

Visible Light Activity of Enhanced Screen-printed Titanium Dioxide

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This research focused on investigating the effect of novel Alpirin as a natural light harvesting pigment for sol-gel derived titanium dioxide with silver plasmon. The absorbance, transmittance, refractive index, optical conductivity, band gap, the crystalline sizes and average dislocation density of TiO₂ were investigated. It was observed that these optical properties were improved as a result of doping with Alpirin. Further significant improvement was observed on the addition of AgNPs that was deposited through one successive ionic layer adsorption and reaction (SILAR) cycle. The average crystalline size of Alpirin doped titanium dioxide was with average dislocation density of and the band gap of 2.52 eV while that of alpirin +AgNPs doped TiO₂ was with average dislocation density of and the band gap of 2.00 eV as against the undoped TiO₂ with average crystalline size of and average dislocation density of and band gap of 3.65 eV. The synergy between alpirin + AgNPs show that the incorporation of metal nanoparticle is beneficial for enhanced photoactivity.

Keywords: Alpirin; Photoactivity; Silver; Titanium Dioxide**Introduction**

Titanium dioxide is a promising photocatalyst for the degradation of organic pollutant [1]. Its specific properties like the optical, electronics, excellent chemical stability, non-toxicity to the environment and relatively cheap nature have given it a wider research interest [2,3]. Unique properties such as high transmittance, high refractive index, relatively high energy conversion efficiency and high stability make it a better prospect for optical applications [4]. When light of appropriate intensity shines on titanium (iv) oxide surface, pairs of electrons and holes are generated inside its crystal lattice. Free electrons are usually produced in the conduction band and the holes at the valence band [5]. However, the major limitation associated with using titanium dioxide as a photoanode is the high electron hole recombination as a result of its wide band gap energy; which causes a small fraction of the solar light from the ultraviolet region to be utilized [67]. To

maximize the photoactivity of TiO₂, it is necessary to reduce the wide band gap energy [1]. Many attempts have been made recently to enhance TiO₂ with metals and non metals such as nitrogen [8], silver [4], iron, gold [9], copper [10]. Recent research has indicated that the use of natural ruthenium dye [11], cynodon dactylon [6], sepia melianin [1] among other dyes which are cheap, abundant, renewable and ecofriendly have significantly modified the photoactivity of titanium dioxide. However, solar cells fabricated with co-doped TiO₂ proved to be more efficient. [10] doped TiO₂ with Fe, Cu and mix Fe-Cu and observed that mix Fe-Cu has more power conversion efficiency than doping with single metal. Deposition of Ag on doped TiO₂ showed enhanced photovoltaic properties due to the synergistic effect between Ag and doped TiO₂, the Ag-NPs has dual effect on the performance of TiO₂ including the enhancement of the absorption coefficient and optical absorption due to surface Plasmon resonance [12,13]. Incorporating a

very small amount of metal into natural dye has not been fully explored. This research area still remains very economical due to the cheap source of the natural dye and its natural abundance and renewability. However the photocatalytic activity of TiO_2 also strongly depends on the preparation methods and on the post-treatment conditions. It has decisive influence on the chemical and physical properties [14,15]. There are different methods that has been used to synthesize TiO_2 . These include gel method [16,17] and vapour deposition method [7], hydrolysis of inorganic salts [3,18] chemical spray pyrolysis, sol-gel technique, hydrothermal treatment, and arc discharge method [19,20]. Currently, sol-gel is one of the most successful techniques on how to prepare nanosized metallic oxides with high photocatalytic activity [3,20]. Screen printing deposition technique is one of the most reported methods of producing the nanostructured metal-oxide layer within DSSCs [21,22]. This deposition technique produces films in large quantity with the use of relatively cheap and simple designs with excellent scales of economy [23]. The aim of this research work is to investigate the doping influence by the novel alpirin natural dye as well as alpirin dye mixed with silver plasmon on the optical and structural properties of sol gel derived titanium iv oxide. Alpirin is a dye extract from *Alpinia purpurata* commonly called red ginger flower and it is not an edible plant.

Materials and Methods

Materials

The sol-gel derived TiO_2 was purchased from Solaronix Renewable Energy. *Alpinia purpurata* flower samples were collected from a flower garden in a residential compound in Abia State. Silver nitrate (AgNO_3), tin (ii) chloride, methanol and soda lime substrate glass were purchased from Allan's Resources. All the other materials used in this research work were supplied by Sheda Science and Technology Complex (SHETCO) Abuja.

