Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Aqueous Extract of Acanthophyllum Laxiusculum Roots as a Renewable Resource for Green Synthesis of Nano-sized Titanium Dioxide Using the Sol - gel method

Z. Madadi[1], T. Bagheri Lotfabad[1,*]

[1]Department of Energy and Environmental Biotechnology, Institute of Industrial and Environmental Biotechnology (IIEB), National Institute of Genetic Engineering and Biotechnology (NIGEB), P.O. Box 14965/161, Tehran, Iran.
**Department of Energy and Environmental Biotechnology, Institute of Industrial and Environmental Biotechnology (IIEB), National Institute of Genetic Engineering and Biotechnology (NIGEB), P.O. Box 14965/161, Tehran, Iran, Tel: +98(21) 44787321, Fax number: +98 (21) 44787399.*

PAPER INFO

Paper history:
Received18 November 2015
Accepted in revised form 16 February 2016

Keywords:
Natural surfactant
TiO_2 nanosphere
Sol-gel process
Electron microscopy
BET

ABSTRACT

In this study, green or eco-friendly synthesis of TiO_2 nanoparticles (NPs) was performed by using the aqueous extract of *Acanthophyllum laxiusculum*. The plant genus *Acanthophyllum* is among the richest sources of saponins. Saponins are glycoside compounds and they are classified as the nonionic surfactants. Sol-gel method as one of the most common techniques widely used in the nano - field was applied to synthesize the titanium dioxide nanoparticles. TiO_2 nanoparticles were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis of X-rays (EDAX). Fourier Transform Infrared Spectroscopy (FTIR) was performed to confirm the lack of the surfactant templates in synthesized NPs. The optical band gap of synthesized TiO_2nanospheres was determined using UV–Vis absorption spectra and further verified by diffuse reflectance spectroscopy analysis.The specific surface area and pore size distribution of this product were evaluated by employing the Brunauer– Emmett–Teller (BET) technique and the Barrett–Joyner–Halenda (BJH) model.

1. INTRODUCTION

In recent years, titania nanoparticles are received increased attention for their interesting optical, dielectric, antimicrobial, antibacterial, chemical stability and catalytic properties. They may be applied as pigments, fillers, catalyst supports and photocatalysts in different industries [1]. Although TiO2 has wide potential application in environmental management and environmental protection, the low photocatalytic efficiency and the difficulty to separate greatly hinder its process of industrialization [2].
Different chemical and physical approaches have been used successfully to produce nanoparticles, but they are often expensive and involve the use of hazardous chemicals. Therefore, substituting the "green" techniques may enhance environmental sustainability [3].A wide variety of natural materials such as vitamins, sugars, plant extracts, biodegradable polymers, and microorganisms as reductants and capping agents have been considered to improve the environmental aspects of nanotechnology [3]. Plant derivatives are the best candidates due to simplicity and cost-effectiveness leading to economical and operational advantages in the large scale synthesis of nanoparticles [4]. Various plant components such as the leaves, roots, latex, seeds, and stem have been used in order to extract the key active agents. Key active agents are the chemical compounds which induce or mediate the green-synthesis of nanoparticles, such as the polyphenols existing in tea being utilized for obtaining Fe-containing nanoparticles [5].
Phytosynthesis of nano-scale metal and metal oxide particles has been reported on silver, iron and iron oxide by a large number of researchers, whereas few studies have been dedicated to gold, titanium (IV) oxide, zinc (II) oxide and copper oxides [3-6].
Titanium (IV) oxide (TiO2) nanoparticles have been prepared through green technology using the solvent extract of Nyctanthes arbor-tristis leaf [1], and/or aqueous extract of Eclipta prostrata leaf [7], Jatropha curcas L. latex [8], Catharanthus roseus leaf [9], Calotropis gigantea flower [10] and Solanum trilobatum

