Materials Letters 68 (2012) 115–117

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Eclipta prostrata leaf aqueous extract mediated synthesis of titanium dioxide nanoparticles

G. Rajakumar [a], A. Abdul Rahuman [a,*], B. Priyamvada [b], V. Gopiesh Khanna [c], D. Kishore Kumar [d], P.J. Sujin [e]

[a] *Unit of Nanotechnology and Bioactive Natural Products, Post Graduate and Research Department of Zoology, C. Abdul Hakeem College, Melvisharam - 632 509, Vellore District, Tamil Nadu, India*
[b] *Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar, Dakshina Kannada District, Mangalore-575 025, India*
[c] *Centre for Nanobiotechnology, School of Biosciences and Technology, VIT University, Vellore-632 014, Tamil Nadu, India*
[d] *ATI, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom*
[e] *Department of Microprocessors and Computers, School of Physics, Madurai Kamaraj University, Madurai-625 0 021, Tamil Nadu, India*

ARTICLE INFO

Article history:
Received 21 June 2011
Accepted 12 October 2011
Available online 18 October 2011

Keywords:
Titanium dioxide nanoparticles
Eclipta prostrata
FTIR
Atomic force microscopy
XRD

ABSTRACT

Eco-friendly, nontoxic, inexpensive, abundantly available hitherto unreported *Eclipta prostrata* leaf extract is used for the biosynthesis of titanium dioxide nanoparticles (TiO_2 NPs). The TiO_2 NPs were characterized by FTIR, XRD, AFM and FESEM analysis. FTIR peak implicated the role of carboxyl group O–H stretching amine N–H stretch in the formation of TiO_2 NPs. XRD characterized in crystallographic plane of rutile phase. AFM showed uneven surface morphology which indicates the presence of both individual and agglomerated nanoparticles. FESEM analysis showed shape in spherical clusters, quite polydisperse and it ranges in size from 36 to 68 nm with calculated average size of 49.5 nm. In this paper, we have demonstrated a novel biological route for the synthesis of TiO_2 NPs.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Materials with nano-sized dimensions have attracted considerable attention of the researchers due to their exponential promises in almost all walks of life [1]. For time immemorial, nature has made noble metal oxide part of our daily life. Metal oxide nanoparticles [2], exemplified by titanium dioxide (TiO_2) are of great technological grandness in the field of heterogeneous catalysis [3]. TiO_2 is used in cosmetic and skin care wareses, particularly in sun blocks, where especially nanosized particles (<100 nm) help to protect skin from UV rays; it is widely used to provide whiteness and opacity to products such as paints, plastics, papers, inks, food colorants and toothpastes [4].

Preparation of nanoparticles using green technologies is advantageous over chemical agents due to their less environmental consequences. In the biosynthesis method, extracts from plant may act both as reducing and capping agents in synthesis of nanoparticles. TiO_2 nanoparticles are known to react with O_2 and –OH adsorbed on the surface to obtain oxygen free radical and hydroxyl free radical which are capable of directly attacking the cell wall and cell membrane.

Eclipta prostrata L. (Asteraceae) commonly known as False Daisy has been used as a traditional medicine [5]. In the present investigation, TiO_2 NPs were synthesized using *E. prostrata* leaf by simple aqueous reduction method.

2. Experimental procedure

The salubrious leaves of *E. prostrata* were collected from C.Abdul Hakeem College, Melvisharam, Vellore, India. $TiO(OH)_2$ was purchased from Himedia Laboratories Pvt. Ltd., Mumbai, India. Aqueous extract of *E. prostrata* was prepared using freshly amassed leaves (10 g). They were surface cleaned with running tap water, followed by distilled water and boiled with 100 mL of double distilled water at 60 °C for 10 min. This extract was filtered through nylon mesh (Spectrum), followed by Millipore hydrophilic filter (0.22 μm) and used for further experiments. For synthesis of TiO_2 NPs, the Erlenmeyer flask containing 100 mL of $TiO(OH)_2$ (5 mM) was stirred for 2 h. 15 mL of the aqueous extract of *E. prostrata* was added in 85 mL of 5 mM TiO_2 at room temperature under stirred condition for 24 h. The pure $TiO(OH)_2$ and aqueous leaf extract of *E. prostrata* didn't show any color change and there was no proof for the formation of nanoparticles. After the reaction of *E. prostrata* extract with $TiO(OH)_2$ the color changed in to light green.

Characterization involved FTIR analysis of the dried powder of synthesized TiO_2 NPs by Perkin–Elmer Spectrum One instrument spectrometer in attenuated total reflection mode and using spectral range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The

---

* Corresponding author. Tel.: +91 94423 10155, +91 04172 269009; fax: +91 04172 269487.
E-mail address: abdulrahuman6@hotmail.com (A.A. Rahuman).

