GREEN SYNTHESIS OF TITANIUM DIOXIDE NANOPARTICLES BY NYCTANTHES ARBOR-TRISTIS LEAVES EXTRACT

M. SUNDRARAJAN*, S. GOWRI
Department of Industrial Chemistry, Green Chemistry Lab, School of Chemistry, Alagappa University, Karaikudi -630 003, Tamilnadu, India.

Biological synthesis of nanoparticles by plant extract is at present under exploitation for the reason that to develop environmentally benign nanoparticles synthesis to avoid adverse effects in biomedical applications. Many plant extracts employed are neem, lemon grass, aloe vera, Indian gooseberry which focuses on the green chemistry principles. In this report we have developed a facile and eco-friendly method for the synthesis of titanium dioxide nanoparticles from titanium isopropoxide solution using nyctanthes leaves extract. The synthesized nanoparticles were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM) and particle size analyzer (PSA). The sharp peaks by XRD pattern show the crystallinity and purity of titanium dioxide nanoparticles. The shape and morphology was studied by SEM analysis. SEM and PSA analysis shows the nanoparticle size in the range from 100 to 150nm. This report added the value for the application of nanoparticles in biomedical and nanotechnology applications with the absence of adverse side effects.

(Received June 27, 2011; Accepted August 02, 2011)

Keywords: Biosynthesis, Titanium dioxide, Nanoparticles, Nyctanthes leaves

1. Introduction

The synthesis of metal and metal oxide nanoparticles has attracted considerable attention in physical, chemical, biological, medical, optical, mechanical and engineering sciences where novel techniques are being developed to probe and manipulate single atoms and molecules. Metal and metal oxide nanoparticles have high surface area and high fraction of atoms which is responsible for their fascinating properties such as antimicrobial, magnetic, electronic and catalytic activity [1-4]. Generally, properties of nanopartices depend on size, shape, composition, morphology and crystalline phase. Among the various metal oxide nanoparticles, titanium dioxide nanoparticles have wide applications in air and water purification, DSSC due to their potential oxidation strength, high photo stability and non-toxicity [5-7]. Moreover titania nanoparticles possess interesting optical, dielectric, antimicrobial, antibacterial, chemical stability and catalytic properties which leads to industrial applications such as pigment, fillers, catalyst supports and photocatalyst [8-12]. Traditionally most of the metal and metal oxide nanoparticles were routinely synthesized by various physical and chemical methods. Some of the commonly used synthetic methods are non-sputtering, solvothermal, reduction, sol-gel technique and electrochemical technique [13-16]. But these methods are costly, toxic, high pressure, high energy requirement, difficult separation and potentially hazardous [17]. Hence developing of reliable biosynthetic, an environment friendly approach has added much importance because of its ecofriendly products, biocompatibility and economic viability in the long run and also to avoid adverse effects during their application especially in medical field. Biosynthesis of nanoparticles is a kind of bottom up approach where the main reaction occurring is reduction/oxidation. The microbial enzyme or the plant phytochemicals with antioxidant or reducing properties are usually responsible for the

*Corresponding author: drmsgreenchemistrylab@gmail.com

preparation of metal and metal oxide nanoparticles. The three ecofriendly and green chemistry perspective for the nanoparticle synthesis are the choice of the solvent medium, reducing agent and non-toxic material respectively for the stabilization of nanoparticles [18-19]. Recently nanoparticle synthesis were achieved with bacteria, fungi, actinomycetes [20-22] and use of plant extract such as neem, camellia sinensis, coriandrum, nelumbo lucifera, ocimum sanctum and several others which is compatible with the green chemistry principles [23-25]. Among the various biosynthetic approaches, the use of plant extracts has advantages such as easily available, safe to handle and possess a broad viability of metabolites. The main phytochemicals responsible for the synthesis of nanoparticles are terpenoids, flavones, ketones, aldehydes amides etc. In continuation of the efforts for synthesizing titanium dioxide nanoparticle, here we report a facile, green and one pot synthesis using the leaf extract of nyctanthes. Nyctanthes has chosen because of its functional anti-inflammatory, antioxidant, antifungal, antidiabetic, antimicrobial, antileishmanial, antipyretic and antinoceptive activities [26-29]. The biosynthetic route for nanoparticles has not yet been extended for the synthesis of titanium dioxide nanoparticles especially with nyctanthes.

