Advances in Bioresearch
Adv. Biores., Vol 5 (3) September 2014:10-16
©2014 Society of Education, India
Print ISSN 0976-4585; Online ISSN 2277-1573
Journal's URL:http://www.soeagra.com/abr.html
CODEN: ABRDC3
ICV 7.20 [Poland]

Advances
in
Bioresearch

ORIGINAL ARTICLE

Ocimum basilicum L. var. *purpurascens* Benth.-LAMIACEAE Mediated Green Synthesis and Characterization of Titanium Dioxide Nanoparticles

Hasna Abdul Salam, Rajeshwari Sivaraj*
Department of Biotechnology, School of Life Sciences, Karpagam University, Coimbatore-641021, Tamil Nadu, India
*Corresponding Author: rajeshwarishivaraj@gmail.com

ABSTRACT

Titanium dioxide nanoparticles enjoy a prominent status among metal oxide nanoparticles due to their potential technological applications. Though conventional physical and chemical approaches for nanoparticle synthesis are capable of meeting the growing demand, it has also invited degradation and deterioration of the environment, as a result of release of toxic substances, during manufacture and processing of the particles. Thus, synthesis of nanoparticles via the "green" route has gained tremendous interest in the recent times due to eco-friendliness, and the current study is the first report for the utilization of Ocimum basilicum L. var. purpurascens Benth.-LAMIACEAE leaf extract, as a novel source, for the synthesis and characterization of titanium dioxide nanoparticles (TiO_2*-NPs). Hexagonal shaped *TiO_2*-NPs with size of 50 nm have been synthesized and characterized using XRD, FTIR, SEM, TEM and EDX.*

Keywords: *TiO_2-NPs, green synthesis, characterization, analysis, nanoparticles*

Received 22/05/2014 Accepted 02/07/2014

How to cite this article:
Hasna A. S, Rajeshwari S. *Ocimum basilicum* L. var. *purpurascens* Benth.-LAMIACEAE Mediated Green Synthesis and Characterization of Titanium Dioxide Nanoparticles Adv. Biores., Vol 5 [3] September 2014: 10-16**.** DOI: 10.15515/abr.0976-4585.5.3.1016

INTRODUCTION

Nano-sized particles have been existing on earth since millions of years and are being utilized since thousands of years. They may or may not exhibit size-related characteristics that differ significantly in comparison to fine or bulk particles [1].They have gained whole lot of attention in recent times due to their increasing ability to be synthesized and manipulated, along with their utility in wide areas like electronic, biomedical, pharmaceutical, cosmetics, energy, environmental, catalytic and material applications [2]. An estimate for the production of engineered nanomaterials has been 2000 tons in 2004, which has been predicted to increase to 58,000 tons by 2020 [3].

Metal oxide nanoparticles is a special field of materials chemistry that has attracted considerable interest due to the potential technological applications of these compounds in a wide range of fields such as medicine, information technology, catalysis, energy storage, and sensing [4].possess high surface area and high fraction of atoms that is contributing to its various fascinating properties like antimicrobial, magnetic, electronic and catalytic activity [5-8]. Among the metal oxide nanoparticles, titanium dioxide nanoparticles possess a prominent status and is widely used in air and water purification and in DSSC (dye-sensitized solar cell) due to their strength of oxidation, high photo stability and non-toxicity [9-16].Titanium dioxide nanoparticles are being manufactured worldwide in huge amounts for a variety of applications like sunscreen and UV blocking pigments, photo catalyst and electronic data storage medium. TiO_2-NPs possess unique physicochemical properties in comparison to their fine particle analogs which may alter their bioactivity. In nanomedicine, intravenous injection is sufficient to deliver TiO_2-NPs carriers directly into the human body [17].

Conventionally, nanoparticles have been mostly synthesized by physical and chemical methods, which are potentially hazardous, requiring high energy along with difficulty in separation process [18-22]. Thus, development of green synthesis methods that employs plants proves an eco-friendly technique for the production of potential nanoparticles. Plant photo chemicals like terpenoids, flavones, ketones, aldehydes amides etc. that possess antioxidant or reducing properties contribute to the formation of metal oxide nanoparticles [23]. *Ocimum basilicum* plant is well known for its culinary, religious and medicinal purposes and with regard to nanoparticles, the particles synthesized so far from the species include silver, gold and platinum [24-29].

Literature provides only one instance of green synthesis of TiO_2-NPs, which has employed *Nyctanthes arbor-tristis* L. leaf extract [23]. Thus, the present study is the first report on the use of a novel source, *Ocimum basilicum* L. var. *purpurascens* Benth.-LAMIACEAE leaf extract, for the synthesis and characterization of TiO_2-NPs, along with titanium (IV) isopropoxide as precursor.