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.10.038

morphology of the plant synthesized TiO_2 NPs was examined using field emission scanning electron microscopy (FESEM, FEI Novanano 600, Netherlands), and for the images it was operated at 15 kV on a 0° tilt position. XRD patterns of all samples were collected in the range of 20–80 °C (2θ) using Phillips PW 1830 instrument (CuKα radiation, $\lambda = 1.5406$ Å), operated at 40 kV and 30 mA. AFM images have been processed using WSxM software ver. 4.0.

3. Results and discussion

TiO_2 NPs synthesized by a novel, biodegradable materials and simple green chemistry procedure using *E. prostrata* leaf extract. The pure $TiO(OH)_2$ without aqueous leaf extract of *E. prostrata* didn't show any color change and there was no proof for the formation of nanoparticles. After the reaction of *E. prostrata* extract with $TiO(OH)_2$ the color changed in to light green. FTIR spectroscopy was used to determine different groups on *E. prostrata* leaf extract and predict their role in nanoparticle synthesis. The FTIR spectrum of the $TiO(OH)_2$ showed characteristic bands at 3417 cm^{-1} and 1632 cm^{-1} correspond to the surface water and hydroxyl group (Fig. 1A). The band intensities in different regions of the spectrum for the powder *E. prostrata* and synthesized TiO_2 NPs test samples were analyzed. There was a shift in the following peaks: 3421 to 3427, 2922 to 2927, 2853 to 2856, 1631 to 1639 and 1103 to 1124 cm^{-1}(Fig. 1 B and C). A comparison of these results with earlier reports [6] indicated that alcohols, phenols, alkanes, primary amines and aliphatic amines in *Eclipta* may be participating in the process of nanoparticle synthesis. The *E. prostrata* leaves contains beta-amyrin, wedelolactone, triterpenoids, flavonoids, luteolin-7-o-glucoside, L-terthienyl methanol and stigmasterol [7]. Water soluble heterocyclic compounds such as flavones are the reducing and capping ligands of the nanoparticles [8]. Functional groups associated with these the cause for the bioreduction of $TiO(OH)_2$ to TiO_2 nanoparticles.

The nanoparticles were characterized by XRD in rutile phase. The positions of principal peaks in XRD were found to be in agreement with the literature [9]. The XRD sample shows dominant peak of $2\theta = 27.811$ which matches the 110 crystallographic plane of the rutile structure indicating that the crystal structure is predominantly rutile dominant (Fig. 2). This pattern reflects the shape of the wave functions of the electronic eigenstates of the Ti–O–Ti–O chain on the TiO_2 (110)/H_2O interface [10]. The particles size estimation was performed by the Scherrer's formula. $d = 0.94\ \lambda/\beta \cos\theta$ where d is the mean diameter of the nanoparticles, λ is wavelength of X-ray

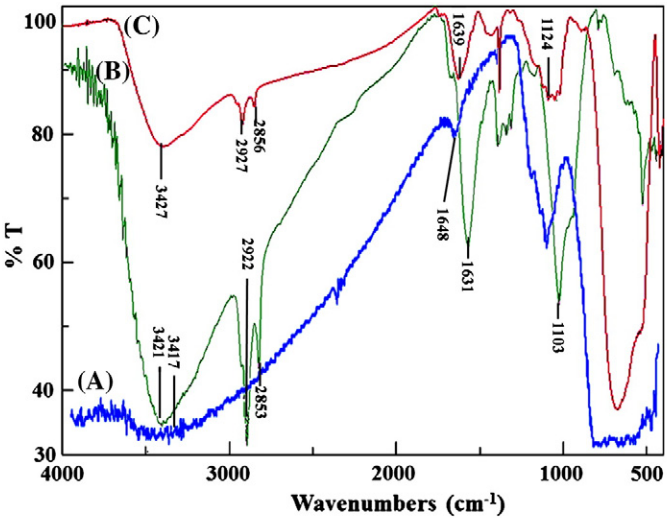

Fig. 1. FTIR spectra of (A) 5 mM $TiO(OH)_2$ (B) dried *E. prostrata* leaf powder (C) TiO_2 NPs synthesized from aqueous leaf extracts of *E. prostrata*.

