Journal of Environmental and Applied Bioresearch
Published online 05 April, 2016 (http://www.scienceresearchlibrary.com)

Vol. 04, No. 01, pp. 35-38
ISSN 2719 8745

Research Article **Open Access**

SYNTHESIS AND CHARACTERISATION OF TITANIUM DIOXIDE NANOPARTICLES VIA ECOFRIENDLY METHOD USING ARTEMISIA PALLENS PLANT EXTRACT

M.Mythreyi, C.Sukumar, S.Pattabi R.Gomathi. S. Senthilkumar

Department of Basic Sciences, PSG College of Technology, Coimbatore- 641004, India.
Department of Environmental Science PSG College of arts and science, Coimbatore-641014, India

Received: 08 January, 2016 / Accepted : 20 February, 2016

Abstract

In the present study, Titanium dioxide nanoparticles were synthesized by sol-gel method with a cleaner technology substituting a bio-extract obtained from the plant Artemisia Pallens containing mainly poly alcohols as a solvent. The structural, optical, particle size and the morphological properties of TiO_2 nanoparticles were analysed using the X-Ray diffraction data, Scanning Electron microscope (SEM) and Transmission electron microseope (TEM). The TiO_2 nanoparticles synthesized using this method is crystalline and spherical in shape. The optical band gap was investigated and found to be 3.4 eV. The Fourier transformer infra red spectroscopy (FT-IR) shows a single band attributed to TiO_2 vibrational band. The successful formation of TiO_2 using the simple aqueous solution based organic solvent free approach is further used as nano carriers for drug delivery system.

Keywords : Nanoparticles, Bio-extract, Synthesized, Drug delivery

*Corresponding authors: mythupriya@gmail.com

Introduction

Nanotechnology is the art of manipulation of materials on atomic and molecular scales to build nanoscale structures and devices. A lot of work is being carried out in the synthesis, design, characterization and application of materials, structures, devices and systems by controlling shape and size at nanometer scale [1]. The most important features their size-dependent properties. Among oxide nanomaterials TiO_2 has been considered as one of the most promising material due to its easy availability, catalytic performance, long term stability and nano toxicity [2]. Titanium dioxide do exist in three crystalline phases anates, brookite and rutile of which anatase is commercial phase of TiO_2 [3]. Titanium dioxide nanoparticles (TiO_2 NPs) are widely used in various manufactured products, including sunscreen, pharmaceuticals, toothpaste, white pigment, cosmetics and in environmental decontamination of air, soil and water[4]. The predominant commercial phase of titaniumdioxide is anatase which has high photocatalytic applications. Anatase is stabilized by heat treatments at 400^o-600^oc [5].

Sol-gel method is widely used for preparation of titaniumdioxide nanocrystals with different shapes and polymorphs [6]. To avoid the use of toxic organic solvents and severe reaction condition such as temperature, pressure and long refluxing time for the prepration of nanomaterials, all new possibilities of preparing nanomaterials in aqueous medium is carried on [7].

Recent days the attention is more on the biosynthetic method using plant extracts than microbial, chemical and physical methods. Authors reported the TiO_2 nano particle from annona peel extract [8], psidium gujava [9], catharanthus roseus leaf extract [10] and bacillus subtulis [11]. The use of plant extracts compensates easy viability of metabolites [12]. Bioextracts do not need any capping or reducing agents as the bio extracts itself acts as the reducing and capping agent and its alcohol free [13]. Solution based approach is more versatile. The morphology of nanoparticles can be controlled by optimizing reactions condition such as pH, concentration of precursors, temperature and reaction time. To prevent nanoparticles become agglomers is most challenging issue because of high surface energy. The use of plant extracts has better compensation such easy available, safe handling and broad availability of metabolites. The important pythochemical responsible for nanoparticle synthesis are terpenoids, flavonoids, carbohydrates, alkaloids and proteins. The attempt was made to extract the natural organics in the artemissia pallens using water, a distillation free from alcohol. The bioextract obtained was used a solvent for the synthesis of TiO_2. The as synthesized TiO_2 was subjected to various characterizations and the results were similar to those synthesized by using alcohol as solvent. The objective of the study is to synthesis of TiO_2 in eco-friendly method by completely replacing alcohol by solvent extracted from artemissia pallens and study the characteristics of as synthesized TiO_2.