MATERIALS AND METHODS

Preparation of crude aqueous leaf extract

The plant collected from Pirayiri, Palakkad District, Kerala, was authenticated at Botanical Survey of India, Coimbatore, India. Fresh leaves were washed thrice with distilled water to remove dust and chopped. The chopped leaves and water were taken in the ratio 1: 10, subjected to continuous stirring for 30 mins at 70^{0}C, cooled, filtered and stored at 4^{0}C for further use [29].

Synthesis of TiO_2-NPs

Titanium (IV) isopropoxide was purchased from Sigma and precursor prepared with ethanol in the ratio 1: 10 by constant stirring for 1 h. The crude aqueous leaf extract and the precursor were taken in the ratio 1: 9 and subjected to stirring for 4 h at 50^{0}C. TiO_2-NPs were obtained by centrifugation at 10000 rpm for 15 mins, washed with ethanol and centrifuged again at 5000 rpm for 10 mins. The separated particles were dried and ground followed by calcination at 500^{0}C for 3 h [23].

Characterization of TiO_2-NPs

The TiO_2-NPs were characterized by XRD, FTIR, SEM, TEM and EDX.

The formation of TiO_2-NPs was analyzed by an X' Pert Pro X-ray diffaractometer (PAN analytical BV, The Netherlands) operated at a voltage of 40 kV and a current of 30 mA with Ni filtered Cu $K\alpha$ radiation in a θ-2θ configuration and the crystallite size was obtained by Scherrer equation [30, 31]. The FTIR spectrum was obtained on KBr pellets using IRA Affinity-1 SHIMADZU. SEM analysis was carried out using Hitachi S 4500 SEM machine in which thin films of the sample were prepared on a carbon coated copper grid which were then allowed to dry under a mercury lamp for 5 mins. TEM analysis was done using JEOL 2000Fx-II HRTEM, a 200 kV analytical HRTEM, to obtain the exact size of the particles. EDX analysis was done using JEOL JEM 2100 high resolution TEM to confirm the presence of titanium and oxygen in the formed particles [6].

RESULTS AND DISCUSSION

Synthesis of TiO_2-NPs

The plant source used in this study was identified at Botanical Survey of India, Coimbatore, India, as *Ocimum basilicum* L. var. *purpurascens* Benth.-LAMIACEAE (BSI/SRC/5/23/2012-13/Tech.954). Crude aqueous leaf extract upon reaction with precursor after subsequent steps produced characteristic white powder which showed resemblance to those obtained using *Nyctanthes arbor-tristis* L. leaf extract [23]. These exhibited similarity to the TiO_2-NPs produced by conventional methods using different precursors. Colloidal solutions of TiO_2 with different particle sizes and stability have been synthesized using acetylacetone-modified $TiO(OPr^i)_4$ and organic solvents that differed in polarity and molar volume [32]. Reports are available for deposits of nanocrystaline TiO_2 from ethanolic solution of titanium isopropoxide and hydrogen peroxide by refluxing at 50^{0}C for 48 h [33]. Titanium tetrachloride ($TiCl_4$) is also another widely used precursor for the synthesis of TiO_2-NPs in which the nanoparticles can be synthesized by thermal hydrolysis of $TiCl_4$ in a propanol-water mixture, and also by hydrolysis of $TiCl_4$ in a strongly acidic aqueous solution in the absence as well as presence of PEG-1000 [34, 35]. Titanium dioxide has also been reported to be synthesized using miscellaneous titanium containing precursors like ammonium dihydroxodilactatotitanate (thermohydrolysis), titanium hydride powder (plasma synthesis), and organic precursors (spray pyrolysis) [36, 37, 38]. The formation of nanoparticles can be attributed to the presence of linalool, a terpene alcohol found in flowers and plants of families Lamiaciae, Lauraceae, birch trees and other plants, from tropical to boreal climate zones, and also in some fungi, which has been reported to reduce metal ions to nanoparticles as in the case of gold nanoparticles from cinnamon phytochemicals [39, 40, 41]. TiO_2-NPs with different phase compositions can be synthesized by varying the temperature, synthesis time and pH of the medium [42].

Characterization of TiO_2-NPs

The characteristic white colored TiO_2-NPs upon characterization by XRD, FTIR, SEM, TEM and EDX, exhibited features that emphasized the elemental identity, size and shape of the synthesized particles.