*Corresponding Author's Email: bagheril@nigeb.ac.ir

leaf [11] as reported by individual researchers. Different experiments resulted in nanoparticles of different sizes, morphologies and crystalline forms without emphasis on the key active agent, except in the report by Hudlikaret al [8]. They introduced curcain (enzymes as the reducing and capping agents) present in the latex of J. curcas L.
In the present study, the aqueous extract of Acanthophyllum laxiusculum roots known as "soap plant" was used for the nano-synthesis of TiO2. Different species of Acanthophyllum have been used traditionally as cleaning agents. Moreover, Acanthophyllum extracts have been the subject of much recent research on immunotherapy methods by saponin adjuvants due to the presence of saponin compounds [12]. Application of the Acanthophyllum root-extracts have not yet been extended for the synthesis of nanoparticles and, in particular, for titanium dioxide. In the present work, the aqueous extract of A. laxiusculum as the surface active compound is proposed as an effective, safer substitute for chemical surfactants used in nanoparticle synthesis by the sol-gel method in an effort to eliminate these potentially carcinogenic chemical compounds.

2. MATERIALS AND METHOD

2. EXPERIMENTAL

2.1. MATERIALS

All chemicals purchased from Merck Co for this study were of analytical grade and were used without further purification. *Acanthophyllum laxiusculum* Schiman-Czeika roots were collected from the steppe regions of Iran, primarily in Qom Province, in June 2013 and were stored at the Iranian Biological Resource Center (voucher number IBRC-1275). Aqueous root-extract provided according to Soltaninejad et al [13] was used as the natural surface active compound (NSAC) and Tween 40 as the chemical one.

2.2. SYNTHESIS OF TITANIUM DIOXIDE NANOPARTICLES

To synthesize TiO_2 NPs, titanium tetraisopropoxide (TTIP) and 2-propanol were mixed in a ratio of 7:50 and stirred for 2 hrs. A solution of NSAC in deionized water was prepared at a concentration of 1.6 g/l and the pH was adjusted to 1.5 using 1M HNO_3 and stirred for 24 hrs. TTIP solution was dropped gradually into 50 ml of NSAC solution at room temperature under stirred conditions for 2 h [14-16]. Precipitates were collected by centrifuging at 7440× g for 5 minutes, were washed 5 times in a solution of ethanol and deionized water (1:1), then were air-dried at 25°C and calcinated at 400°C for 4 hours [14-17]. The same procedure was followed to prepare TiO_2 powders using the Tween 40 solution and pure water as the chemical and control powders, respectively.

2.3. CHARACTEREIZATION OF SYNTHESIZED TITANIUM DIOXIDE NANOPARTICLES

The morphology and particle size of the TiO_2 nanopowders were analyzed by scanning electron microscopy using the MIRA\\TESCAN. Moreover, NSAC mediated NPs was further studied by transmission electron microscopy (Kev 100, EM 208, Philips) [18]. TEM images were used for investigation of the morphology and size of TiO_2 nanoparticles.
The band gap and optical properties of the TiO_2 NPs were measured using a UV–vis diffuse reflectance spectrophotometer (UV–vis DRS, Shimadzu UV-2501, Mpc-2200). UV–vis absorption spectra were recorded on a UV–vis spectrophotometer in the wavelength range 200-800 nm using ethanol as a dispersion medium.
Removal of surfactant templates was verified using Fourier transform infrared spectroscopy (FTIR) on Shimadzu 8400s FTIR spectrometer using KBr pellet technique. Moreover, the NPs prepared in the presence of NSAC were compositionally analyzed through the energy dispersive analyses of X-rays (EDAX) by using the instrument attached to the SEM (MIRA\\TESCAN). The specific surface areas were measured by nitrogen adsorption at 77 K through the Brunauer–Emmett–Teller (BET) technique. The samples were degassed at 200 °C for 3 hrs prior to nitrogen adsorption measurements. In addition, the pore size distribution was determined from the nitrogen desorption branch of the isotherm curve using the Barrett–Joyner–Halenda (BJH) model. The crystal structure and phase of the TiO_2 nanopowder was determined by X-ray diffraction (XRD, PW 1800, Philiples) with CuKα radiation (λ=1.5418 Å) in the 2θ range 4° to 60° and the crystal size was calculated by using the Scherrer equation [18,19].