2. Experimental details

The healthy leaves of nyctanthes arbor-tristis were collected from the local places of Sivaganga District, Tamil Nadu, India. The collected leaves were gently washed to remove dust. Leaves were shade dried at room temperature for about 15 days under dust free condition. Dried leaves were cut into fine pieces, grinded and sieved to get the finest powder. One gram of the dried leaves were mixed with 50mL of ethanol and extracted under reflux condition at 50°C. After five hours, the ethanolic leaf extract was obtained by filtering the mixture through Whatmann No.1 filter paper and either directly used in the synthesis of titanium dioxide nanoparticles or stored at 4°C for further experiments.

For the synthesis of titanium dioxide nanoparticles, the Erlenmeyer flask containing 0.4M of titanium tetraisoproxide in ethanolic leaf extract was reacted under stirring at 50°C. After four hours of continuous stirring, the formed titanium dioxide nanoparticles was acquired by centrifugation at 10000 rpm for 15 minutes. Then the centrifuged particles were washed with ethanol and again subjected to centrifugation at 5000rpm for 10 minutes. Separated titanium dioxide nanoparticles were dried and grinded to calcinate at 500°C in muffle furnace for about 3 hours. The calcined titanium dioxide nanopowder was used for further analytical techniques.

Crystal phase identification of titanium dioxide nanoparticles were characterized by powder X-ray diffraction using a Panlytical X Pert PRO Diffractometer with K_α radiation(λ = 1.5406 Å). Titanium dioxide nanoparticles was loaded on a 0.4mm Kapton capillary tube, sealed at both ends under N_2 in a glovebox and mounted on standard goniometer heads to determine the grain size and phase. A beam of 21 keV(wavelength = 0.5904 Å) was used. The beam size was 3 mm (h) x 1mm (r). Mythen strip detector was used to collect the data for five minutes. The particle size and morphology of the titanium dioxide nanoparticles were examined using Scanning electron microscopic observations. SEM measurements were performed on a JEOL JSM 6390 instrument operated at an accelerating voltage at 15kV. The particle size of the nanoscale materials was measured by nanotract type: Ultra Serial Number: U2475ES. The sample was sonicated prior to examination for uniform distribution.

3. Results and discussion

The formation of titanium dioxide nanoparticles synthesized using nyctanthes arbor-tristis leaves extract was supported by X-ray diffraction measurements. XRD analysis showed six distinct diffraction peaks at 25.3°, 37.8°, 47.9, 54.5°, 62.8°, 69.5° and 75.1° which indexed the planes 101, 004, 200, 105, 204, 116 and 215 respectively of the cubic face centered titanium dioxide((JCPDS No.21-1272). The average grain size formed in the biosynthesis was determined using Scherrer's formula, $d = 0.89\lambda/\beta\cos\theta$ was estimated as 100nm for the higher intense peak (Fig.1). The sharp peaks and absence of unidentified peaks confirmed the crystallinity and higher purity of prepared nanoparticles.