The XRD pattern (Fig. 1) projected distinct peaks at 2θ=27.7, 37.9, 48.2, 55.1, 63.1, 68.7 and 74.7 that showed close proximity to those obtained by *Nyctanthes arbor-tristis* L. leaf extract mediated synthesis and gives probable indication of the nanoparticles to possess cubic face centered lattice [23]. The crystallite structure of the synthesized particles was found to be 6.97 nm as per Scherrer equation. The peaks further seem to indicate that the TiO_2-NPs may be of monolithic anatase phase that may possess length dependent toxicity and bioactivity [43]. The obtained peaks also showed similarity to those obtained for synthesis of TiO_2-NPs by hydrothermal method where peaks at 2θ=25.28, 36.95, 38.58, 48.05, 53.89 and 62.69 have been attributed to anatase tetragonal crystal structure and those at 2θ=30.68 have been related to brookite orthorhombic crystal structure [44]. The presence of sharp peaks confirmed the crystallinity and purity of the particles.

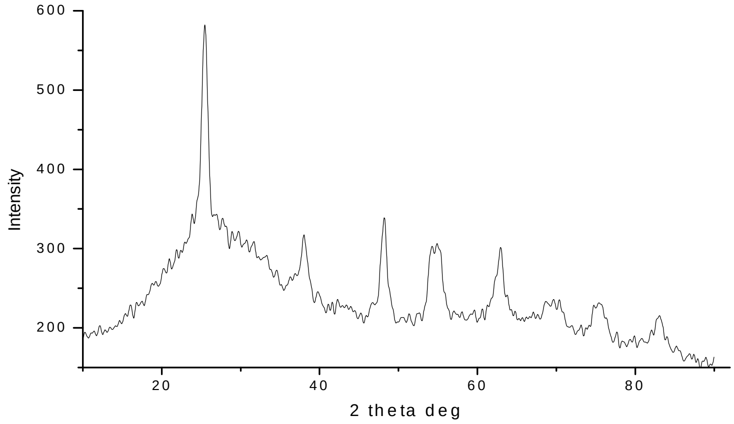

Fig. 1: XRD pattern of the green synthesized titanium dioxide nanoparticles

The FTIR spectrum (Fig. 2) showed characteristic peaks at 3425.58 cm^{-1}, 1685.79 cm^{-1} and 1633.71 cm^{-1} that respectively corresponds to N-H stretching vibration of secondary amine, C=O stretching vibration of hydrogen bonded chelate esters, and C=C stretching medium intensity vibration of alkenes. These results showed correlation with the spectral pattern of pure titanium dioxide which had been compared upon modification with silica [45]. IR spectroscopic studies of titanium dioxide produced by pyrolysis of homogenous TiO_2 gels prepared by hydrolysis of titanium isopropoxide pretreated with formic and oxalic acids have shown the products to contain Ti-O-Ti fragments, formate groups and oxalate groups coordinated with titanium and non-hydrolyzed titanium isopropoxide [46, 47].