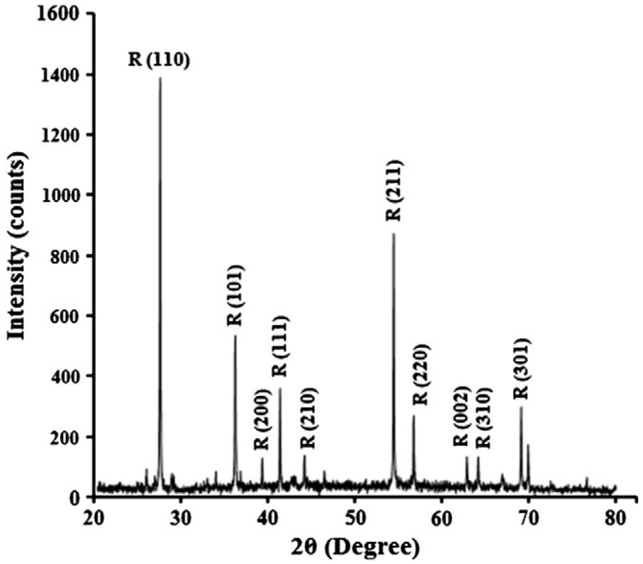

Fig. 2. XRD pattern of the TiO_2 NPs synthesized from aqueous leaf extracts of *E. prostrata*.

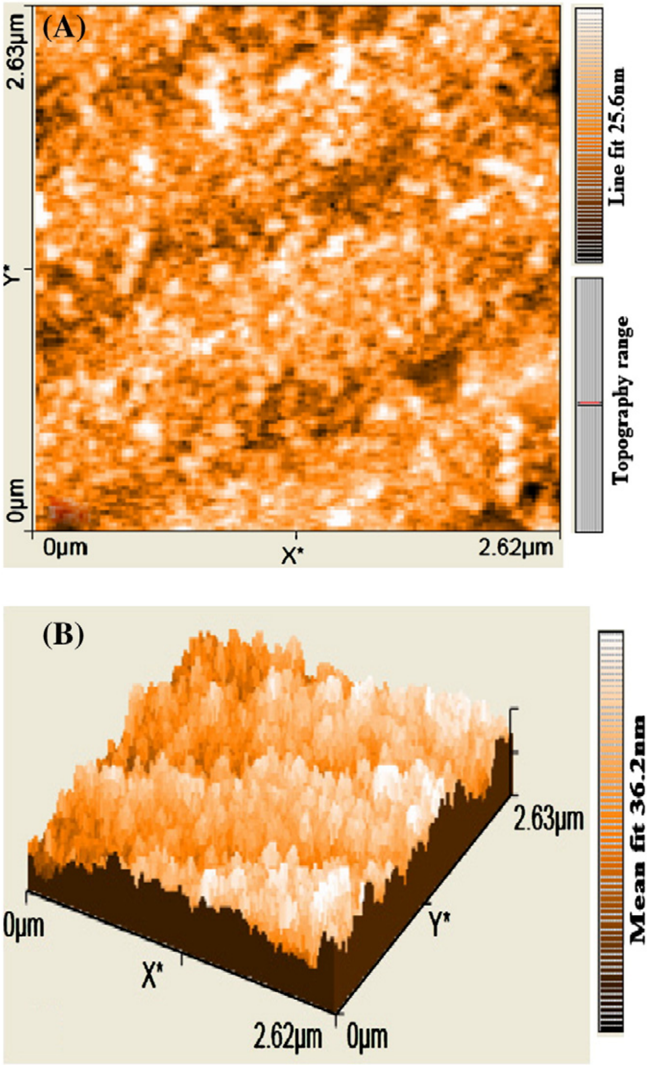

Fig. 3. Atomic force microscopic (AFM) image of the synthesized of TiO_2. (A) Topographic view, (B) three-dimensional visualization.