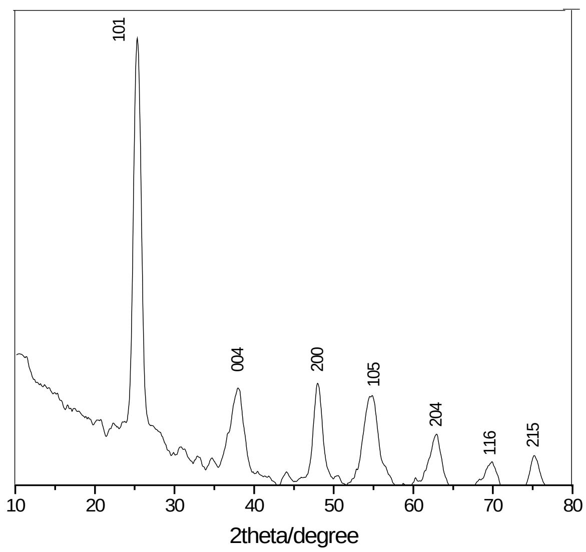

Fig. 1. XRD Pattern of TiO_2 nanoparticles

Fig. 2 shows the SEM images of titanium dioxide nanoparticles obtained with Nyctanthes arbor-tristis leaf extract at 50°C. The formation of titanium dioxide nanoparticles as well as their morphological dimensions in the SEM study demonstrated that the average size was from 100-150nm with interparticle distance, whereas the shapes were uniformed spherical.