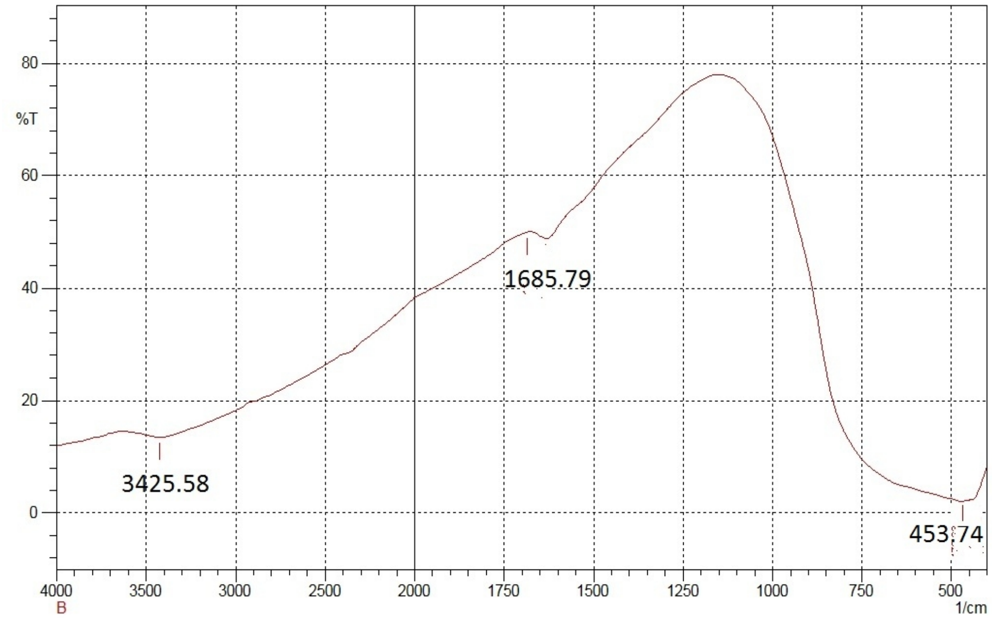

Fig. 2: FTIR spectrum of the green synthesized titanium dioxide nanoparticles

The SEM image (Fig. 3) of the particles showed that the nanoparticles obtained had an average size of 50 nm, with hexagonal morphology. Titanium dioxide nanospheres of approximate diameter 60-200 nm have been previously reported for length-dependent toxicity and bioactivity [43]. The TiO_2-NPs, of sizes 9.3 nm, 5.9 nm and 1.5 nm, produced by low-pressure pyrolysis (LPSP) method using organic precursors, showed that nanoparticles produced by this method were primarily crystals and that the crystallization improved with increase in reaction temperature. Besides, in such instances, the particles may become irregular and fragmented, with each fragment holding nanoparticles inside them [37]. The SEM data points to a considerable increase in homogeneity and uniformity of TiO_2 films and their high specific surface area in the presence of dispersants like methylcellulose [42].

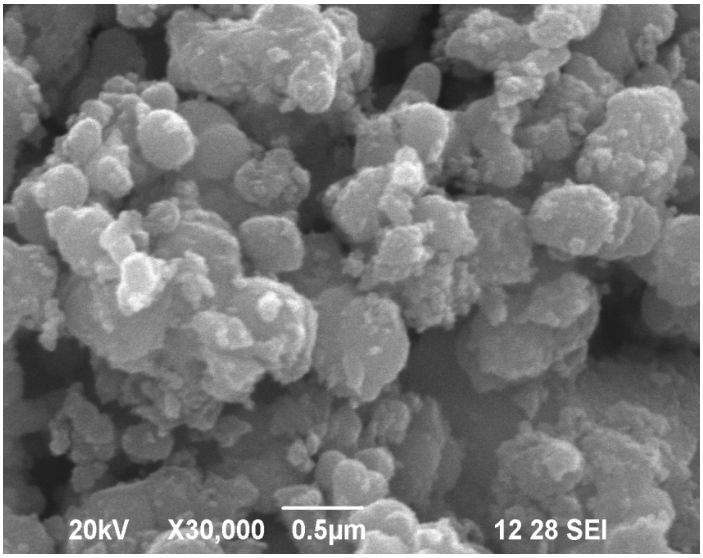

Fig. 3: SEM image of the green synthesized titanium dioxide nanoparticles

The TEM image (Fig. 4) further confirmed the hexagonal morphology of the TiO_2-NPs with the size of 50 nm. Titanium dioxide crystalline nanotubes of 8-10 nm, possessing multiple shells have been reported [48]. TEM analysis of spherical anatase TiO_2-NPs, produced using ethanolic solution of titanium isopropoxide and hydrogen peroxide, showed that though the morphology was retained with increase in temperature, size increased from 5 nm to 10 nm [33]. TEM analysis further explains that the growth and agglomeration of titanium dioxide nanoparticles can be affected by the presence of materials like silica and also that the morphology varies with increase in temperature [44, 45]. Anatase TiO_2-NPs produced by hydrolysis of $TiO(OPr^i)_4$ showed that strong acidic conditions were responsible for their spherical morphology [49].

EDX pattern (Fig. 5) showed high intensity peaks that confirmed the elemental presence of titanium and oxygen, besides showing the absence of any other elemental impurities and the weight percentage of titanium and oxygen were found to be 49.70 and 50.30, respectively. Similar pattern has been reported for the synthesis of TiO_2-NPs generated by hydrolysis of titanium tetra isopropoxide in a mixture of ethanol and water [50]. The analysis of TiO_2-NPs from human lung fibroblasts that were exposed to the particles for study of cyto- and genotoxic potential showed that the NPs had composition as 56% titanium and 41% oxygen, along with 3% carbon [51]. Single nanoparticles plus spherical aggregates of 50 nm, isolated from waste water treatment plants were presumably found to contain titanium and oxygen [52]. TiO_2-NPs with 54% titanium and 46% oxygen have also been reported [53]. Among personal care products, toothpastes and sunscreens have been reported to contain 1% to 10% titanium by weight [54].As EDX analysis is a technique for detection of elements under study as well as impurities, if any, it further suggests that the existence of lighter elements such as hydrogen ought to be ignored, as in the case of nanotubes, and must referred to as TiO_x nanotube [48].