Deposition of TiO_2

The substrate glass was cleaned with deionized water and ultrasonicated in isopropanol for about 10 minutes. TiO_2 nanoparticles were gradually screen printed unto soda lime substrate glass with the help of squeegee at annealing temperature of 500°C for seventy minutes. The films were allowed to cool down to room temperature. That was a necessary condition to remove thermal stresses and avoid cracking of the glass or peeling off the TiO_2 film [24].

Deposition of silver nanoparticles

The substrate glass was cleaned using cotton wool soaked with sodium lauryl sulphate and rinsed with de-ionized water. Later dipped into a mixture of H_2SO_4 and chromic acid to make the surface hydrophilic and was thereafter rinsed with distilled water. It was then immersed in 0.1 M tin (ii) chloride (SnCl_2) for 20 mins then rinsed with distilled water for 20 mins and immersed in 0.01M silver nitrate (AgNO_3) and rinsed with a mixture of distilled water and hydrochloric acid (HCl). This process gave the structure glass/ TiO_2 /AgNPs with one complete SILAR cycle. SILAR method is relatively simple, cheap, and time-saving and can be carried out at room temperature. It offers an easy control to the thickness of the film or nanoparticle.

Dye extraction

The flowers of *Alpinia purpurata* were air dried under room temperature for about thirty (30) days until they became invariant in weight and were well blended to very fine particles. 1g of the flower sample was measured using electronic chemical balance and soaked in methanol and HCl mixed in the ratio of 99:1 to form acidified methanol. The solution was vibrated on a magnetic Stirrer Hotplate78-1(PEC medicals USA) for twenty (20) mins at uniform acidity (pH of 3). Dye extract at the pH of 3 displays broad absorption peak in the 480-560nm range resulting from $\pi - \pi^*$ transitions due to the mixed contributions of the yellow-orange betaxanthins (480 nm) and of the red-purple betacyanin (540 nm) [25; 26]. It was filtered to separate the solid residue from the clear dye solution.

Doping process

The samples with structures; glass/ TiO_2 and glass/ TiO_2 /AgNPs were doped with *alpirin* for 48 hours. As reference, another sample with structure of glass/ TiO_2 was left undoped.

Characterization and measurement

The thicknesses of both doped and undoped samples were measured using a Veeco Dektak 150 profilometer. Each sample went through the optical study using the UV/Vis/NIR spectrophotometer (6.2.0.1588 spectrophotometer). The scanning for each sample was done thrice in the wavelength interval of 0 nm to 1000 nm and the various averaged curves were taken in order to obtain the absorbance, transmittance, reflectance, refractive index and optical conductivity. The reflectance was obtained using Equation (1)

$$A + T + R = 1 \quad \text{----- (1)}$$

Where A is the absorbance, T is the transmittance, R is the reflectance. From Equation (1) the reflectance values were obtained as shown in Equation (2) given by [27].

$$1 - (A + T) = R \quad \text{----- (2)}$$

The refractive index (n) determines the extent of permeability at which light rays can travel through a medium.

Refractive index values of the samples were obtained from equation (3) as given by [4,28].

$$n = \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})} \quad \text{----- (3)}$$

Extinction coefficient (k) for the samples were calculated using equation (4) given by [29].

$$k = \frac{\alpha \lambda}{4\pi} \quad \text{----- (4)}$$

Where α is the absorption coefficient, λ is the wavelength and π is equal to 3.142.

The X-ray diffraction pattern was recorded on a Rigaku Ultima IV X-ray diffractometer.

Results and Discussions

Optical analysis

The thickness of the samples shows that they are all thin films with the thickness of about 75 nm. Figure 1 shows the UV-Vis absorption spectra of undoped and doped TiO₂ samples within the wavelength range 0 – 1000 nm. It is obvious that the absorption edge was shifted to the visible region due to doping. However the shift went higher as a result of the Ag nanoparticles. The optical absorption enhancement is attributed to the intensified near-field surface plasmon resonance (SPR) of metallic AgNPs, which interacted with the dye molecule thereby enhancing dye absorption. This result is in agreement with those obtained by [2,13,28]. Figure 2 shows the variation of transmittance with wavelength for undoped and doped TiO₂ samples. High transmittance for all the samples was observed. We also observed a slight drop with TiO₂ doped with alpirin, the transmittance dropped further for sample doped with alpirin + silver nanoparticles within the visible spectrum. This shows that the film can be used as optical windows in solar cell. This result agrees with those obtained by [2].