3. RESULTS AND DISCUSSION

3.1. SEM AND TEM ANALYSES

SEM images showed *A. laxiusculum* extract (here-named NSAC) to be an innovative, biocompatible substance which mediated the simple green synthesis of TiO_2 nanospheres and led to an average size of 20-25 nm (Figure 1a) which was comparable to the synthesis seen in the presence of Tween 40 (Figure 1b).
Lack of surface active agents caused an increase in particle size to ca. 50-70 nm and hunk formation (Figure 1c). Furthermore, TEM image (Figure 2) confirmed the SEM analyses for naturally synthesized NPs. The results

are satisfactory in comparison with those previously reported by other researchers.

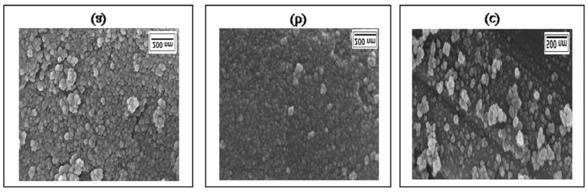

Figure 1. SEM images of titania NPs synthesized in presence of (a) NSAC, (b) Tween 40 and (c) in lack of surfactant.

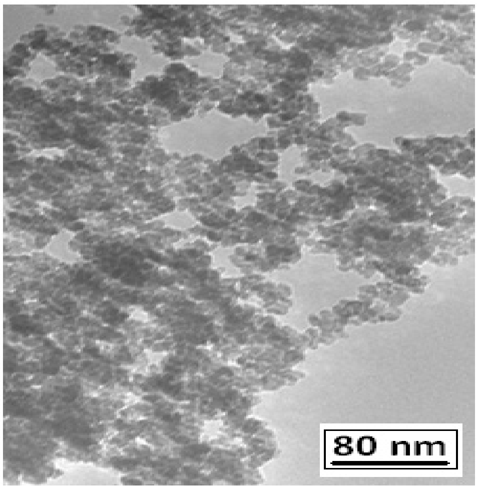

Figure 2. TEM image of titania NPs synthesized in presence of NSAC

Sundrarajan et al reported the synthesis of titanium (IV) oxide nanoparticles (100–150 nm) from titanium isopropoxide solution using *Nyctanthes* leaf extract [1]. Alternatively, TiO_2 nanoparticles (25–100 nm) have been prepared by using 0.3% aqueous extract prepared from latex of Jatropha curcas L. [8].

3.2. UV-VIS DIFFUSE REFLECTANCE SPECTROSCOPY (UV/DRS)

The UV–vis absorbance spectra of the TiO_2 nanopowder is shown in Figure 3. An absorption band-edge around 350 nm (corresponding to the optical band gap = 3.5eV) is observed for both powders synthesized by NSAC and Tween 40. The band gap is blue shifted compared to the bulk band gap of TiO_2 (3.2 eV) due to the particle-size reduction effect [20]. This is further investigated by the diffuse reflectance plot shown in the inset of Figure 3. The band gap energy (E) was calculated by equation of $E = hç/\lambda$, where h is the Plank's constant, 6.626×10^{-34} J s, c is the speed of light, 3.0×10^{8} m/s and λ is the wavelength (nm) [20, 21].

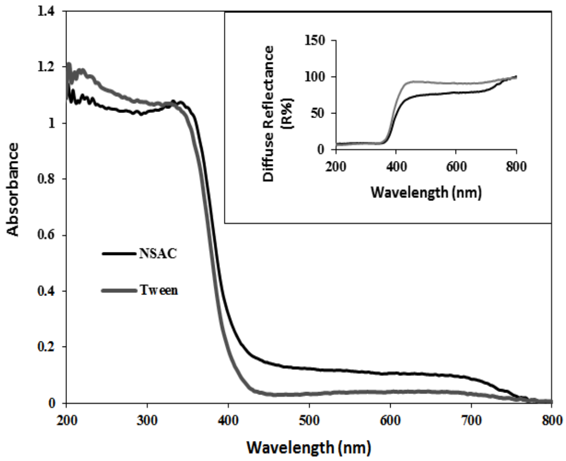

Figure 3. UV-absorbance spectra for TiO_2nanospheres synthesized by adding NSAC and Tween 40.