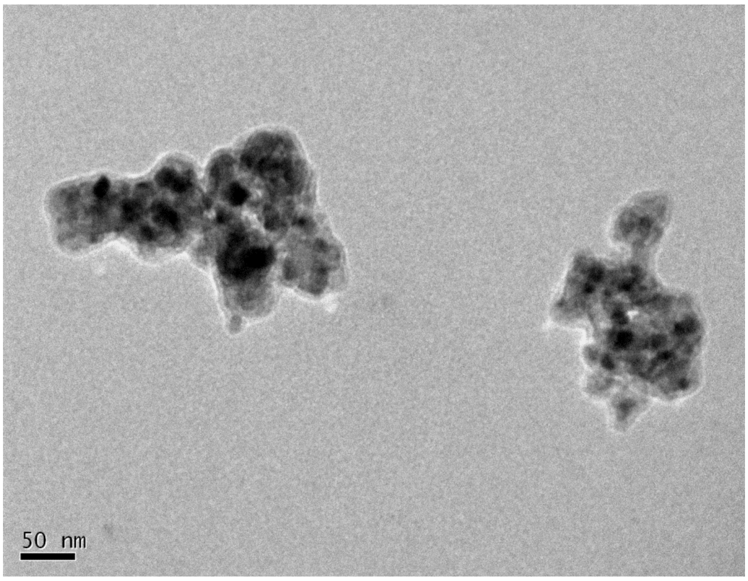

Fig. 4: TEM image of the green synthesized titanium dioxide nanoparticles

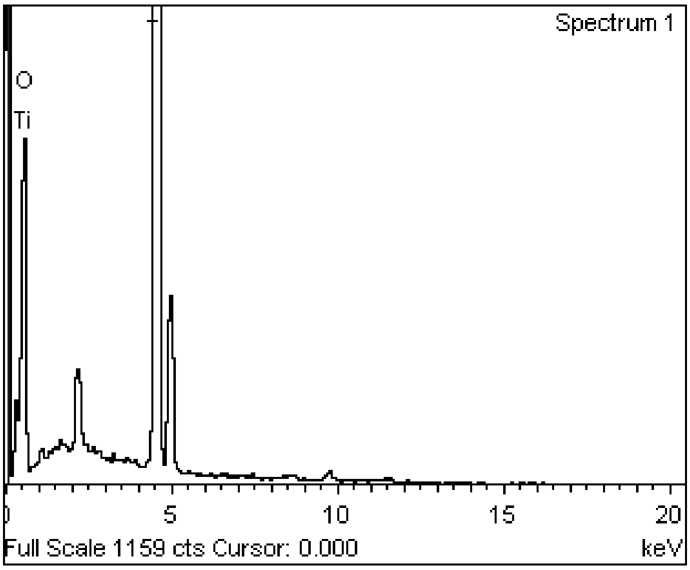

Fig. 5: EDX pattern of the green synthesized titanium dioxide nanoparticles

CONCLUSION

A common plant (*Ocimum basilicum* L. var. *purpurascens* Benth.-LAMIACEAE) has been utilized for the rapid synthesis of titanium dioxide nanoparticles. Various characterization techniques confirmed the elemental analysis of the hexagonal shaped nanoparticles of size 50 nm. The present report emphasizes that leaf extracts can be cost-effective precursors for large-scale preparation of TiO_2-NPs, besides being environment-friendly and economically viable.

ACKNOWLEDGEMENT

The authors whole-heartedly thank the Management of Karpagam University, Coimbatore, India, and Dr. Avadhani, IISC, Bangalore, India, for provision of necessary amenities for the work.

REFERENCES

1. Buzea, C., Pacheco, I.I. & Robbie, K. (2007). Nanomaterials and nanoparticles: Sources and toxicity. Biointerphases, 2 (4): MR17-MR71.
2. Bernd, N. & Thomas, D.B. (2007). Occurrence, behavior and effects of nanoparticles in the environment. Environ. Pollut., 150 (1): 5-22.
3. Maynard, A.D. (2006). Nanotechnology: A Research Strategy for Addressing Risk. Woodrow Wilson International Center for Scholars, Washington, DC.

