ISSN 2286-4822
www.euacademic.org

EUROPEAN ACADEMIC RESEARCH
Vol. VII, Issue 4/ July 2019

Impact Factor: 3.4546 (UIF)
DRJI Value: 5.9 (B+)

Advantages and applications of sustainable and green synthesis titania: A review

MUHAMMAD AZRI MUHAMAD YUSOP
CHE AZURAHANIM CHE ABDULLAH
Department of Physics, Faculty of Science
University Putra Selangor, Malaysia

Abstract

The methods that applicable to synthesis titanium dioxide (TiO_2) nanoparticles have been thoroughly reviewed. In this review, the focus will be on both the chemical and green synthesis of TiO_2. Presently, green synthesis innovated by various researchers to prepare TiO_2 nanoparticles due to their advantages offers where green synthesis does not require high quantity of chemical reagents and its offers sustainability. Green synthesis consists of and not limited to plant based, it can also originate from an aquatic animal, as well as enzymes where all of these categorized as natural resources that can be exploited for the green synthesis of nanomaterials coupled with the low cost and non-toxic final product. Although the chemical synthesis approach capable in producing large batch of nanoparticles, the disadvantages is it can harm the ecosystem due to their byproduct's formation. In addition, green synthesis will produce minimum chemical waste in comparison to chemical synthesis. Herein, details comparisons between these two approaches are properly reviewed.

Keywords: titanium dioxide (TiO_2), Green synthesis, chemical synthesis

INTRODUCTION

Nanotechnology is a well-known branch of science and listed as one of the important parts nowadays. The nanoparticle that play crucial role in this field are classified into two: mineral and mineral oxide nanoparticles. Nanoparticles can be easily defined as set of substances that has a single critical dimension less than 100 nanometers [1,2]. These nanoparticles possess distinctive biological, physical and also chemical properties which advances large number of applications mainly in medical application [3]. Mesoporous silica nanoparticles are an example of nanomaterial that have been applied in medical field [4]. Antimicrobial, magnetic, electronic and crystalline phase properties due to its high surface to volume ratio are key characteristics that attract numerous scientists to give attention to nanoparticles. Mineral oxides nanoparticles hold a crucial role in a large number of physics, chemistry as well as materials science. On top of that, the mineral oxides have been applied in the fabrication process of sensors, fuel cells, microelectronic circuit and coating for the passivation of surface against corrosion [5, 6]. However, instead of all of the advantages offers by metal oxide that been discovered, scientist is still struggled to understand on how nanoparticles move in different water media such as rivers, seawater and groundwater and contaminate the water sources [7]. So, in order to reduce the environmental impact of the nanoparticles, the chemical method of synthesis will be tune to green synthesis.

Titanium dioxide nanoparticle or TiO_2 nanoparticles also sometimes been called as titanium pigment is categorized as metal oxides and the most efficacious photo catalyst for self-cleaning [8, 9]. TiO_2 been classified as binary metal oxide and this property is very important in the making of electronic devices such as thin film transistors [10]. It is also having profound impact on the performance where the tensile moduli of the composites increase [11]. TiO_2 is white in color, nonflammable, thermally stable and considered as non-hazard material [12-14]. Although TiO_2 nanoparticles have many advantages, TiO_2 is poorly soluble. Properties that possess by TiO_2 nanoparticles have made it as an important nanomaterial in field of advanced materials. Recent trend focusses on the biosynthesis of TiO_2 nanoparticles based on aquatic lives such as fish, algae and plankton and study its effect towards environment [15, 16].

In order to synthesize TiO_2, there are two main method namely green synthesize and chemical synthetize. Nowadays, green synthesize is preferable among the researchers due to its eco-friendly and low cost. So, it is more suitable to prepare the TiO_2 nanoparticle via using green synthesize approach. Chemical synthesis required many substances to produce a good TiO_2 nanoparticle for commercialization purposes and one of the methods is called sol gel method [17-18]. Both method either chemical or green synthesis process of nanoparticles will usually produce anatase structure of TiO_2 rather rutile phase [19-20].