2. MATERIALS AND METHODS

2.1 Preparation of Artemisia pallens extract:

The artemissia pallens plant was collected fresh and was washed in tap water to remove the soil and dirt. The plant leaf along with stem was cut into small pieces and was grinded with distilled water. The grinded puree was subjected to distillation with 150ml of double distilled water with proper water circulation. The condensed liquids were collected in an air-tight container. To understand the chemical composition, the bio extract was subjected to GC-MS Analysis (GCMS-QP2010 PLUS Shimadzu)

and FT-IR spectrum analysis. This bio-extract was used as a solvent for the synthesis of nano TiO_2.

2.2 Synthesis of nano TiO_2 using bio-extract:

The precursor used for the synthesis of TiO_2 nano particles was titanium isopropoxide. The hydrolysis solution is the bio-extract from artemissia pallens. 20ml of the bio-extract is added to the 500ml of round bottom flask; 7gms of titanium isopropoxide is weighed and added to the round bottom flask containing bio extract. The mixture is allowed is stirred for about two hours by a magnetic stirrer. Another 25ml of the bio-extract is added to the burette and is added drop by drop to the refluxing mixture for another six hours. After the addition of complete extract allow the mixture for further one hour stirring. Cover it with aluminium foil and is aged for 12 hours. The aged mixture is then transferred to a 50 ml beaker and is kept in oven of 100 ^oC till is dried. The dried mixture is then calcined at 500 ^oC for 1 hour to remove the excess moisture. The powder was then subjected to characterize.

Crystal structure identification and crystal size analysis were performed with Shimadzu XRD6000 X-Ray diffractometer. Scanning Electron Microscopy (SEM) was performed with a Philips X130 ESEMFEG. The Transmission Electron Microscopy (TEM) analysis was done with a Tecnai F300 Transmission Electron Microscope, the UV-Vis absorption spectra were obtained using UV-1700, Shimadzu. The IR spectral data were obtained using Perkin Elmer FT-IR Spectrophotometer 1725

The chemical were supplied by Merck and used as such without any purification. The glassware supplied by Scotch-Duran. Double distilled water was used in for all purpose.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of Artemissia Pallens plant extract.

3.1.1 GC-MS chromatogram of Artemisia pallens

The GC-MS chromatogram of the Artemisia Pallens water extracts is represented in fig 1. It showed 7 prominent peaks with very narrow retention time. The fragmentation patterns for some of the peaks were comparable with the standard compounds. Data shown in tableI 1. GC-MS analysis revealed that the derivative of the compound 5-hepten-3-one was predominantly present in water based extract with the retention time of 17.12 min. this compound shows a molecular ion peak at 236 and a base peak at 111, (NIST08s.LIE CAS: 20482-11-5). The second largest compound extracted out with the retention time of 6.644 min was found to be 5, 5-Dimethyl-2(5H)-Furanone. This derivative shows a molecular ion peak at 112 and a base peak at 97.05, (WILEY8. LIE CAS: 20019-64-1). The third major derivative extracted out with retention time at 2,406 min was found to be 2- pentanol. This compound has a molecular ion peak at 73 and a base peak at 45.0, (WILEY8.LIE CAS: 6032-29-7). It was expected that the above major compounds along with the other derivatives present in the water-based extract from the plant material are responsible for the formation of tio2 through hydrolysis and condensation reactions.