4. Corr, S.A. (2013). Metal oxide nanoparticles (Eds. O'Brien, P. and P. Paul), Nanoscience, The Royal Society of Chemistry, p. 180-207.
5. Zhao, G. & Stevens Jr, S.E. (1998). Multiple parameters for the comprehensive evaluation of the susceptibility of *Escherichia coli* to the silver ion. Biometals, 11 (1): 27-32.
6. Crabtree, J.H., Burchette, R.J., Siddiqi, R.A., Huen, I.T., Hadnott, L.L. and Fishman, A. (2003). The efficacy of silver-ion implanted catheters in reducing peritoneal dialysis-related infections. Perit. Dial. Int., 23 (4): 368-374.
7. Krolikowska, A., Kudelski, A., Michota, A. & Bukowska, J. (2003). SERS studies on the structure of thioglycolic acid monolayers on silver and gold. Surf. Sci., 532: 227-232.
8. Catauro, M., Raucci, M.G., De Gaaetano, F. & Marotta, A. (2004). Antibacterial and bioactive silver-containing $Na_2O.CaO.2SiO_2$ glass prepared by sol-gel method. J. Mater. Sci. Mater. Med., 15 (7): 831-837.
9. Barbe, C.J., Arendse, F., Comte, P., Jirousek, M., Lenzmann, F., Shklover, V. & Gratzel, M. (1997). Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications. J. Am. Ceram. Soc., 80 (12): 3157-3171.
10. Ito, S., Inoue, S., Kawada, H., Hara, M., Iwaski, M. & Tada, H. (1999). Low-Temperature Synthesis of Nanometer-Sized Crystalline TiO_2 Particles and Their Photoinduced Decomposition of Formic Acid. J. Colloid Interface Sci., 216 (1): 59-64.
11. Monticone, S., Tufeu, R., Kanaev, A.V., Scolan, E. & Sanchez, C. (2000). Quantum size effect in TiO_2 nanoparticles: does it exist? Appl. Surf. Sci., 162-163: 565-570.
12. Al-Salim, N.I., Bagshaw, S.A., Bittar, A., Kemmtt, T., Mcquillan, A.J., Mills, A.M. & Ryan, M.J. (2000). Characterization and activity of sol-gel-prepared TiO_2 photocatalysts modified with Ca, Sr or Ba ion additives. J. Mater. Chem., 10: 2358-2363.
13. Boujday, S., Wunsch, F., Portes, P., Bocquet, J.-F. & Justin, C.C. (2004). Photocatalytic and electronic properties of TiO_2 powders elaborated by sol-gel route and supercritical drying. Solar Energy Mater. Solar Cells, 83 (4): 421-433.
14. Carp, O., Huisman, C.L. & Reller, A. (2004). Photoinduced reactivity of titanium dioxide. Prog. Solid State Chem., 32 (1-2): 33-177.
15. Ruiz, A.M., Sakai, G., Cornet, A., Shimanoe, K., Morante, J.R. & Yamazoe, N. (2004). Microstructure control of thermally stable TiO_2 obtained by hydrothermal process for gas sensors. Sens. Actuators B: Chem., 103 (1-2): 312-317.
16. Li, Y., White, T.J. & Lim, S.H. (2004). Low-temperature synthesis and microstructural control of titania nano-particles. J. Sol. State Chem., 177 (4-5): 1372-1381.
17. Shi, H., Magaye, R., Castranova, V. & Zhao, J. (2013). Titanium dioxide nanoparticles: a review of current toxicological data. Part. Fibre Toxicol., 10 (4): 1-33.
