.1016/j.arabjc.2017.03.007

[17] A. Nur, A. Purwanto, A. Jumari, E. R. Dyartanti, S. D. P. Sari, and I. N. Hanifah, "Synthesis of TiO_2 by electrochemical method from $TiCl_4$ solution as anode material for lithium-ion batteries." p. 030003.

[18] G. Rajakumar, A. A. Rahuman, S. M. Roopan, I.-M. Chung, K. Anbarasan, and V. Karthikeyan, "Efficacy of larvicidal activity of green synthesized titanium dioxide nanoparticles using Mangifera indica extract against blood-feeding parasites," *Parasitology research*, vol. 114, no. 2, pp. 571-581, 2015.
https://doi.org/10.1007/s00436-014-4219-8

[19] T. Santhoshkumar, A. A. Rahuman, C. Jayaseelan, G. Rajakumar, S. Marimuthu, A. V. Kirthi, K. Velayutham, J. Thomas, J. Venkatesan, and S.-K. Kim, "Green synthesis of titanium dioxide nanoparticles using Psidium guajava extract and its antibacterial and antioxidant properties," *Asian Pacific journal of tropical medicine*, vol. 7, no. 12, pp. 968-976, 2014.
https://doi.org/10.1016/S1995-7645(14)60171-1

[20] E. Kordouli, K. Bourikas, A. Lycourghiotis, and C. Kordulis, "The mechanism of azo-dyes adsorption on the titanium dioxide surface and their photocatalytic degradation over samples with various anatase/rutile ratios," *Catalysis Today*, vol. 252, pp. 128-135, 2015.
https://doi.org/10.1016/j.cattod.2014.09.010

[21] A. Calia, M. Lettieri, M. Masieri, S. Pal, A. Licciulli, and V. Arima, "Limestones coated with photocatalytic TiO_2 to enhance building surface with self-cleaning and depolluting abilities," *Journal of Cleaner Production*, vol. 165, pp. 1036-1047, 2017.
https://doi.org/10.1016/j.jclepro.2017.07.193

[22] B. Naufal, S. G. Ullattil, and P. Periyat, "A dual function nanocrystalline TiO_2 platform for solar photocatalysis and self cleaning application," *Solar Energy*, vol. 155, pp. 1380-1388, 2017.
https://doi.org/10.1016/j.solener.2017.08.005

[23] B. N. Sousa, "Biological and Photocatalytic Degradation of Mycotoxins in Corn for Use in Bio-Fuel Production," 2017.

[24] B. Bhanvase, T. Shende, and S. Sonawane, "A review on graphene–TiO2 and doped graphene–TiO_2 nanocomposite photocatalyst for water and wastewater treatment," *Environmental Technology Reviews*, vol. 6, no. 1, pp. 1-14, 2017.
https://doi.org/10.1080/21622515.2016.1264489

[25] M. Borges, M. Sierra, E. Cuevas, R. García, and P. Esparza, "Photocatalysis with solar energy: sunlight-responsive photocatalyst based on TiO_2 loaded on a natural material for wastewater treatment," *Solar Energy*, vol. 135, pp. 527-535, 2016.
https://doi.org/10.1016/j.solener.2016.06.022

[26] M. N. Chong, Z. Y. Tneu, P. E. Poh, B. Jin, and R. Aryal, "Synthesis, characterisation and application of TiO_2–zeolite nanocomposites for the advanced treatment of industrial dye wastewater," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 50, pp. 288-296, 2015.
https://doi.org/10.1016/j.jtice.2014.12.013

[27] J. Liqiang, S. Xiaojun, C. Weimin, X. Zili, D. Yaoguo, and F. Honggang, "The preparation and characterization of nanoparticle TiO_2/Ti films and their photocatalytic activity," *Journal of Physics and Chemistry of solids*, vol. 64, no. 4, pp. 615-623, 2003.
https://doi.org/10.1016/S0022-3697(02)00362-1

[28] J. Aguado, R. Van Grieken, M. Lopez-Munoz, and J. Marugán, "Removal of cyanides in wastewater by supported TiO_2-based photocatalysts," *Catalysis Today*, vol. 75, no. 1-4, pp. 95-102, 2002.
https://doi.org/10.1016/S0920-5861(02)00049-4

[29] H. Yin, Y. Wada, T. Kitamura, S. Kambe, S. Murasawa, H. Mori, T. Sakata, and S. Yanagida, "Hydrothermal synthesis of nanosized anatase and rutile TiO_2 using amorphous phase TiO_2," *Journal of Materials Chemistry*, vol. 11, no. 6, pp. 1694-1703, 2001.
https://doi.org/10.1039/b008974p

[30] S. K. Gupta, R. Desai, P. K. Jha, S. Sahoo, and D. Kirin, "Titanium dioxide synthesized using titanium chloride: size effect study using Raman spectroscopy and photoluminescence," *Journal of Raman Spectroscopy: An International Journal for Original Work in all Aspects of Raman Spectroscopy, Including Higher Order Processes, and also Brillouin and Rayleigh Scattering*, vol. 41, no. 3, pp. 350-355, 2010.

[31] F. Behar-Cohen, G. Baillet, T. de Ayguavives, P. O. Garcia, J. Krutmann, P. Peña-García, C. Reme, and J. S. Wolffsohn, "Ultraviolet damage to the eye revisited: eye-sun protection factor (E-SPF®), a new ultraviolet protection label for eyewear," *Clinical ophthalmology (Auckland, NZ)*, vol. 8, pp. 87, 2014.

[32] J. Luan, Y. Shen, L. Zhang, and N. Guo, "Property Characterization and Photocatalytic Activity Evaluation of $BiGdO_3$ Nanoparticles under Visible Light Irradiation," *International journal of molecular sciences*, vol. 17, no. 9, pp. 1441, 2016.
https://doi.org/10.3390/ijms17091441

[33] R. Dobrucka, "Synthesis of titanium dioxide nanoparticles using *Echinacea purpurea* herba," *Iranian journal of pharmaceutical research: IJPR*, vol. 16, no. 2, pp. 756, 2017.

[34] S. M. Roopan, A. Bharathi, A. Prabhakarn, A. A. Rahuman, K. Velayutham, G. Rajakumar, R. Padmaja, M. Lekshmi, and G. Madhumitha, "Efficient phyto-synthesis and structural characterization of rutile TiO_2 nanoparticles using Annona squamosa peel extract," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 98, pp. 86-90, 2012.
https://doi.org/10.1016/j.saa.2012.08.055

[35] K. Qi, B. Cheng, J. Yu, and W. Ho, "Review on the improvement of the photocatalytic and antibacterial activities of ZnO," *Journal of Alloys and Compounds*, 2017.
https://doi.org/10.1016/j.jallcom.2017.08.142

M.M. Ngandjou Douanla was born in Cameroon, in 1992, obtaining Baccalaureus Technologiae's degree in Biomedical Technology (Biotechnology) in 2016, and the National Diploma in Biotechnology in 2015, both at the Cape Peninsula University of Technology, Cape Town, South Africa. Prior to this, she matriculated in 2011 at the high school of Bepanda. Currently, she is a Master of Engineering: Chemical Engineering student, at the Cape Peninsula University of Technology, Cape Town, South Africa.