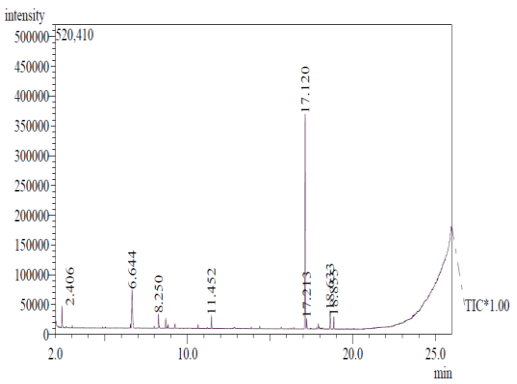


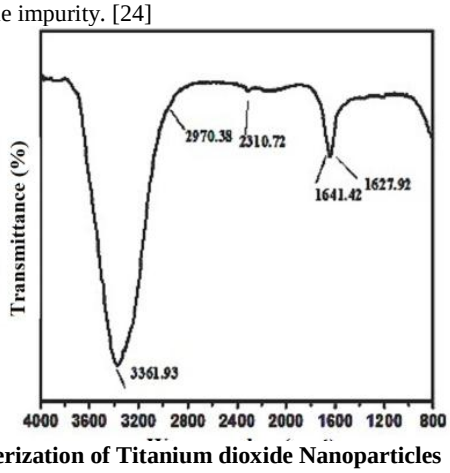
Fig 1. GC-MS chromatogram of Artemisia pallens water extracts.

Peak#	R.Time	Area	Area%	Peak Report TIC Height	Height%	A/H	Name
1	2.406	58191	4.59	34623	6.03	1.68	2-PENTANOL
2	6.644	216359	17.07	65116	11.34	3.32	2(5H)-FURANONE, 5,5-DIMETHYL-
3	8.250	42213	3.33	23240	4.05	1.82	2(3H)-Furanone, 5-ethenyldihydro-5-met
4	11.452	31477	2.48	21733	3.79	1.45	ETHANONE, 1-(5-ETHENYLTETRAH
5	17.120	771165	60.84	360771	62.84	2.14	5-Hepten-3-one, 2-(5-ethenyltetrahydro-5
6	17.213	33551	2.65	16841	2.93	1.99	
7	18.633	79423	6.27	30677	5.34	2.59	2-(1-HYDROXY ETHYL)-5-METHYL-5
8	18.855	35064	2.77	21124	3.68	1.66	4-HEPTEN-3-ONE, 2-(5-ETHENYLTET
		1267443	100	574125	100		

Table 1. Fragmentation patterns compared to standard compounds

3.1.2 FTIR Spectrum of Artemisia Pallens plant extracts

The FTIR spectrum of Artemisia Pallens plant extracts is shown below in fig 2. A sharp free hydroxyl band was observed in the vapour phase, in very dilute solution in non polar solvents or hindered OH groups are expected to develop intermolecular hydrogen bonding, which results bands at low frequencies, 3500-3200 cm-1 due to free hydroxyl bonds. The strong absorption band appeared at 3361.93-1 arise due to polymeric structure of intermolecular OH stretching vibrations due to free hydroxyl present in plant extract. Absorption peak at 3361.93cm-1 corresponding to hydroxyl group is found in IR spectrum of Artemissia Pallens plant extract can be confirmed by GCMS data (Table 1) indicating the presence of 2-Pentanol with retention time2.408 min and molecular ion peak at 73 and base peak at 45. The band at 2970.38cm-1 corresponds to asymmetric C-H stretching. A small sharp peak was observed at 1641.42cm-1 was observed and can be attributed to the presence of aromatic ring. A significant small ketonic derivative peak observed at 1627.92 cm-1. This peak at 1627.92cm-1 present in Artemissia Pallens plant extract indicating the presence of ketonic derivatives can be confirmed by GCMS data (Table 1) which shows the presence of the 5-hepten-3-one with retention time 17.12 min and molecular ion peak at 236 and base peak at 111. Other ketonic derivatives given in GCMS Data are 5,5-Dimethyl-2(5H)-Furanone with retention time 6.642 and molecular ion peak at 112 and base peak at 43. Absorption peak at 2310.72 cm-1 is due to atmospheric carbondioxide impurity. [24]