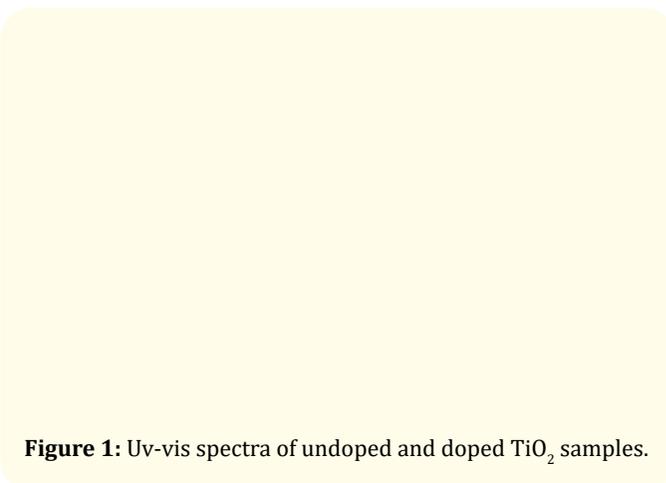


Figure 1: Uv-vis spectra of undoped and doped TiO₂ samples.

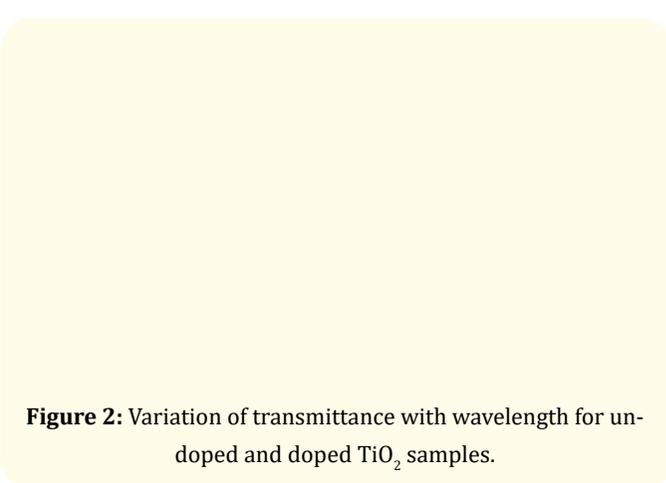


Figure 2: Variation of transmittance with wavelength for undoped and doped TiO₂ samples.

From the results obtained in figure 3 we observed high reflectance in the visible region for the sample doped with alpirin. The reflectance increased further on doping with AgNPs + alpirin as compared to the undoped sample. This result is in agreement with [28].

The results obtained in figure 4 indicate high refractive index within the visible region for the doped samples. It is observed that the refractive index increased for sample doped with alpirin and increased further on doping with AgNPs + alpirin. This shows that the medium is highly permeable for light rays and very good for solar cell applications.

Figure 5 show the variation in extinction coefficient with wavelength for undoped and doped TiO₂. We observed that the extinction coefficient increased on doping with alpirin with peak at

400 nm and also increased further on doping with AgNPs + alpirin a peak at 447 nm.

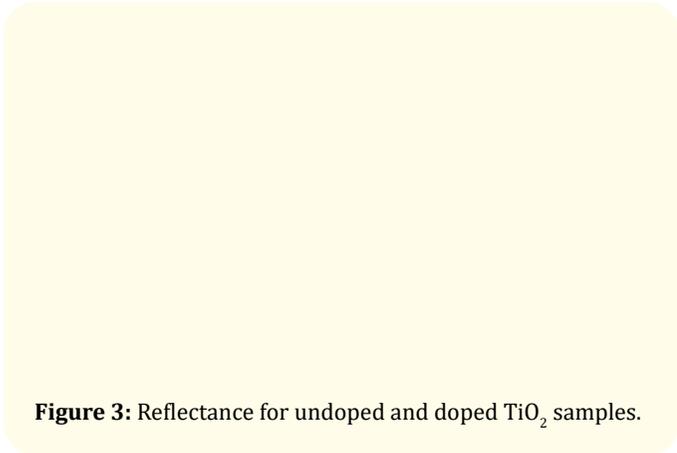


Figure 3: Reflectance for undoped and doped TiO₂ samples.