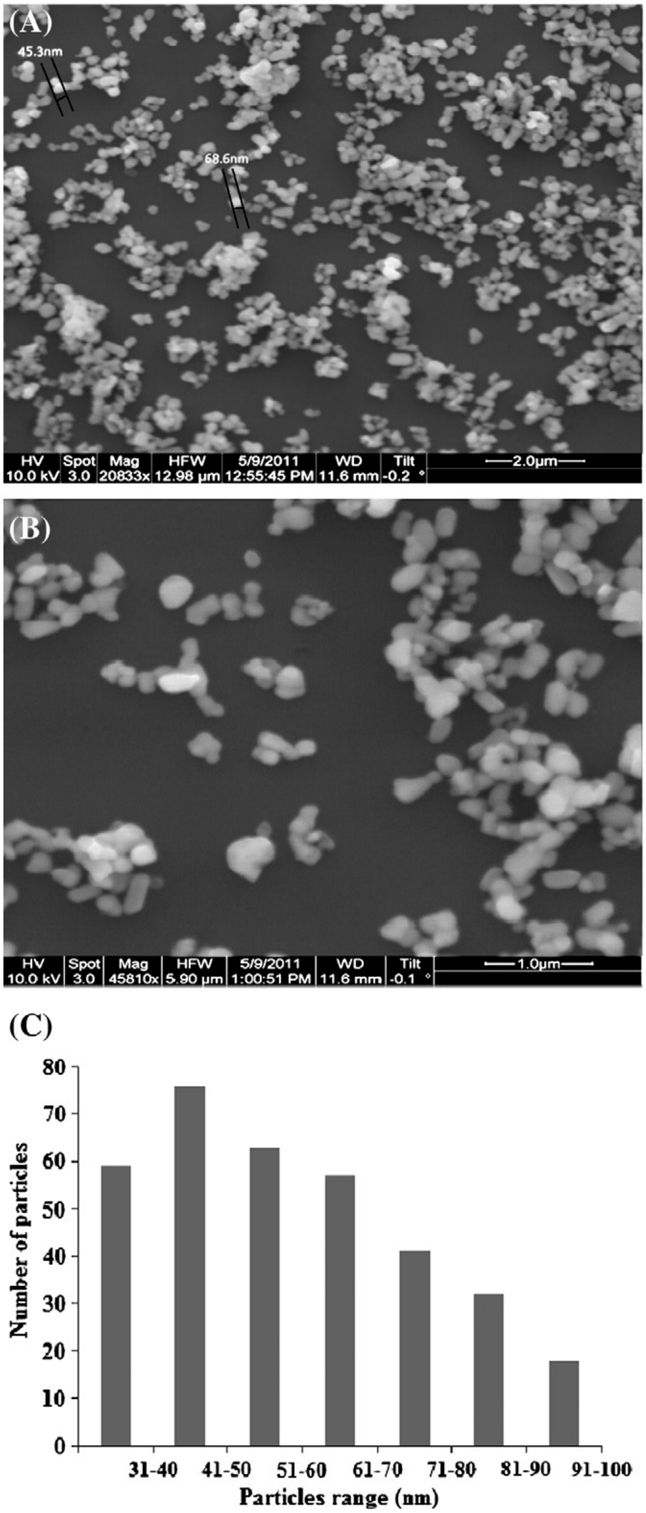

Fig. 4. FESEM images of the TiO_2 nanoparticles formed by the reaction of 5 mM TiO_2 and *E. prostrata* leaf broth (A) 20833X (B) 45810 X (C) particle size distribution.

radiation source, β is the angular FWHM of the XRD peak at the diffraction angle θ and the data obtained was matched with the database of Joint Committee on Powder Diffraction Standards (JCPDS) file No. 89-4202. The plant synthesized TiO_2 nanoparticles are quite polydisperse and ranges in size from 36 to 68 nm with calculated average size of 49.5 nm. Characterization of the synthesized nanoparticles using AFM offered a three-dimensional visualization. The uneven surface morphology explained by the presence of both individual and agglomerated nanoparticles. The strong crystalline nature can be seen in the form of diagonal formations with ridges (Fig. 3 A and B).

The surface of synthesized nanoparticles was characterized using FESEM. The micrograph shows nano-scaled TiO_2 particles with the detailed surface morphology of nanoparticles (NPs) and microspheres. The nanoparticles are poorly dispersed with spherical clusters with agglomeration size up to 95 nm. Agglomeration makes it difficult to study individual nanoparticles (Fig. 4 A and B). The particle size distribution is shown in Fig. 4C.

4. Conclusion

In conclusion, the present novel method is capable of producing TiO_2 nanoparticles with *E. prostrata* leaf extracted solution as a solvent instead of organic solvents. The advantages of this method include (i) use of cheap, nontoxic and environmentally benign precursors and (ii) simple procedures without time-consuming polymerization and problem with treatment of a highly viscous polymeric resin. This method can be used to prepare nanocrystalline oxides of other interesting materials for diverse fields of coating, cosmetics, food additive, etc.

Acknowledgments

The authors are grateful to C. Abdul Hakeem College Management, Dr. W. Abdul Hameed, Principal, Dr. Hameed Abdul Razack, HOD of Zoology Department, for providing the facilities to carry out this work.

References

[1] Roopan SM, Khan FN. Chem Pap 2010;64:812–7.
[2] Roopan SM, Khan FN. Med Chem Res 2011;20:732–7.
[3] Biener J, Farfan-Arribas E, Biener M, Friend CM, Madix RJ. J Chem Phys 2005;123: 0947051–6.
[4] Trouiller B, Reliene R, Westbrook A, Solaimani P, Schiestl RH. Cancer Res 2009;69: 8784–9.
[5] Anon. CSIR, New Delhi 1952; 3.
[6] Inbakandan D, Venkatesan R, Ajmal KS. Colloids Surf B 2010;81:634–9.
[7] Yoganarasimhan SN. TRI, Bangalore, India 2000; 206.
[8] Raut RW, Kolekar NS, Lakkakula JR, Mendhulkar VD, Kashid SB. Nano-Micro Lett 2010;2:106–13.
[9] Wang C, Deng ZX, Li Y. Inorg Chem 2001;40:5210–4.
[10] Kobayashi E, Matsuda K, Mizutani G, Ushioda S. Surf Sci 1999;427:294–7.