3.3. FT-IR SPECTROSCOPY

FTIR analysis in Figure 4 shows the effective removal of the surfactant templates for both the NPs synthesized by adding NSAC and Tween 40. Peaks at 457 and 470 cm^{-1} showed O–Ti–O bonding in anatase morphology for TiO_2 NPs obtained by adding NSAC and Tween 40, respectively. Moreover, the bands appeared at 1641 cm^{-1} and 3407 cm^{-1} for NSAC-synthesized NPs and 1618 $cm^{-1}$and 3417 $cm^{-1}$for the NPs synthesized by Tween 40 and demonstrated the presence of surface-adsorbed water and hydroxyl (-OH) groups [20]. These peaks appear due to stretching and bending vibrations of -OH groups [22]. EDAX analyses for NPs prepared by NSAC (data not shown) showed distinct elemental signals of titania (TiO_2) and also confirms the presence of the Ti-O-Ti and revealed that the nanoparticles were essentially TiO_2 with no indication of contamination.

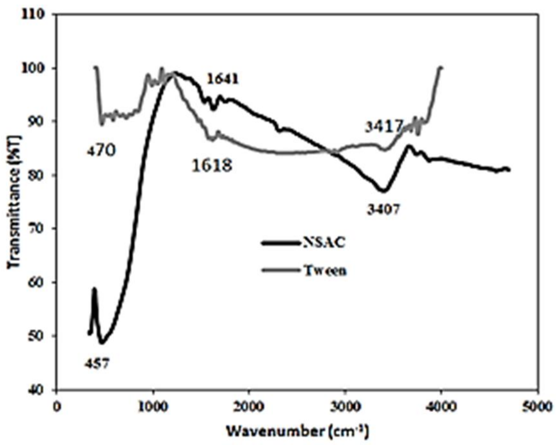

Figure 4. FTIR spectra for TiO_2nanospheres synthesized by adding NSAC and Tween 40.

3.4. BET AND BJH ANALYSES

BET adsorption of nitrogen gas demonstrated high specific surface area for TiO_2-NPs synthesized by NSAC (116.82 m^2 $g^{-1)}$ compared to that obtained by Tween 40 (98.62 m^2 g^{-1}). TiO_2- NPs produced in the presence of NSAC had larger BET specific surface areas and was further studied. The adsorption and desorption isotherm curves shown in Figure 5 revealed a distinct hysteresis loop in the range of $0<P/P_0<1$, which indicates the category of type V [23]. The BJH method by means of the adsorption branch of the nitrogen isotherm was applied to determine the pore size distribution of this product. The BJH plot shown in the inset of Figure 5 reveals that the pore radius (r_p) for this nanostructure is centered at 2.71nm.

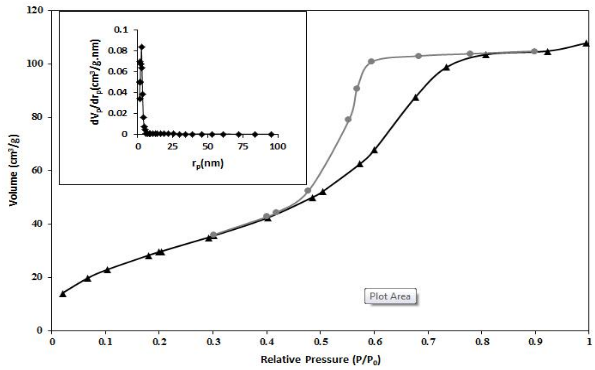

Figure 5. Nitrogen adsorption (▲) and desorption (•) isotherms for TiO_2 NPs in presence of NSAC. The inset shows BJH plot of this product.