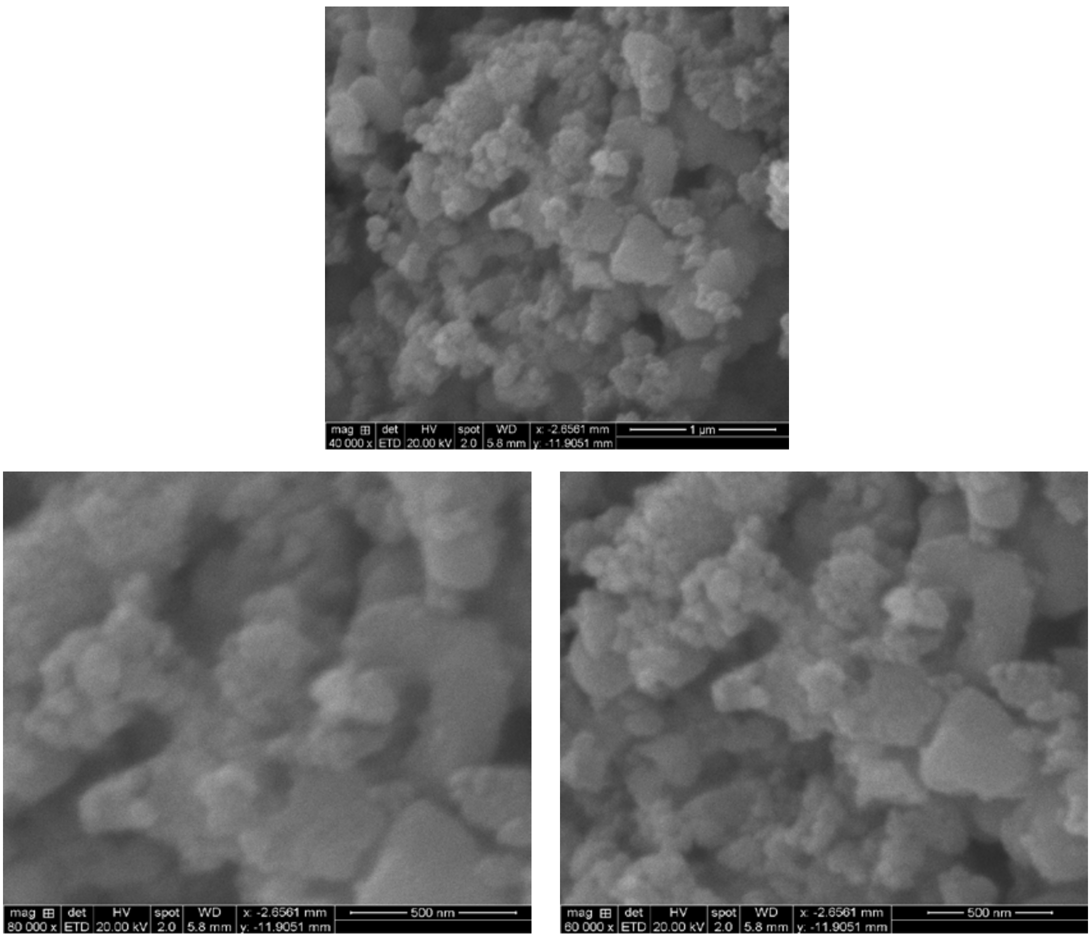

Fig. 2. SEM micrographs of TiO_2 nanoparticles

The particle size of as-synthesized titanium dioxide powders measured by PSA was approximately 150nm. Figure 3 shows the cumulative size distribution of nanoparticles. Approximately most of the nanoparticles were found to be smaller than 150nm.

..

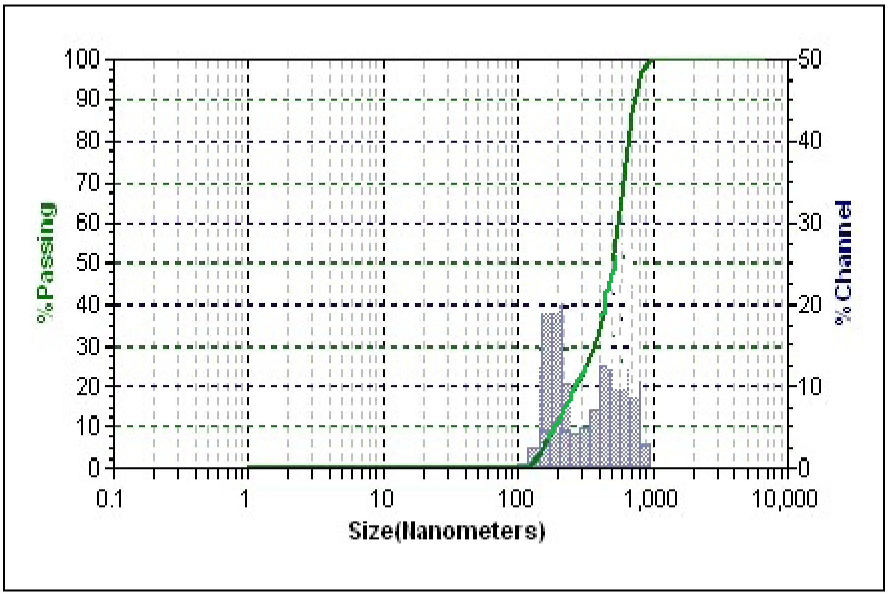

Fig. 3. Particle size distribution of TiO_2 nanoparticles

4. Conclusions

The rapid synthesis of stable titanium dioxide nanoparticles using nyctanthes leaves extract solution has been demonstrated. Structural and morphological properties of synthesized nanoparticles were characterized. XRD analysis showed that the TiO_2 samples are cubic with higher crystallinity and purity. The prepared nanoparticles exhibit spherical morphology and particle size in the range of 100-150nm by SEM and PSA. The present work proves that the Nyctanthes leaf extracted solution synthesis is a new useful method using cheap precursors for the preparation of titanium dioxide nanoparticles. This simple, cost effective, time saving and environmental friendly synthetic method gives a potential avenue for various applications. The eco-friendly green chemistry approach by the use of these leaf extracts for the synthesis of nanoparticles will increase their economic viability and sustainable management. So the exploration of the plant systems as the potential nanofactories has heightened interest in the biological synthesis of nanoparticles.