18. Taleb, A., Petit, C. & Pileni, M.P. (1997). Syntheses of highly monodisperse silver nanoparticles from AOT reverse micelles: a way to 2D and 3D self-organization. Chem. Mater., 9 (4): 950-959.
19. Rodriguez-Sanchez, L., Blanco, M.C. & Lopez-Quintela, M.A. (2000). Electrochemical synthesis of silver nanoparticles. J. Phys. Chem. B, 104 (41): 9683-9688.
20. Krishna, B. & Dan, V.G. (2009). Silver nanoparticles for printable electronics and biological applications. J. Mater. Res., 24 (9): 2828-2836.
21. Tripathi, R.M., Saxena, A., Gupta, N., Kapoor, H. & Singh, R.P. (2010). High antibacterial activity of silver nanoballs against *E. coli* MTCC 1302, *S. typhimurium* MTCC 1254, *B. subtilis* MTCC 1133 and *P. aeruginosa* MTCC 2295. Dig. J. Nanomater. Biostruc., 5 (2): 323-330.
22. Saxena, A., Tripathi, R.M. & Singh, R.P. (2010). Biological synthesis of silver nanoparticles using onion (*Allium cepa*) extract and their antibacterial activity. Dig. J. Nanomater. Biostruc., 5 (2): 427-432.
23. Sundrarajan, M. & Gowri, S. (2011). Green synthesis of titanium dioxide nanoparticles by *Nyctanthes arbor-tristis* leaves extract. Chalcogenide Lett., 8 (8): 447-451.
24. Naheed, A., Md, K.A., Singh, V.N., Salman, F.S. & Seema, S. (2009). Ocimum Mediated Biosynthesis of Silver Nanoparticles. In: ICMENS'09 Proceedings of the 2009 Fifth International Conference on MEMS NANO, and Smart Systems, 80-84.
25. Garima, S., Riju, B., Kunal, K., Ashish, R.S. & Rajendra, P.S. (2011). Biological synthesis of silver nanoparticles using *Ocimum sanctum* (Tulsi) leaf extract and screening its antimicrobial activity. J. Nanopart. Res., 13 (7): 2981-2988.
26. Kiruba Daniel, S.C.G., Kumar, R., Sathish, V., Sivakumar, M., Sunitha, S. & Anitha, S.T. (2011). Green Synthesis (*Ocimum tenuiflorum*) of Silver Nnoparticles and Toxicity Studies in Zebra Fish (*Danio rerio*) Model. Int. J. NanoSci. Nanotechnol., 2 (2): 103-117.
27. Mallikarjuna, K., Narasimha, G., Dilip, G.R., Praveen, B., Shreedhar, B., Sree Lakshmi, C., Reddy, B.V.S. & Deva Prasad Raju, B. (2011). Green synthesis of silver nanoparticles using *Ocimum* leaf extract and their characterization. Dig. J. Nanomater. Biostruc., 6 (1): 181-186.
28. Soundarrajan, C., Sankari, A., Dhandapani, P., Maruthamuthu, S., Ravichandran, S., Sozhan, G. & Palaniswamy, N. (2012). Rapid biological synthesis of platinum nanoparticles using *Ocimum sanctum* for water electrolysis applications. Bioprocess Biosyst. Eng., 35 (5): 827-833.
29. Singhal, G., Riju, B., Ashish, R.S. & Rajendra, P.S. (2012). Ecofriendly Biosynthesis of Gold Nanoparticles Using Medicinally Important *Ocimum basilicum* Leaf Extract. Adv. Sci. Engg. Med., 4: 62-66.
30. Jayakumar, S., Thyagarajan, T.K., Ananthapadmanabhan, P.V., Sreekumar, K.P., Perumal, K., Mishra, S.C., Su, L.T. & Tok, A.I.Y. (2010). Synthesis of nano-ZrO_2 by Reactive Plasma Processing. In: Proceedings of 55th DAE Solid State Physics Symposium, Manipal, 257-258.