Synthesis of TiO_2 via chemical methods

Countess industry and companies nowadays prefer to use chemical methods in order to manufacture nanoparticles including TiO_2. There are numerous techniques or methods that commonly used to manufacture TiO_2 such as hydrothermal, sol gel method, solution combustion, solvothermal, microwave assisted, co precipitation, electrospinning, sonoelectrochemical as well as chemical vapour deposition technique [3]. Hydrothermal process and sol gel process usually produce a very well-structured anatase TiO_2. The difference of these process are the starting materials that required to manufacture anatase compound. Hydrothermal methods initiated with $TiCI_4$, $TiOCI_2$ and amorphous TiO_2 solutions. On the other hand, sol gel method is based on the usage of titanium alkoxides[21]. One of the advantages that can be crucial for hydrothermal method is it has a very high purity end product and the product obtained from this method mostly in the form of anatase phase [22]. Besides that, solution combustion approach also globally chosen in many fields including materials production. Unfortunately, this method is quite complicated and required excessive quantities of chemicals such as phenol, glycine, acetic acid, nitric acid and hydrogen peroxide [23]. Solution combustion commonly dictate a self-sustained reaction in mixture of minerals nitrates and dissimilar fuels [24]. Basically, solution combustion is amalgam of ignition and solution that highly sensitive to other materials and it is include in the methods that required high temperature in order to produce nanoparticles especially TiO_2.

Apart from solution combustion, sol gel method is basically tailored where one particle able to possess general monodisperses particles in large quantities. This phenomenon will occur when the initial process used fully potential of a condensed, high viscous hydroxide gel as a matrix for the process of growing particles to inhibit their coagulation [25]. Other than that, sol-gel method has been known as one of the best methods for the synthesis of noble metal-dielectric nanocomposites and it had been applied countless in the past few years [26]. Microwave assisted process is a unique process that will involve the radiation in order to complete the synthesis. This process requires some chemical materials as well as at least typical microwave oven that operating at the frequency of $2.450s^{-1}$[27]. Instead of requiring chemical materials and radiation, this process is fast compared to the other processes. This is because it can perform under atmospheric pressures and doesn't require high pressure. Microwave-assisted process also been acknowledged as a high-quality process of synthesis for nanoparticles because the size of nanoparticles that needed can be easily controlled and crystallinity is high. In fact, high quality of nanoparticles [28]. The most complicated process and require high cost to produces nanoparticles is called chemical vapor deposition. This process required certain reactor such as radio frequency plasma enhanced chemical vapor deposition (RF PECVD) reactor. The middle tool of the reactor consists two parallel stainless-steel electrodes then divided by high glass cylinder. This process also needs high power of energy at least 300W and required controlled pressure during the process [29]. Besides that, production of high quality of thin film also required chemical vapor deposition. By applying this method, synthesis of TiO_2 will produce a brookite phase of TiO_2 with the morphology of it structures consisting a pyramidal feature and highly crystalline [30]. Solvothermal process is a very good process in order to require a good reactive and high quality of TiO_2 in the form of anatase which mostly (001) surface [31]. Yet, same as other process, this method would produce a quite big average size of anatase but this event can be prevent by increase the ratio of alcohol/water to decrease the size of TiO_2 nanoparticles [32]. Very recently, one promising method that been known as electrospinning have introduce among researchers. This method basically uses ethanol together with vinyl pyrrolidone and titanium tetraisopropoxide ($C_{12}H_{28}O_4Ti$) with help the of electric field to produce amorphous TiO_2. To change the TiO_2 into anatase phase, calcination is required and the temperature for calcination is about 500^oC [33]. Sonoelectrochemical method is a new method and known as a fast process to fabricate TiO_2. This method required applied voltage in the range of 5-20V to collect a high quality of TiO_2 and doubtless sonoelectrochemical can be used widely in industry that need fast production of TiO_2 [34]. The main reason why chemical techniques chosen in producing the nanoparticles by industries in order to have rapid production are due to simple and vastly applicable. Without doubt chemical methods are remarkable method that can help in order to synthesis the nanoparticles such as TiO2.