3.5. XRD ANALYSIS

The XRD pattern for TiO_2 synthesized with NSAC and calcinated at 400ºC (Figure 6) shows only the anatase phase structure. The anatase phase was well confirmed by the Joint Committee on Powder Diffraction Standard (JCPDS) file no. 21-1272. The peaks at 2θ=25.24°, 37.72°, and 47.96° corresponded to the (101), (004), and (200) planes of anatase.
The average crystallite size of the NPs was ≃25 nm using the most intense XRD peak (101) when applying the Scherrer equation, $D=K\lambda/\beta\cos\theta$. Where D is the crystal size, λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα, K is usually taken as 0.89, and β is the line width at half-maximum height (FWHM) of the diffraction peak (radian), and θ is the diffracting angle of the peak maximum. The sharp peaks and absence of unidentified peaks confirmed the crystallinity and higher purity of prepared nanoparticles.

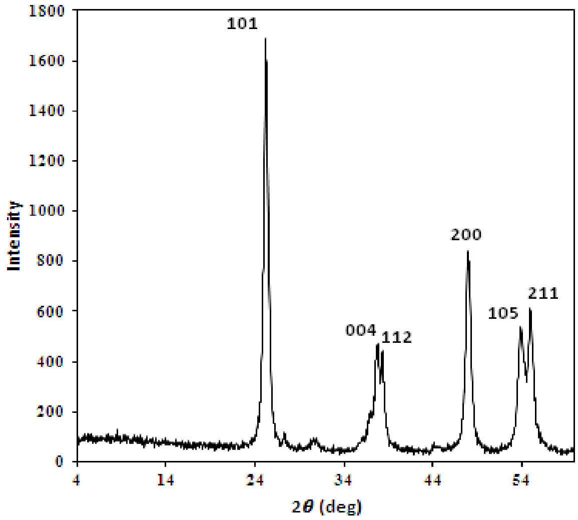

Figure 6. XRD pattern of TiO_2 nanoparticles prepared in presence of NSAC.

Most of previous research on synthesis of TiO_2 nanoparticles in the presence of different natural extracts reported crystalline rutile form of titanium dioxide [7, 10, 11]. Velayutham *et al* evaluated the *Catharanthus roseus* leaf extract-mediated biosynthesis of titanium dioxide nanoparticles. TiO_2 nanoparticles clearly showed the clustered and irregular shapes, mostly aggregated and having the size of 25–110 nm. Analyses obviously depicted the formation of the rutile and anatase forms in the TiO_2 NPs [9]. Sundrarajan *et al* developed a facile and eco-friendly method for the synthesis of titanium dioxide nanoparticles from titanium isopropoxide solution using *nyctanthes* leaves extract. They reported the sharp peaks by XRD pattern showed the crystallinity and purity of titanium dioxide nanoparticles. Moreover, they observed size distribution in the range from 100 to 150 nm for TiO_2 nanoparticles [1].
Hudlikar *et al* reported green synthesis of TiO_2 nanoparticles by using 0.3% aqueous extract prepared from the latex of *Jatropha curcas L.* They observed broad peaks in the XRD pattern indicated that particles had very small crystallite size and were semi-crystalline in nature. The lattice parameters obtained for TiO_2 nanoparticles corresponded to anatase phase.

The TiO_2 nanoparticles showed two broad size distributions, first having diameter from 25 to 50 nm with mostly spherical shape and the rest having some larger and uneven shapes. However, nanoparticles should be treated by sodium dodecyl sulfate (SDS) to remove the protein/peptide caps to be used in practical applications [8].
However, anatase form of TiO_2 as a metastable phase usually exhibits the most photocatalytic active due to a low recombination rate of photo-generated electrons and holes. On the contrary, the most stable rutile phase is less

active or not active at all [24]. Therefore, the NSAC synthesized TiO_2 due to being in anatase crystalline form and size ranging between 20-25 nm has heightened interest in the biological synthesis of nano TiO_2.

