Materials Research Express

PAPER

Structural, optical and conductivity study of hydrothermally synthesized TiO2 nanorods

N Santhosh Kumar 1, S K Naveen Kumar 1,2 and L Yesappa 2

1 Department of Electronics, Mangalore University, Mangalagangothri—574199, India
2 Department of Physics, University of Agricultural Sciences, Raichur—584104, India
3 Author to whom any correspondence should be addressed.

E-mail: nave12@gmail.com

Keywords: TiO2 nanorods, P25, structural and optical properties, conductivity study, I-V characteristics

Abstract

TiO2 nanorods are synthesized by hydrothermal method using the commercially available TiO2 nanopowder (P25) as a precursor. This work mainly focused on the study of the various properties and comparison among the P25, 20 mg TiO2 nanorods and 40 mg TiO2 nanorods by different characterizations. Fourier Transform Infrared Spectroscopy (FTIR) was carried out and the results confirmed the formation and presence of TiO2 nanorods by shifting peak positions from 1433 cm\(^{-1}\) to 1424 cm\(^{-1}\) and 1420 cm\(^{-1}\). The x-ray diffraction (XRD) results indicate that the crystallinity of TiO2 nanorods increased significantly and was confirmed by the variation in the diffraction peak intensity and the peak at 2\(\theta\) = 25.23\(^\circ\) is confirmed the anatase phase. The Field Emission Scanning Electron Microscope (FESEM) images clearly show the formation and presence of TiO2 nanorods. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) reveal that increasing in thermal stability and differential scanning calorimeter (DSC) evaluates the increase in melting temperature of TiO2 nanorods. The UV–vis absorption spectra show the absorption peak redshift towards higher wavelength and it leads to expansion of optical activities of TiO2 nanorods. The optical band gap energy was found to be decreased to 5.3, 5.2 and 4.9 eV for P25, 20 and 40 mg respectively. The dielectric constant has increased twice and the dielectric loss by almost ten times compared to P25. The current versus voltage (I-V) characteristics show the linear curve which reveals the easy flow of current is more in TiO2 nanorods. From the obtained results, it could be concluded that TiO2 nanorods are suitable for potential applications.

1. Introduction

In the recent years, Metal oxides play a major role in the field of Nano electronics, physics, chemistry and materials science [1]. Metal oxides and combination of Metal oxides are used in both dielectric and conducting applications. Metal oxides are used in different applications like sensors, microelectronic circuits, piezoelectric devices and fuel cells. Metal oxides can be classified into four groups namely high conductors (e.g. SrRuO3), superconductors (e.g. YBa2Cu3O7), semiconductors (e.g. TiO2, ZnO, SnO2, CuAlO2) and insulators (e.g. Al2O3, MgO, BeO). Metal oxides based semiconductors and insulators have more application oriented properties as they play the key role in electronics domain [2]. Among the available metal oxides, TiO2 is one of the best materials in the field of medical electronics due to their properties such as nontoxic, biocompatible, chemically stable, high band gap, high dielectric constant and inexpensive [3]. In addition to that, TiO2 has also unique physical, chemical and electronic properties [4]. The TiO2 nanoparticles belong to transition metal oxides family. The naturally occurring TiO2 crystal has three polymorphs (phases) namely rutile, anatase and brookite [4]. Among those polymorphs rutile and anatase have wider application but rutile is the most stable than both anatase and brookite at room temperature. TiO2 is available in different forms such as bulk material, nanoparticles, nanowires, nanorods, nanotubes etc TiO2 nanoparticles have uniqueness in their physical and chemical properties due to their limited particle size and a high volume density. TiO2 nanoparticles are one of
the most important metal oxide nanoparticles compared to others and are used in various number of fields. TiO$_2$ nanoparticles are very popular for their enormous and miscellaneous applications. TiO$_2$ nanoparticles are used in day to day products such as foods, paints, pharmaceuticals, cosmetics, plastics, toothpaste, glazes and enamel etc [5]. In advanced applications, TiO$_2$ nanoparticles play major role such as energy field like storage cells, photovoltaic cells and environmental field like water purification, air purification, photo catalysts [6] and also biomedical fields like biosensing, drug delivery etc TiO$_2$ bulk material and TiO$_2$ nanoparticles are inexpensive but nanotube, nanowires and nanorods are quite expensive, to overcome this, the work concentrates to fabricate TiO$_2$ nanorods inexpensively by hydrothermal method using P25 (Titanium nanopowder) as a precursor. The major existing methods to fabricate TiO$_2$ nanorods are surfactant directed, electrochemical, microwave irradiation, alumina templating and hydrothermal. Among all, hydrothermal method is the best for fabrication of TiO$_2$ nanorods with some advantages like fabricated materials have high quality with small diameters of about 10nm, also inexpensive and very convenient [7]. This method has some advantages like not harmful, temperature can be controlled manually, duration of the process is short and it can be setup easily within the room as user friendly. In this paper, TiO$_2$ nanorods are prepared by hydrothermal method using commercially procured P25 to study the various properties such as structure, surface morphology, optical, thermal and electrical conductivity properties. The comparison among P25, 20 mg and 40 mg TiO$_2$ nanorods is the major aim of this work. According to the results, among those ratios 40 mg TiO$_2$ nanorods are best in thermal stability, crystal size, structure and conductivity. These studies help to state that the TiO$_2$ nanorods are suitable for potential application. Finally the paper concludes that, the 40 mg TiO$_2$ nanorods are the best ratio for potential applications against P25 and 20 mg TiO$_2$ nanorods and it is well explained in the paper.