TiO_2 synthesis via green approach

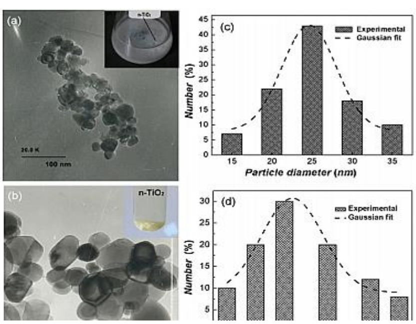
Scientist currently struggle to minimize the waste of chemical materials and implementation of sustainable processes through adoption of 12 fundamental principles in the process extraction of nanoparticles including TiO_2. Those 12 fundamentals are prevention, atom economy, less hazardous chemical syntheses, designing safer chemicals, safer solvents and auxiliaries, use of renewable feedstocks, reduce derivatives, catalysis, design for degradation, real-time analysis for pollution prevention and inherently safer chemistry for accident prevention. [35]. Lately, countless experiments successfully conducted to use plant extract in producing nanoparticle such as silver, gold as well as TiO_2. Table 1 shows several green extractions of TiO_2 from natural extract materials. Even though green synthesis been applied material production, results that obtained for TiO_2 may be different based on various properties especially when working with various green resources.

Table 1. Review of green synthesis of the TiO_2 nanoparticles

Sources	XRD	Type of TiO_2	Grain sizes	FTIR	TEM	AFM	References
Nyctanthes arbor-tristis (Jasmine)	25.3° (101)	Anatase	100.00nm	-	-	Formation off uneven surface morphology due to presence of individual and agglomerated nanoparticles.	**[36]**
Eclipta prostrata (Bhangra)	27.8° (110)	Rutile	49.50nm	Alcohols (3427cm^{-1}) Phenols (2927cm^{-1}) Alkenes (2856cm^{-1}) Primary amines (1639cm^{-1}) Aliphatic amines (1124cm^{-1})			**[37]**
Euphorbia prostrata (Prostrate spurge)	27.6° (110)	Rutile	83.22±1.50nm	Titania (2926cm^{-1}) O-H (3420cm^{-1}) C-H (2926cm^{-1}) NH (1618cm^{-1}) Phenols (1377cm^{-1}) Cyclic Ethers (1071cm^{-1}) Thioethers (649cm^{-1})	Spherical and quite polydisperse in shape.	-	**[38]**
Psidium guajava (Guava)	27.6° / 41.4° (110) / (111)	Anatase/Rutile	32.58nm	0-H (3420cm^{-1}) Alkenes (2922cm^{-1}) Carboxylic acid (1659cm^{-1}) Aromatic (1065cm^{-1})	-	-	**[39]**
Catharanthus Roseus (Madagascar periwinkle)	27.4°	Anatase	100.00nm	Titania (714cm^{-1}) Amines (1076cm^{-1}) N-H (1642cm^{-1}) 0-H (3426cm^{-1})	Clustered and irregular shape, mostly aggregated	Formation of rutile and anatase, surface morphology is uneven due to the presence of some aggregates.	**[40]**

In order to utilize green synthesis methods, it requires some characteristics such that the materials produced are environmental friendly and nontoxic. Usually green synthesis used plant extract. Today, nanoparticles was successfully prepared from the extraction of microorganisms also considered as green synthesis since it involved ecofriendly and none of the of the byproducts is toxic [41]. For example, a fungus called *Fusarium oxysporum* can produce silica and titanium particles [42]. This finding has shown that scientists or researchers can take advantage on the microorganisms ability or capability in producing low cost and safe nanomaterials. Another example is microorganisms belongs to bacterium kingdom and called *Lactobacillus sp*. *Lactobacillus sp* which was discovered by Moro in 1990 with properties such as non-sporeforming and non-flagellated rods found to be able producing TiO_2 along with yeast which is categorized under kingdom of fungus. The outcome from the experiment was quite promising where anatase and rutile phase TiO_2 been produced with different lattice parameters and the average particle sizes in the range of 30nm and 18nm for *Lactobacillus sp* and yeast, respectively [43-44]. The figure 1 below is the TEM results showing the images and particle size distribution for *Lactobacillus sp* and yeast respectively.

Figure 1; TEM images for *Lactobacillus sp* and yeast respectively. Image taken from [45].