4. CONCLUSION

A desire for environmental sustainability has led to a growing tendency among researchers to establish new strategies based on green or eco-friendly chemistry. This emphasizes the need to develop simple and economical approaches for the synthesis of nano-materials. Nano-crystalline anatase TiO_2 nanoparticles were successfully synthesized via sol-gel method using titaniumtetraisopropoxide. Based on XRD patterns the average particle size obtained for anatase form calculated by Scherrer's equation was 25 nm. FTIR indicates the presence of Ti-O-Ti peak at around 457 cm^{-1}. BET surface area was found to be 116.82 m^2g^{-1} for anatase TiO_2. SEM and TEM images presented the spherical form of TiO_2 NPs, specific for anatase phase and also confirmed the nanometer particle size. The present work provides an alternative eco-friendly technique for the fabrication of TiO_2nanoparticles based on feasibility, reproducibility and low costs, which are advantages that can recommend it for optimized, large-scale production.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of Nastooh Commercial Engineering Co. for this research.

REFERENCES

1. C Sundrarajan, M., and Gowri, S., "Green synthesis of titaniumdioxide nanoparticles by Nyctanthes arbor-tristis leaves extract", ***ChalcogenideLett***, Vol. 8, (2011), 447–451.
2. Kamil, F., Hubiter, K. A., Abed, T.K., and Al-Amiery, A. A., "Synthesis of Aluminum and Titanium Oxides Nanoparticles via Sol-Gel Method: Optimization for the Minimum Size", ***J Nanoscience and Technology***, Vol. 2, (2016), 37–39.
3. Kharissova, O.V., Rasika Dias, H.V., Kharisov, B.I., Pérez B.O., and Jiménez Pérez, V.M., "the greener synthesis of nanoparticles" , ***Trends Biotechnol***, Vol. 31, (2013), 240–248.
4. Mittal, J., Batra, A., Singh, A., and Sharma, M.M. "Phytofabrication of nanoparticles through plant a nanofactories", ***Adv Nat Sci: Nanosci Nanotechnol***, Vol. 5,(2014), 1-10.
5. Hoag, G.E., Collins, J.B., Holcomb, J.L., Hoag, J.R., Nadagouda, M.N, and Varma, R.S., "Green synthesis of metal nanoparticles using plant extracts", ***J Mater Chem***, Vol. 19, (2009), 8671–8677.
6. Rahimi-Nasrabadi, M., Pourmortazavi, S.M., Shandiz, S.A.S., Ahmadi, F., and Batooli, H., "Green synthesis of silver nanoparticles using Eucalyptus leucoxylon leaves extract and evaluating the antioxidant activities of extract, ***Natural Product Research***, Vol. 28, (2014), 1964–1969.
7. Rajakumar, G., Rahuman, A.A., Priyamvada, B., GopieshKhanna, V., Kishore Kumar, D., and Sujin, P.J., "Ecliptaprostrata leaf aqueous extract mediated synthesis of titanium dioxide nanoparticles", ***Mater Lett***, Vol. 68, (2012), 115–117.
8. Hudlikar, M., Joglekar, S., Dhaygude, M., and Kodam, K., "Green synthesis of TiO_2 nanoparticles by using aqueous extract of Jatropha curcas L. latex", ***Mater Lett***, Vol. 75, (2012), 196–199.
9. Velayutham, K., Rahuman, A.A, Rajakumar, G., Santhoshkumar, T., Marimuthu, S., Jayaseelan, C., and et al., "Evaluation of Catharanthusroseus leaf extract-mediated biosynthesis of titanium dioxide nanoparticles against Hippoboscamaculata and Bovicolaovis" , ***ParasitolRes***, Vol. 111,(2012), 2329–2337.
10. Marimuthu, S., Rahuman, A.A, Jayaseelan, C., Kirthi, A.V., Santhoshkumar, T., Velayutham, K., and et al., "Acaricidal activity of synthesized titanium dioxide nanoparticles using Calotropisgigantea against Rhipicephalusmicroplus and Haemaphysalisbispinosa", ***Asian Pac J Trop Med***, Vol. 6, (2013), 682–688.