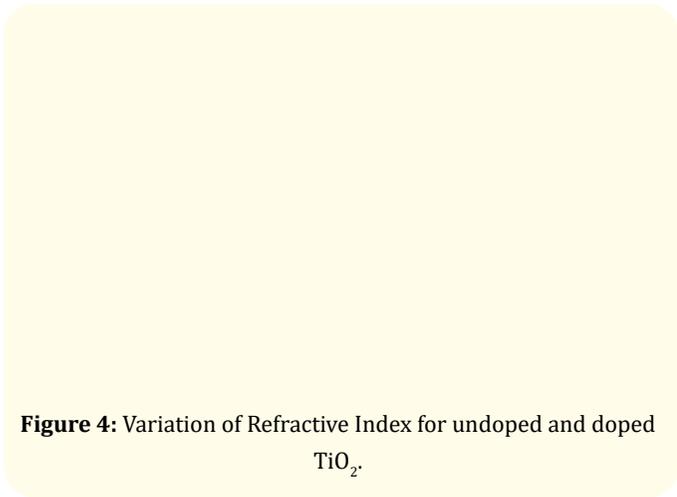


Figure 4: Variation of Refractive Index for undoped and doped TiO₂.

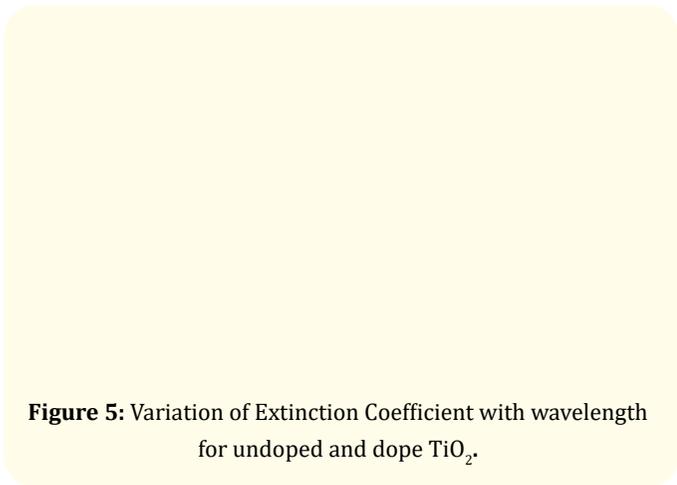


Figure 5: Variation of Extinction Coefficient with wavelength for undoped and doped TiO₂.



Figure 6: Direct band gap for (a) undoped TiO₂ (b) TiO₂ doped with alpirin (c) doped with AgNPs and alpirin.

The direct energy band gap of the films was evaluated at the intercept of zero y-axis of linear extrapolation of the plot. Figure 6 gives the direct band gap of (a) 3.65 eV for undoped TiO₂, (b) 2.45 eV for Alpirin/TiO₂ and 2.10 eV for Alpirin/AgNO₃/TiO₂. From these results, it is obvious that optical band gap energy of pure undoped TiO₂ decreased on doping with Alpirin which allows delay in recombination of ion and increases photoactivities of TiO₂.

The X-ray diffraction

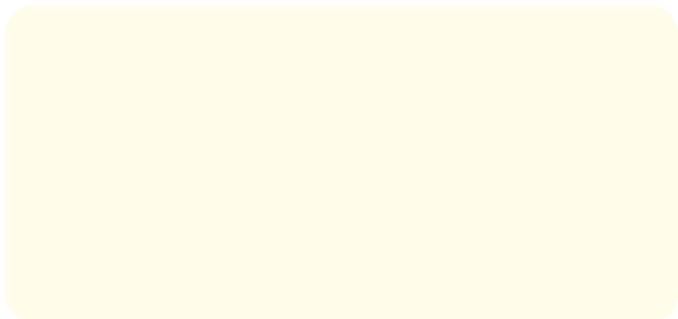


Figure 7: XRD pattern for (a) undoped TiO₂ (b) TiO₂ doped with alpirin (c) doped with AgNPs and alpirin.