Based on this finding, it reveals that microorganism such as fungus and bacterium can be utilize in the production of nanoparticles and can be used in various field such as biomedical and engineering. Latest, enzymes based biosynthesis of TiO_2 nanoparticles is one of the remarkable achievement that researcher explored. One of the enzymes that ever took in the process is called silicate and this enzyme will undergo the process of purification from glassy skeletal element of a marine sponge [45]. Alpha amylase from *Aspergillus oryzae* is other enzymes that scientist used in the production of TiO_2 [46].

Applications of TiO_2

Countless industries had realized that TiO_2 is a type of nanoparticles that may provide innumerable benefits or advantages for their products as well as things that involving cost. Table 2 and figure 2 shows the applications of TiO_2 widely in the world or in big industries.

Table 2. Applications of TiO_2 in industries based on the types of TiO_2

No	Methods	Types of TiO_2	Applications	References
1	- Microwave-Assisted - Sol gel method	Anatase	Photocatalyst, hydrogen evolution and pigment.	[48] [49]
2	- Hydrothermal -Typical synthesis	Rutile	Photodegradation and dye-sensitized solar cells.	[50] [51] [52]
3	-Sol gel method -Thermolysis	Brookite	Lithium ion batteries	[53] [54] [55]

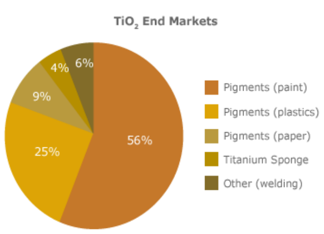


Figure 2: TiO_2 applications worldwide. Image adapted from [56].

CONCLUSION

To conclude, various methods can be applied in producing TiO_2 based on the final aim of the end products and several other factors such as time taken in producing TiO_2, the cost, the environmental impact and the vast production. Chemical process might provide rapid products for industries but at the same time will lead to the production of waste that might be harmful to the ecosystem not only to animals but also to mankind itself. So, green synthesis offers sustainability, ecofriendly and non-toxic TiO_2 which will open up the applications of TiO_2 into various medical and health sciences. Green synthesis also offers minimum consumption of toxic materials.

REFERENCES

[1] Jeng, H. A., & Swanson, J. (2006). Toxicity of metal oxide nanoparticles in mammalian cells. *Journal of Environmental Science and Health Part A*, *41*(12), 2699-2711.

[2] Zhang, L., Gu, F. X., Chan, J. M., Wang, A. Z., Langer, R. S., & Farokhzad, O. C. (2008). Nanoparticles in medicine: therapeutic applications and developments. *Clinical pharmacology & therapeutics*, *83*(5), 761-769.

[3] Azam, A., Ahmed, A. S., Oves, M., Khan, M. S., Habib, S. S., & Memic, A. (2012). Antimicrobial activity of metal oxide nanoparticles against Gram-positive and Gram-negative bacteria: a comparative study. *International journal of nanomedicine*, *7*, 6003.

[4] Mamaeva, V., Sahlgren, C., & Lindén, M. (2013). Mesoporous silica nanoparticles in medicine—Recent advances. *Advanced drug delivery reviews*, *65*(5), 689-702.

[5] Fernández- García, M., & Rodriguez, J. A. (2011). Metal oxide nanoparticles. *Encyclopedia of inorganic and bioinorganic chemistry*.

[6] Tao, S. W., & Irvine, J. T. (2006). A stable, easily sintered proton- conducting oxide electrolyte for moderate- temperature fuel cells and electrolyzers. *Advanced Materials*, *18*(12), 1581-1584.

[7] Keller, A. A., Wang, H., Zhou, D., Lenihan, H. S., Cherr, G., Cardinale, B. J., ... & Ji, Z. (2010). Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environmental science & technology*, *44*(6), 1962-1967.

[8] Chen, X., & Mao, S. S. (2006). Synthesis of titanium dioxide (TiO2) nanomaterials. *Journal of nanoscience and nanotechnology*, *6*(4), 906-925.

[9] Sulaiman, S. N. A., Noh, M. Z., Adnan, N. N., Bidin, N., & Ab Razak, S. N. (2018, May). Effects of photocatalytic activity of metal and non-metal doped Tio2 for Hydrogen production enhancement-A Review. In *Journal of Physics: Conference Series* (Vol. 1027, No. 1, p. 012006). IOP Publishing.