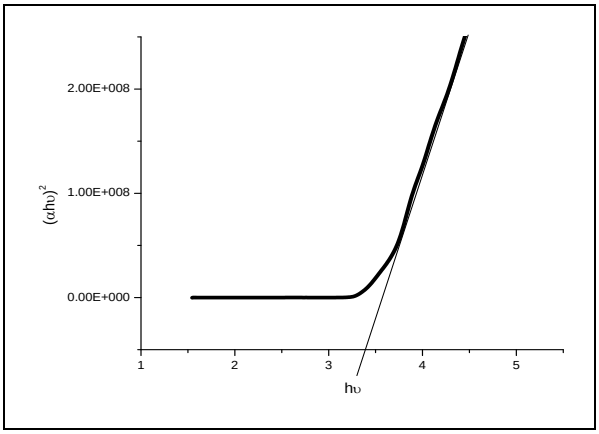


3.2 Characterization of Titanium dioxide Nanoparticles

3.2.1 UV- Vis spectroscopy

With an increase of ph from base to a stronger base, a blue shift of the adsorption edge can be noticed due to the decrease of the crystallite size from 16 to 13nm[ref] where the blue shift of the adsorption edge is noticed with the bio-extract formulated TiO_2 of crystalline size ~ of 13nm. The determination of the energy band gap using Tacu's relationship is presented in the fig.3. It can be observed that the energy band gap of bulk TiO_2 (Eg=3.2) where as the band gap of the green solvent synthesized TiO_2 is 3.41 which is higher. The increase in band gap can be correlated to the reduction of the crystallite size that determine the quantum size effect, which induce a blue shift of the absorption edge in the optical absorbance. The band gap of TiO_2 in anatase phase is 3.2 eV. The variation is due to change in the particle size. The band gap increases with decreasing particle size and the adsorption edge is shifted to a higher energy (blue shift) with decreasing particle size.

UV band gap

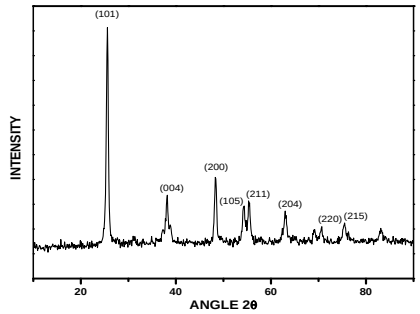


3.2.2 FTIR

FTIR spectra of TiO_2 nanoparticles is shown in fig 4. The peak in the region between 400-600cm^{-1} is attributed to Metal-Oxygen. The spectrum shows a band at 435 cm^{-1} corresponding to metal-oxygen (Ti-O). The hydroxyl group band found in IR spectrum of Artemissia Pallens plant extract is not found in IR spectrum of TiO_2 nanoparticles, which clearly indicates, after calcinations, there is no traces of hydroxyl group and synthesized TiO_2 nanoparticles is pure. The band at 1618cm^{-1} is attributed to the presence of plane bending vibrations of O-H and CO_2 molecules. The absorption band at 1438cm^{-1} might be expected to be C-O-H bending band, usually appears near 1440-1395cm^{-1} with moderate intensity and occurs in the same region as the CH_2 scissoring vibrations of the CH_2 group adjacent to the carbonyl.