11. Rajakumar, G., Rahuman, A.A., Jayaseelan, C., Santhoshkumar, T., Marimuthu, S., Kamaraj, C., and et al., "Solanumtrilobatum extract-mediated synthesis of titanium dioxide nanoparticles to control Pediculushumanuscapitis, Hyalommaanatolicumanatolicum and Anopheles subpictus", ***Parasitol Res***, Vol. 113, (2014), 469–479.
12. Khatuntseva, E.A., Men'shov, V.M., Shashkov, A.S., Tsvetkov, Y.E., Stepanenko R.N, Vlasenko R.Y, and et al., "Triterpenoid saponins from the roots of Acanthophyllum gypsophiloides Regel", ***Beilstein J Org Chem***, Vol. 8, (2012), 763–775.
13. Soltaninejad, H., Madadi, Z., Bagheri Lotfabad, T., Pirani, A., and Ebadipour, N., "Physico-chemical features of aqueous extract of Acanthophyllum laxiusculum roots from natural steppe habitats of Iran: evaluating surface activity and thermal behavior of partially purified extract", ***Iran. Chem. Commun***, Vol. 4 (2016), 1-9.
14. Das, D., Shivhare, A., Saha, S., and Ganguli, A.K.," Room temperature synthesis of mesoporous TiO_2 nanostructures with high photocatalytic efficiency", ***Mater Res Bull***, Vol. 47, (2012), 3780–3785.
15. Chibowski, E., Holysz, L., Terpilowski, K., and Wiacek, A.E., "Influence of Ionic Surfactants and Lecithin on Stability of Titanium Dioxide in Aqueous Electrolyte Solution" ***,Croat ChemActa***, Vol. 80, (2007), 395–403.
16. Valencia, S., Marín, J.M., and Restrepo, G., "Study of the Bandgap of Synthesized Titanium Dioxide Nanoparticules Using the Sol-Gel Method and a Hydrothermal Treatment", ***Open Mater Sci J***, Vol. 4,(2010),9-14.
17. Galkina, O.L., Vinogradov, V.V., Agafonov, A.V., and Vinogradov, A.V., "Surfactant-Assisted Sol-Gel Synthesis of TiO_2 with Uniform Particle Size Distribution", ***Int J InorgChem***, Vol. 2011, (2012),1-8.
18. Abdolazizi, S., Naghizadeh, R., and Baghshahic, S., "The Comparison of MgO and TiO_2 Additives Role on Sintering Behavior and Microstructures of Reaction-Sintered Alumina-Zirconia-Mullite Composite", ***ACERP***, Vol. 1, 2015,11-17.
19. Wetchakun, N., Incessungvorn, B., Wetchakun, K., and Phanichphant, S., "Influence of calcination temperature on anatase to rutile phase transformation in TiO_2 nanoparticles synthesized by the modified sol–gel method", ***Mater Lett***, Vol. 82, (2012),195–198.
20. Bagheri, S., Shameli, K., Abd Hamid, S.B., "Synthesis and Characterization of Anatase Titanium Dioxide Nanoparticles Using Egg White Solution via Sol-Gel Method", ***J Chem***, Vol. 2013, (2012), 1-5.

21. Sahu K, Murty V.V.S., " Novel sol gel method of synthesis of pure and Aluminium doped TiO_2 nano particles useful for dye sensitized solar cell applications*",* ***IRJET*****,** Vol. 2,(2015), 567-571.
22. Asjadi, F., Salahi, E., Mobasherpour, I., "Titanium and Fluoride Co-substitution in Hydroxyl Apatite", ***ACERP***, Vol. 1, (2015),18-23.
23. Tadjarodi, A., Izadi, M., and Imani, M., "Synthesis and characterization of the special ZnO nanostructure by mechanochemical process" , ***Mater Lett*****,** Vol. 92, 2013, 108–110.
24. Wang, G. J., "Hydrothermal synthesis and photocatalytic activity of nanocrystalline TiO_2 powders in ethanol-water mixed solutions", ***Mol. Catal. A: Chem*** , Vol. 274, (2007),185-191.