[10] Dunbar, T. D. (2009). *U.S. Patent No. 7,507,618*. Washington, DC: U.S. Patent and Trademark Office.

[11] Selvin, T. P., Kuruvilla, J., & Sabu, T. (2004). Mechanical properties of titanium dioxide-filled polystyrene microcomposites. *Materials Letters*, *58*(3-4), 281-289.

[12] Patidar, V., & Jain, P. (2017). Green Synthesis of TiO2 Nanoparticle Using Moringa Oleifera Leaf Extract. *Int. Res. J. Eng. Technol.*, *4*, 470-473.

[13] Rao, K. G., Ashok, C., Rao, K. V., Chakra, C. S., & Tambur, P. (2015). Green synthesis of TiO 2 nanoparticles using Aloe vera extract. *Int. J. Adv. Res. Phys. Sci*, *2*(1A), 28-34.

[14] Jalill, R. D. A., Nuaman, R. S., & Abd, A. N. (2016). Biological synthesis of Titanium Dioxide nanoparticles by Curcuma longa plant extract and study its biological properties. *World Scientific News*, *49*(2), 204-222.

[15] Siddiqi, K. S., ur Rahman, A., & Husen, A. (2016). Biogenic fabrication of iron/iron oxide nanoparticles and their application. *Nanoscale research letters*, *11*(1), 498.

[16] Hund-Rinke, K., & Simon, M. (2006). Ecotoxic effect of photocatalytic active nanoparticles (TiO2) on algae and daphnids (8 pp). *Environmental Science and Pollution Research*, *13*(4), 225-232.

[17] Khodadadi, B. (2017). TiO2/SiO2 prepared via facile sol-gel method as an ideal support for green synthesis of Ag nanoparticles using Oenothera biennis extract and their excellent catalytic performance in the reduction of 4-nitrophenol. *Nanochemistry Research*, *2*(1), 140-150.

[18] Liang, Y., Sun, S., Deng, T., Ding, H., Chen, W., & Chen, Y. (2018). The preparation of TiO2 film by the sol-gel method and evaluation of its self-cleaning property. *Materials*, *11*(3), 450.

[19] Kormann, C., Bahnemann, D. W., & Hoffmann, M. R. (1988). Preparation and characterization of quantum-size titanium dioxide. *The Journal of Physical Chemistry*, *92*(18), 5196-5201.

[20] Tadros, M. E., Adkins, C. L., Russick, E. M., & Youngman, M. P. (1996). Synthesis of titanium dioxide particles in supercritical CO2. *The Journal of Supercritical Fluids*, *9*(3), 172-176.

[21] Yin, H., Wada, Y., Kitamura, T., Kambe, S., Murasawa, S., Mori, H., ... & Yanagida, S. (2001). Hydrothermal synthesis of nanosized anatase and rutile TiO2 using amorphous phase TiO2. *Journal of Materials Chemistry*, *11*(6), 1694-1703.

[22] Zhang, Y. X., Li, G. H., Jin, Y. X., Zhang, Y., Zhang, J., & Zhang, L. D. (2002). Hydrothermal synthesis and photoluminescence of TiO2 nanowires. *Chemical Physics Letters*, *365*(3-4), 300-304.

[23] Sivalingam, G., Priya, M. H., & Madras, G. (2004). Kinetics of the photodegradation of substituted phenols by solution combustion synthesized TiO2. *Applied Catalysis B: Environmental*, *51*(1), 67-76.

[24] Mukasyan, A. S., & Dinka, P. (2007). Novel approaches to solution-combustion synthesis of nanomaterials. *International Journal of Self-Propagating High-Temperature Synthesis*, *16*(1), 23-35.

[25] Sugimoto, T., Zhou, X., & Muramatsu, A. (2003). Synthesis of uniform anatase TiO2 nanoparticles by gel–sol method: 3. Formation process and size control. *Journal of colloid and interface science*, *259*(1), 43-52.

[26] Epifani, M., Giannini, C., Tapfer, L., & Vasanelli, L. (2000). Sol–gel synthesis and characterization of Ag and Au nanoparticles in SiO2, TiO2, and ZrO2 thin films. *Journal of the American Ceramic Society*, *83*(10), 2385-2393.