The XRD pattern for the undoped TiO₂ with peaks at $2\theta = 25^\circ, 38^\circ, 48^\circ, 54^\circ, 55^\circ, 63^\circ$ and 75° which correspond to miller indices [101], [004], [200], [105], [211], [204], [116], and [215] is shown in Figure 7(a). The patterns of deposited sample are attributed to reflections of anatase phase with tetragonal crystal structure. The results correspond to those obtained by [20;4]. In Figure 7(b), there was phase transformation from amorphous to anatase and to rutile. It was also observed that the anatase phase with the tetragonal crystal structure has more peaks than the rutile phase. It is considered widely that this is as a result of improved charged carrier separation, possibly through the trapping of electrons in rutile and the consequent reduction in electron-hole recombination. This result corresponds to those obtained by [30]. There are three additional peaks at, and as shown in figure 7(c). The x-ray diffraction patterns is also attributed to reflections of anatase phase with tetragonal crystal structure, there is also the presence of Silver chlorargyrite AgCl. Using Debye-Scherer Equation.

The average crystalline sizes were for undoped TiO₂, for TiO₂ doped with alpirin and for TiO₂ doped with Ag + alpirin. The average dislocation densities were; for undoped TiO₂, for TiO₂ doped with alpirin and TiO₂ doped with Ag + alpirin. The XRD of the synthesized nanoparticles are very broad which indicates large crystallite sizes. Anatase TiO₂ is seen as the main polymorph present in the samples. The diffraction angles indicate a body centered tetragonal crystalline structure of TiO₂. The peaks of the

doped samples were shifted to the higher diffraction angles as compared to that of the undoped TiO₂ sample. The results show that average crystallite size of TiO₂ slightly increases when it was doped with alpirin and decreases when it was doped with Ag + alpirin.

Conclusion

The impact of alpirin and Ag + alpirin on the optical and structural properties of TiO₂ nanoparticles synthesized of TiO₂. The UV-vis spectroscopy showed the shifting of absorption edge of doped TiO₂ to the visible spectrum as compared with the undoped TiO₂. The transmittance for the TiO₂ samples was high which lends good application as optical window solar cells. The refractive index increases for TiO₂ doped with alpirin and went higher on doping with Ag + alpirin. The average dislocation densities increase with decreasing particle size. These properties show high permeability as required in optical windows.

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Bibliography

1. Mbonyiriyvuzze A., *et al.* "Titanium Dioxide Nanoparticles Biosynthesis for Dye Sensitized Solar Cells application: Review". *Physics and Materials Chemistry/Science and Education Publishing*, 3 (2015): 12-17.
2. Ozuomba JO and Ekpunobi A J. "A Study of The Band Gap of Sensitized Titanium Dioxide Nanoparticles and Their Photovoltaic Applications". *Moldavian Journal of the Physical Sciences* 12.3-4 (2013): 165-171.
3. Kralova M., *et al.* "Preparation and characterization of doped titanium dioxide printed layers". *Catalysis Today*, Elsevier, 230 (2014): 188-196.
4. Arishi JI., *et al.* "Influence of Ag-doping on Optical and Structural Properties of TiO₂ Thin Films Deposited dye Electrohydrodynamic Spray Pyrolysis". *Journal of Materials Science Research and Reviews* 2.3 (2019): 1-10.
5. Donald RA. "The Science and Engineering of Materials". New York, NY: Wadsworth, Inc (1985).
6. Ozuomba JO., *et al.* "The viability of a natural dye extracted from paw paw leaves as photosensitizer for sensitized solar cell". *International Science Research Journal* 3 (2011): 3-5.