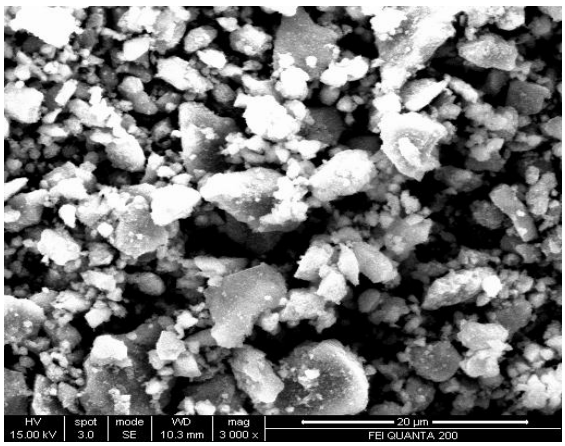
3.2.3 XRD

The XRD pattern of the TiO_2 nanoparticles is shown in fig.5. There are two prominent peaks observed at 2 theta=25.65o, 48.37o and corresponds to (101), (200) reflection. The other diffraction peaks. The other diffraction peaks observed at 2theta= 38.2o, 54.0o, 55.3o, 63.3o, 75.0o, corresponds to (004), (105), (211), (204), (220), (215) planes are observed. The crystalline size was calculated using Debye-Scherer equation and found to be 9-16nm. The hexagonal shape of TiO_2 nanoparticles is observed from the diffraction pattern. The diffraction patterns matches with the standard JCPDS card no 89-4921. The lattice constants, a and c of as- synthesized TiO_2 nanoparticles were calculated using Braggs law. The obtained values of a and c are a=4.0055 Ao, c=6.9378 Ao.



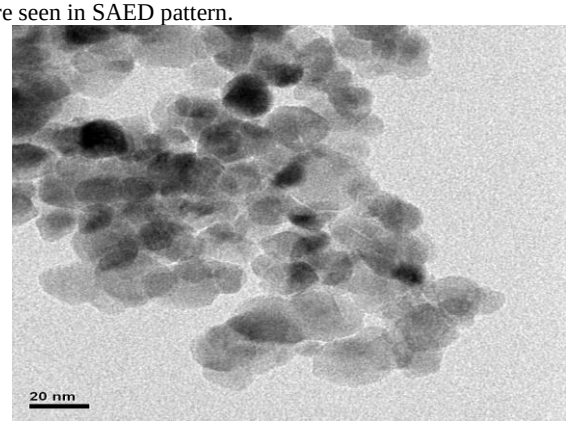
3.2.4 SEM

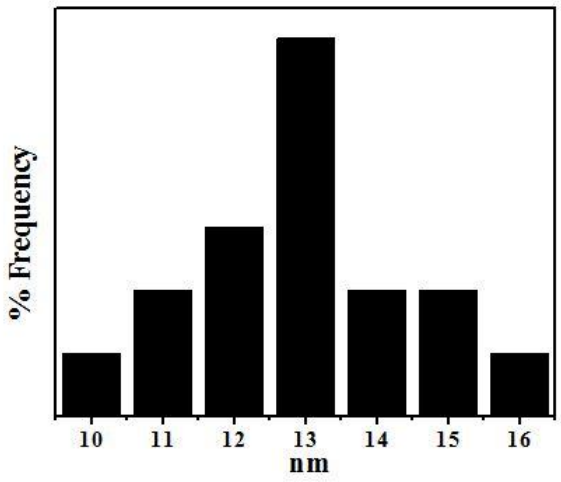
The SEM image of TiO_2 nano powders Fig 6. The green synthesized TiO_2 nanoparticle by sol-gel method shows the tetragonal shapes of various sizes. The average crystalline size of TiO_2 is not clearly seen in image due to agglomeration of the nano particles. The particle morphology was obtained by sem image.



3.2.5 TEM

TEM Image of TiO2 nanopowder is presented in fig,7, the green synthesized TiO2 nano particles shows the particle size, crystallinity and the morphology. The synthesized nano particles have relatively uniform structures with the mean particle range from 9nm-16nm and a hexagonal shape. The image also reveals the lattice fringes that are continous across the particle. The selective area diffraction pattern SAED was in good agreement with the XRD observations, thus confirming the XRD observations, thus confirming the presence of anatase phase. The characteristic diffraction rings corresponding to anatase phase were seen in SAED pattern.





4. CONCLUSION.

Titanium dioxide nano particles were synthesized by sol-gel technique using a green solvent from Artemissia Pallens instead of chemical solvent (alcohol). The structural, optical, partical size and morphological properties of TiO2 nanoparticles were analysed using XRD, UV-Vis, FTIR, SEM and TEM. The TiO2 particles were crystalline, have smaller particle size and spherical shape compared to other method of synthesis. The band gap of synthesized TiO2 is 3.41 ev, where as it is higher than the bulk TiO2.