31. Jegadeeswaran, P., Rajeshwari, S. & Venckatesh, R. (2012). Green synthesis of silver nanoparticles from extract of *Padina tetrastomatica* leaf. Dig. J. Nanomter. Biostruc., 7 (3): 991-998.
32. Chen, H.J., Wang, L. & Chiu, W.Y. (2007). Chelation and solvent effect on the preparation of titania colloids. Mater. Chem. Phys., 101 (1): 12-19.
33. Kim, D.H., Ryu, H.W., Moon, J.H. & Kim, J. (2006). Effect of ultrasonic treatment and temperature on nanocrystalline TiO_2.J. Power Sources, 163 (1): 196-200.
34. Fang, C.S. & Chen, Y.W. (2003). Preparation of titania particles by thermal hydrolysis of $TiCl_4$ in n-propanol solution. Mater. Chem. Phys., 78 (3): 739-745.
35. Chu, R., Yan, J., Lian, S., Wang, Y., Yan, F. & Chen, D. (2004). Shape-controlled synthesis of nanocrystalline titania at low temperature. Solid State Commun., 130 (12): 789-792.
36. Mockel, H., Giersig, M. & Willig, F. (1999). Formation of uniform size anatase nanocrystals from bis (ammonium lactato) titanium dihydroxide by thermohydrolysis. J. Mater. Chem., 9 (12): 3051-3056.
37. Wang, W., Lenggoro, I.L., Terashi, Y., Kim, T.O. & Okuyama, K. (2005). One-step synthesis of titanium oxide nanoparticles by spray pyrolysis of organic precursors. Mater. Sci. Engg. B, 123 (3): 194-202.
38. Padmanabhan, P.V.A., Sreekumar, K.P., Thyagarajan, T.K., Satpute, R.U., Bhanumurthy, K., Sengupta, P., Dey, G.K. & Warrier, K.G.K. (2006). Nano-crystalline titanium dioxide formed by reactive plasma synthesis. Vacuum, 80 (11-12): 1252-1255.
39. Maria, G.V.S., Maria, I.L.M., Afranio, A.C., Jose, W.A., Francisco, J.A.M. & Monica, C.M. (1998). Essential Oils from Leaves and Inflorescence of *Ocimum basilicum* var. *purpurascens* Benth. from Northeastern Brazil. J. Essential Oil Res., 10 (5): 558-560.
40. Maria, G.V.S., Francisco, J.A.M., Maria, I.L.M. & Afranio, A.C. (2003). Essential oils of *Ocimum basilicum* L., *O. basilicum.* var. *minimum* L. and *Ocimum basilicum* var. *purpurascens* Benth. grown in north-eastern Brazil. Flavour Fragrance J., 18 (1): 13-14.
41. Chanda, N., Shukla, R., Zambre, A., Mekapothula, S., Kulkarni, R.R., Katti, K., Bhattacharya, K., Fent, G.M., Casteel, S.W., Boote, E.J., Viator, J.A., Upendran, A., Kannan, R. & Katti, K.V. (2011). An Effective Strategy for the Synthesis of Biocompatible Gold Nanoparticles Using Cinnamon Phytochemicals for Phantom CT Imaging and Photoacoustic Detection of Cancerous Cells. Pharm. Res., 28 (2): 279-291.
42. Ismagilov, Z.R., Tsykoza, L.T., Shikina, N.V., Zarytova, V.F., Zinoviev, V.V. & Zagrebelnyi, S.N. (2009). Synthesis and stabilization of nano-sized titanium dioxide. Russ. Chem. Rev., 78 (9) 1-13.
43. Raymond, F.H.J., Nianqiang, W., Dale, P., Mary, B., Michael, W. & Andrij, H. (2009). Particle length-dependent titanium dioxide nanomaterials toxicity and bioactivity. Part. Fibre Toxicol., 6 (12): 1-11.
44. Anwar, N.S., Kassim, A., Lim, H.N., Zakarya, S.A. & Huang, N.M. (2010). Synthesis of Titanium Dioxide Nanoparticles via Sucrose Ester Micelle-Mediated Hydrothermal Processing Route. Sains Malaysiana, 39 (2): 261-265.
45. Zhijie, L., Bo, H., Yao, X., Dong, W. & Yuhan, S. (2005). Hydrothermal synthesis, characterization, and photocatalytic performance of silica-modified titanium dioxide nanoparticles. J. Colloid Interface Sci., 288: 149–154.
46. Campostrini, R., Ischia, M. & Palmisano, L. (2003). Pyrolysis study of Sol-gel derived TiO_2 powders: Part I. TiO_2-anatase prepared by reacting titanium (IV) isopropoxide with formic acid. J. Therm. Anal. Calorim., 71 (3): 997-1010.
47. Campostrini, R., Ischia, M. & Palmisano, L. (2003). Pyrolysis study of Sol-gel derived TiO_2 powders: Part I. TiO_2-anatase prepared by reacting titanium (IV) isopropoxide with oxalic acid. J. Therm. Anal. Calorim., 71 (3): 1011-1022.
48. Du, G.H., Chen, Q., Che, R.C., Yuan, Z.Y. & Peng, L.-M. (2001). Preparation and structure analysis of titanium oxide nanotubes. Appl. Phys. Lett., 79 (22): 3702-3704.
49. Mahshid, S., Askari, M. & Ghamsari, M.S. (2007). Synthesis of TiO_2 nanoparticles by hydrolysis and peptization of titanium isopropoxide solution. J. Mater. Process Technol., 189 (1-3): 296-300.
50. Muneer, M.B., Abdul Amir, H.K., Abu, B.M., Mohd, S.K. & Kamaruzzaman, S. (2012). Synthesis and Catalytic Activity of TiO_2 Nanoparticles for Photochemical Oxidation of Concentrated Chlorophenols under Direct Solar Radiation. Int. J. Electrochem. Sci., 7 (6): 4871-4888.
51. Kunal, B., Maria, D., Jens, B., Roels, P.F.S., Eik, H. & Elke, D. (2009). Titanium dioxide nanoparticles induce oxidative stress and DNA-adduct formation but not DNA-breakage in human lung cells. Par. Fibre Toxicol., 6 (6): 1-11.
52. Kiser, M.A., Westerhoff, P., Benn, T., Wang, Y., Perez-Rivera, J. & Hristovski, K. (2009). Titanium Nanomaterial Removal and Release from Wastewater Treatment. Environ. Sci. Technol., 43 (17): 6757-6763.
53. Yongli, S., Feng, W., Jibao, H., Santosh, Y. & He, W. (2010). Titanium dioxide nanoparticles cause apoptosis in BEAS-2B cells through the caspase 8/t-Bid-independent mitochondrial pathway. Toxicol. Lett., 196 (1): 21-27.
54. Alex, W., Paul, W., Lars, F., Kiril, H. & Natalie von, G. (2012). Titanium Dioxide Nanoparticles in Food and Personal Care Products. Environ. Sci. Technol. 46 (4): 2242-2250.