7. Liu, J. X., *et al.* "Sol-gel deposited TiO₂ film on NiTi surgical alloy for biocompatibility improvement". *Thin Solid Films* 429 (2013): 225-230.
8. Mehdizadeh P., *et al.* "Visible Light Activity of Nitrogen-Doped TiO₂ by Sol-Gel Method Using Various Nitrogen Sources". *Journal of Nanostructure* 10.2 (2020): 307-316.
9. Monsefi M., *et al.* "Size-Controlled Synthesis of Gold Nanostars and Their Characterizations and Plasmon Resonances". *Journal of Nanostructure* 10.2 (2020): 198-205.
10. Alwan DB., *et al.* "Improving the efficiency of dye-sensitized solar cells with doping and co-doping titanium dioxide". *Iraqi Journal of Science* 57.3C (20156): 2228-2233.
11. Anees Ur R., *et al.* "Analyze the Absorption Properties and I-V Characterization of Dye Sensitized Solar Cell Using Ruthenium Dye". *Pakistan, American Journal of Engineering and Applied Science* 37.8 (2014): 611-621.
12. Su Pei L., *et al.* "Boosting Photovoltaic Performance of Dye-Sensitized Solar Cells Using Silver Nanoparticle-Decorated N, S-Co-Doped-TiO₂ Photoanode". *Scientific Reports* 5 (2015): 1-14.
13. Danladi E., *et al.* "Photoelectrochemical performance of dye-sensitized organic photovoltaic cells based on natural pigments and wide-bandgap nanostructured semiconductor". *Physical Science International Journal* 10.2 (2016): 1-7.
14. Govindasamy G., *et al.* "Investigations on the Synthesis, Optical and Electrical Properties of TiO₂ Thin Films by Chemical Bath Deposition (CBD) method". *Materials Research* 19 (2016): 413-419.
15. Huaimin C., *et al.* "Hydrothermal Synthesis and Electrochemical Properties of TiO₂ Nanotubes as an Anode Material for Lithium Ion Batteries". *International Journal of Electrochemistry* 13 (2018): 2118-2125.
16. Aliev SA., *et al.* "Properties of TiO₂ films with gold nanoparticles". Conference Series. Russia, International Conference of Photonics and Information Optics IOP Publishing Journal of Physics 737 (2016): 1-8.
17. Yu M., *et al.* "Optical Properties TiO₂ Thin Films". Elsevier; Science Direct (2015): 100-107.
18. Bregadiolli B A., *et al.* "Easy and Fast Preparation of TiO₂ -based Nanostructures Using Microwave Assisted Hydrothermal Synthesis". *Materials Research* 20.4 (2017): 912-919.
19. Valtierra J M., *et al.* "Formation of smooth and rough TiO₂ thin films on fibreglass by sol-gel method". *Journal of the Mexican Chemical Society* 50.1 (2006): 8-13.
20. Chenari HM., *et al.* "Titanium Dioxide Nanoparticles: Synthesis, X-Ray Line Analysis and Chemical Composition". *Materials Research Study* 1 (2016): 1-5.
21. Vetrivel V., *et al.* "Synthesis and characterization of Pure Titanium dioxide nanoparticles by Sol-gel method". *International Journal of ChemTech Research* 7.3 (2015): 1090-1097.
22. Johnson JC. "Inkjet Printing of Titanium Dioxide Photoanodes for Dye Sensitized Solar Cells". Grand Valley State, GVSU ScholarWork (2013).
23. Foster CW., *et al.* "Screen-Printing Electrochemical Architectures". Springer Briefs in Applied Science and Technology 3 (2016): 13-23.
24. Khalil E J. "Natural Dye-Sensitized Solar Cell Based on Nanocrystalline TiO₂". *Sains Malaysiana*, 41.8 (2012): 1011-1016.
25. Kasim U I., *et al.* "Betalain pigments as natural photosensitizers for dye-sensitized solar cells: the effect of dye pH on the photoelectric parameters". Springer, 3 (2014): 2-6.
26. Barness and Alexander. "Impact of extraction methods upon light absorbance of natural organic dyes for dye sensitized solar cells application". *Journal of Energy and Natural Resources* 3 (2014): 38-45.
27. Shine MH., *et al.* "Preparation of High Transmittance TiO₂ Thin Films by Sol-Gel Technique as Antireflection Coating". *Journal of Physics: Conf. Series* 1032.012018 (2018): 1-12.
28. Dike I Ijeoma and Ozuomba O Okanandu. "Effect Of 0.1m Silver Nanoparticles on The Optical and Structural Properties of TiO₂ Doped with Alpinin Dye ASPJ for SSE". 1.1 (2020): 219-234.
29. Tezel F M., *et al.* "The Effects of pH on Structural and Optical Characterization of Iron oxide Thin Films". *Surface Review and Letters* 24.4 (2017): 1-10.
30. Dorian AH Hanaor and Charles C Sorrell. "Review of the Anatase to Rutile Phase Transformation". *Springer Journal of Materials Science* 46.4 (2016): 855-874.