REFERENCE

Md. Motasim Bellah, Shawn M. Christensen, and Samir M. Iqbal Nanostructures for Medical Diagnostics Journal of Nanomaterials Volume 2012, Article ID 486301, 21 pages

Md. Selim Arif Sher Shah, A Reum Park, Kan Zhang, Jong Hyeok Park, and Pil J. Yoo. The Green Synthesis of Biphasic TIO2- Reduced Graphene Oxide Nanocomposite with Highly Enhanced Photocatalytic Activity. *ACS Applied Materials & Interfaces* 2012,4, 3893-3901

M.A.Behnajady, H.Eskandarloo, N.Modirshahla, M.Shokri. Investigation of the effect of sol-gel synthesis variables on structural and photocatalytic properties of TiO2 nanoparticles. Desalination 278(2011) 10-17

Bing Li, Xiaohong Yu, Suxin Gui, Yi Xie, Jie Hong, Xiaoyang Zhao, Lei Sheng, Xuezi Sang, Qingqing Sun, Ling Wang, Weide Shen, and Fashui Hong. Titanium Dioxide Nanoparticles Relieve Silk Gland Damage and Increase Cocooning of Bombyx mori under Phoxim-Induced Toxicity. J. Agric. Food Chem. 2013, 61, 12238-12243.

Andrea Molea, Violeta Popescu, Neil A. Rowson, Adrian M. Dinescu. Influence of pH on the formulation of TiO2 nano-crystalline powders with high photocatalytic activity. Powder Technology 253(2014) 22-28

M. Sasani Ghamsari, S. Radiman, M. Azmi Abdul Hamid, S. Mahshid, Sh. Rahmani. Room temperature synthesis of highly crystalline TiO2 nanoparticles. Materials Letters 92 (2013) 287-290

Thirunavukkarasu Santhoshkumar, Abdul Abdul Rahuman, Chidambaram Jayaseelan, Govindasamy Rajakumar, Sampath Marimuthu, Arivarasan Vishnu Kirthi, Kanayairam Velayutham, John Thomas, Jayachandran Venkatesan, Se-Kwon Kim. Green synthesis of titanium dioxide nanoparticles using *Psidium guajava* extract and its antibacterial and antioxidant properties. Asian Pacific Journal of Tropical Medicine (2014)968-976

Roopan SM, Bharathi A, Prabhakaran A, Rahuman AA, Velayutham K, Rajakumar G, et al. Efficient phyto-synthesis and structural characterization of rutile TiO2 nanoparticles using Annona squamosa peel extract. Spectrochim Acta A Mol Biomol Spectrosc 2012; 98: 86-90.

Velayutham K, Rahuman AA, Rajakumar G, Marimuthu S, Santhoshkumar T, Jayaseelan C, et al. Evaluation of Catharanthus roseus leaf extract-mediated biosynthesis of titanium dioxide nanoparticles against Hippobosca maculate and Bovicola ovis. Parasitol Res 2011; 111(6): 2329-2337.

Krithi AV, Rahuman AA, Rajakumar G, Marimuthu S, Santhoshkumar T, Jayaseelan C, et al. Biosynthesis of titaniumdioxide nanoparticles using bacterium Bacillus subtulis, Mat Lett 2011;65:2745-2747

Serigo Valencia, Ximena Vargas, Luis Rios, Gloria Restrepo, Juan M. Marin. Sol-gel and low-temperature solvothermal synthesis of photoactive nano-titanium dioxide. Journal of Photochemistry and photobiology A: Chemistry 251; (2013): 175-181.

Anju A. Vargeese, Krishnamurthi Muralidharan. Effect of anatase-brookite mixed phase titanium dioxide nanoparticles on the high temperature decomposition kinetics of ammonium perchlorate. Materials Chemistry and Physics 139; (2013): 537-542.

Synthesis of mesoporous TiO2 in aqueous alcoholic medium and evaluation of its photocatalytic activity