References

[1] M. Catauro, MG. Raucci, F. De Gaaetano, A. Marotta, J. Mater Sci Mater Med. **15**, 831 (2004).
[2] J. H. Crabtree, RJ. Burchette, IT. Siddiqi Ra,Huen, LL. Hadnott, A. Fishman, Perit Dial Int. **23**, 368 (2003).
[3] A. Krolikowska , A. Kudelski , A. Michota , Bukowska, J. Surf Sci. **532**, 227 (2003).
[4] G . Zhao, Stevens, J. Se. Biometals **11**, 27 (1998).
[5] Y. Li, T. J. White and S. H. Lim, Journal of solid state chemistry **177**, 1372 (2004).
[6] N. I. Al-Salim, S. A. Bagshaw, A. Bittar, T. Kemmtt, A. J. Mcquillan, A. M. Mills, M. J. Ryan, J. Mater. Chem. **10**, 2358 (2010).
[7] S. Ito, S. Inoue, H. Kawada, M. Hara, M. Iwaski, H. Tada, J. Colloid Interface Sci. **216**, 59 (1999).

[8] C. J. Barbe, F. Arendse, P. Comte, M. Jirousek, M. Gratzel, J. Am. Ceram. Soc. **80**, 3157 (1997).
[9] R. Monticone, A.V. Tufeu, E. Kanaev, C. Scolan, Sanchez, Appl. Surf. Sci. **162**, 565 (2000).
[10] S. Boujday, F.Wunsch, P. Portes, J.-F. Bocquet, C.C. Justin, Solar Energy Mater. Solar Cells **83**, 421 (2004).
[11] O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem. **32**, 133 (2004).
[12] A. M. Ruiz, G. Sakai, A. Cornet, K. Shimanoe, J.R. Morante, N. Yamazoe, Sens. Actuators B: Chem. **103**, 312 (2004).
[13] Balantrapu Krishna, V. Goia Dan, Journal of materials research **24**, 2828 (2009).
[14] R.M.Tripathi, Antariksh Saxena, Nidhi Gupta, Harsh Kapoor, R.P.Singh, Digest Journal of Nanomaterials and Biostrucutres **5**, 427 (2010).
[15] L. Rodriguez-Sanchez, M. C. Blanco, M. A. Lopez-Quintela, J. Phys. Chem. **104**, 41 (2000).
[16] A. Taleb, C. Petit, M. P. Pileni, Chemistry of Materials **9**, 950 (1997).
[17] Antariksh Saxena, R.M. Tripathi, R. P. Singh, Digest Journal of Nanomaterials and Biostructures **5**, 427 (2010).
[18] P. Mohanpuria, K. N. Rana, S. K. Yadav, Journal of nanoparticle research **10**, 507 (2008).
[19] Prathna T.C., Lazar Mthew, N. Chandrasekaran, Ashok M. Raichur and Amitava Mukherjee, Biomimetic synthesis of nanoparticles: Science, technology and applicability, Biomimetics-Learning from nature 1-20, (2010).
[20] Lengke Maggy, Southam Gordon, Acta. **70**, 3646 (2006)
[21] P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S. R. Sainkar , M. I. Khan, R. Parishcha, P. V. Ajaykumar, M. Alam , R. Kumar, M. Sastry, Nano Lett. **1**, 515 (2001).
[22] J. D Holmes, P. R Smith, R Evans-Gowing, D. J Richardson, D. A. Russel, J. R Sodeau, Arch. Microbiol. **163**, 143 (1995).
[23] N. A. Begum, S. Mondal, S. Basu, R. A. Laskar, D. Mandal, Colloids and Surfaces B: Biointerfaces **1**, 113 (2009).
[24] D. Philip, Spectrochimica Acta: Part A **73**, 374 (2009).
[25] K. Badri Narayanan, N. Sakthivel, Mat. Lett. **62**, 4588 (2008).
[26] R. S. Saxena, B. Gupta , K. K. Saxena , R. C. Singh , D. N. Prasad J. Ethnopharmacol. **11**, 319 (1984).
[27] S. Jitesh, A. Shyam, C. Subrata, Food Chemistry **103**, 1350 (2007).
[28] R. S. Saxena, B. Gupta B, S. Lata, J. Ethnopharmacol. **81**(3) 321 (2002).
[29] V. Suresh, S Jaikumar, Arunachalam, Research Journal of Pharmaceutical, Biological and Chemical Sciences **1**, 311 (2010).