[27] Suprabha, T., Roy, H. G., Thomas, J., Kumar, K. P., & Mathew, S. (2009). Microwave-assisted synthesis of titania nanocubes, nanospheres and nanorods for photocatalytic dye degradation. *Nanoscale research letters*, *4*(2), 144.

[28] Ding, K., Miao, Z., Liu, Z., Zhang, Z., Han, B., An, G., ... & Xie, Y. (2007). Facile synthesis of high quality TiO2 nanocrystals in ionic liquid via a microwave-assisted process. *Journal of the American Chemical Society*, *129*(20), 6362-6363.

[29] Sobczyk-Guzenda, A., Owczarek, S., Wojciechowska, A., Batory, D., Fijalkowski, M., & Gazicki-Lipman, M. (2018). Fluorine doped titanium dioxide films manufactured with the help of plasma enhanced chemical vapor deposition technique. *Thin Solid Films*, *650*, 78-87.

[30] Alotaibi, A. M., Sathasivam, S., Williamson, B. A., Kafizas, A., Sotelo-Vazquez, C., Taylor, A., ... & Parkin, I. P. (2018). Chemical vapor deposition of photocatalytically active pure brookite TiO2 thin films. *Chemistry of Materials*, *30*(4), 1353-1361.

[31] Yang, H. G., Liu, G., Qiao, S. Z., Sun, C. H., Jin, Y. G., Smith, S. C., ... & Lu, G. Q. (2009). Solvothermal synthesis and photoreactivity of anatase TiO2 nanosheets with dominant {001} facets. *Journal of the American Chemical Society*, *131*(11), 4078-4083.

[32] Liao, J., Shi, L., Yuan, S., Zhao, Y., & Fang, J. (2009). Solvothermal synthesis of TiO2 nanocrystal colloids from

peroxotitanate complex solution and their photocatalytic activities. *The Journal of Physical Chemistry C*, *113*(43), 18778-18783.
[33] Li, D., & Xia, Y. (2003). Fabrication of titania nanofibers by electrospinning. *Nano letters*, *3*(4), 555-560.
[34] Mohapatra, S. K., Misra, M., Mahajan, V. K., & Raja, K. S. (2007). A novel method for the synthesis of titania nanotubes using sonoelectrochemical method and its application for photoelectrochemical splitting of water. *Journal of Catalysis*, *246*(2), 362-369.
[35] Raveendran, P., Fu, J., & Wallen, S. L. (2003). Completely "green" synthesis and stabilization of metal nanoparticles. *Journal of the American Chemical Society*, *125*(46), 13940-13941.
[36] Sundrarajan, M., & Gowri, S. (2011). Green synthesis of titanium dioxide nanoparticles by Nyctanthes arbor-tristis leaves extract. *Chalcogenide Lett*, *8*(8), 447-451.
[37] Rajakumar, G., Rahuman, A. A., Priyamvada, B., Khanna, V. G., Kumar, D. K., & Sujin, P. J. (2012). Eclipta prostrata leaf aqueous extract mediated synthesis of titanium dioxide nanoparticles. *Materials Letters*, *68*, 115-117.
[38] Zahir, A. A., Chauhan, I. S., Bagavan, A., Kamaraj, C., Elango, G., Shankar, J., ... & Singh, N. (2015). Green synthesis of silver and titanium dioxide nanoparticles using Euphorbia prostrata extract shows shift from apoptosis to G0/G1 arrest followed by necrotic cell death in Leishmania donovani. *Antimicrobial agents and chemotherapy*, *59*(8), 4782-4799.
[39] Santhoshkumar, T., Rahuman, A. A., Jayaseelan, C., Rajakumar, G., Marimuthu, S., Kirthi, A. V., ... & Kim, S. K. (2014). Green synthesis of titanium dioxide nanoparticles using Psidium guajava extract and its antibacterial and antioxidant properties. *Asian Pacific journal of tropical medicine*, *7*(12), 968-976.
[40] Velayutham, K., Rahuman, A. A., Rajakumar, G., Santhoshkumar, T., Marimuthu, S., Jayaseelan, C., ... & Elango, G. (2012). Evaluation of Catharanthus roseus leaf extract-mediated biosynthesis of titanium dioxide nanoparticles against Hippobosca maculata and Bovicola ovis. *Parasitology research*, *111*(6), 2329-2337.
[41] Bar, H., Bhui, D. K., Sahoo, G. P., Sarkar, P., De, S. P., & Misra, A. (2009). Green synthesis of silver nanoparticles using latex of Jatropha curcas. *Colloids and surfaces A: Physicochemical and engineering aspects*, *339*(1-3), 134-139.

[42] Bansal, V., Rautaray, D., Bharde, A., Ahire, K., Sanyal, A., Ahmad, A., & Sastry, M. (2005). Fungus-mediated biosynthesis of silica and titania particles. *Journal of Materials Chemistry*, *15*(26), 2583-2589.

[43] Gomes, A. M., & Malcata, F. X. (1999). Bifidobacterium spp. and Lactobacillus acidophilus: biological, biochemical, technological and therapeutical properties relevant for use as probiotics. *Trends in Food Science & Technology*, *10*(4-5), 139-157.

[44] Jha, A. K., Prasad, K., & Kulkarni, A. R. (2009). Synthesis of TiO2 nanoparticles using microorganisms. *Colloids and Surfaces B: Biointerfaces*, *71*(2), 226-229.

[45] Sumerel, J. L., Yang, W., Kisailus, D., Weaver, J. C., Choi, J. H., & Morse, D. E. (2003). Biocatalytically templated synthesis of titanium dioxide. *Chemistry of materials*, *15*(25), 4804-4809.

[46] Ahmad, R., Mohsin, M., Ahmad, T., & Sardar, M. (2015). Alpha amylase assisted synthesis of TiO2 nanoparticles: structural characterization and application as antibacterial agents. *Journal of hazardous materials*, *283*, 171-177.

[47] Ding, K., Miao, Z., Liu, Z., Zhang, Z., Han, B., An, G., ... & Xie, Y. (2007). Facile synthesis of high quality TiO2 nanocrystals in ionic liquid via a microwave-assisted process. *Journal of the American Chemical Society*, *129*(20), 6362-6363.

[48] Zhang, X. Y., Li, H. P., Cui, X. L., & Lin, Y. (2010). Graphene/TiO 2 nanocomposites: synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting. *Journal of Materials Chemistry*, *20*(14), 2801-2806.

[49] Ge, M., Li, J. W., Liu, L., & Zhou, Z. (2011). Template-free synthesis and photocatalytic application of rutile TiO2 hierarchical nanostructures. *Industrial & Engineering Chemistry Research*, *50*(11), 6681-6687.

[50] Kumar, A., Madaria, A. R., & Zhou, C. (2010). Growth of aligned single-crystalline rutile TiO2 nanowires on arbitrary substrates and their application in dye-sensitized solar cells. *The Journal of Physical Chemistry C*, *114*(17), 7787-7792.

[51] Cao, Y., He, T., Chen, Y., & Cao, Y. (2010). Fabrication of rutile TiO2− Sn/anatase TiO2− N heterostructure and its application in visible-light photocatalysis. *The Journal of Physical Chemistry C*, *114*(8), 3627-3633.

[52] Lee, B. I., Wang, X., Bhave, R., & Hu, M. (2006). Synthesis of brookite TiO2 nanoparticles by ambient condition sol process. *Materials letters*, *60*(9-10), 1179-1183.
[53] Lee, D. H., Park, J. G., Jin Choi, K., Choi, H. J., & Kim, D. W. (2008). Preparation of Brookite- Type TiO2/Carbon Nanocomposite Electrodes for Application to Li Ion Batteries. *European Journal of Inorganic Chemistry*, *2008*(6), 878-882.
[54] Pottier, A., Chanéac, C., Tronc, E., Mazerolles, L., & Jolivet, J. P. (2001). Synthesis of brookite TiO2 nanoparticlesby thermolysis of TiCl4 in strongly acidic aqueous media. *Journal of Materials Chemistry*, *11*(4), 1116-1121.
[55] http://pventerprises.in/wp-content/uploads/2017/09/main-qimg-cf0c5ebc8a3018771897a967defe76eb.png