2. Experimental work

2.1. Materials used
TiO$_2$ nanopowder (P25) purchased by sigma Aldrich USA with high purity, sodium hydroxide (NaOH) AR grade and hydrochloric acid (HCl) AR grade was purchased from FINAR for synthesis of TiO$_2$ nanorods.

2.2. Preparation of TiO$_2$ nanorods
The TiO$_2$ nanopowder (P25) is used as precursor, 10N NaOH is dissolved in 40 ml of distilled water and the solution is transferred to the Teflon lined autoclave by adding 0.5 gm of P25 to the above solution and hydrothermally treated for 24 h at 130 °C then allowed to cool for 4 to 5 h at room temperature. After cooling, the collected precipitation from the autoclave is washed with deionised water for 2 to 3 times called water treatment followed by an acid treatment (HCl) to obtain the pH value of the precipitation become 7 (neutralization). Finally the powder was dried at 60 °C to produce TiO$_2$ nanorods. The synthesis process was clearly shown in the scheme 1.
2.3. Preparation of TiO$_2$/PVA film
1.98 gm of poly vinyl alcohol (PVA) is dissolved in 30 ml of distilled water and stirred for 6 h. On the other hand the synthesized 20 and 40 mg TiO$_2$ nanorods were dissolved in 10 ml of distilled water, sonicated the solution for 5 min, add sonicated TiO$_2$ nanorods solution drop wise to the PVA solution and stirred for 3 h to get homogeneous mixture, pour the solution to the petri dish and allow solvent to evaporate at room temperature. The film peeled off is used for further characterizations.

2.4. Characterization techniques
The x-ray diffractometer (Rigaku Mini flex II) was used to study the structural properties of the samples between 0 to 60° with the scanning rate 5° per minute. The chemical composition and functional groups of the samples are examined by using Fourier transform infrared spectroscopy (FTIR, ALPHA BRUKER), spectral range between 4000 cm$^{-1}$ to 500 cm$^{-1}$ wavenumber. The surface morphology of the samples was studied with Field emission scanning electron microscope (FESEM, sigma Zeiss) with operating voltage 15 kV and at the magnification 2μm. The various thermal studies like Thermogravimetric analysis (TGA), Differential thermal analysis (DTA) and Differential scanning calorimeter (DSC) were studied by the instrument (SDT Q600 TA Instruments) with temperature range between room temperature and 800 °C at the scanning rate 10 °C per minute with a nitrogen flow rate of 20 ml per minute. The two probe work station instrument (Keithley workstation) is used to examine the current voltage (I-V) characteristics of the samples in the voltage range between −5V and +5V. The dielectric studies of the samples were carried out by using Impedance Analyzer (Agilent 4294A Precision Impedance Analyzer) in the frequency range from 40 Hz to 10 kHz.

3. Result and discussions

3.1. Fourier transform infrared analysis
The Fourier transform infrared spectroscopy (FTIR) analysis helps to examine the functional groups and chemical composition recorded under the wavenumber 4000–500 cm$^{-1}$ of TiO$_2$ nanorods as shown in figure 1. For the sample P25 the peak at 3311 cm$^{-1}$ indicates the hydroxyl group (−OH) and that band shifted to 3304 cm$^{-1}$ in 20 mg and to 3291 cm$^{-1}$ in 40 mg due to the formation of TiO$_2$ nanorods and the broad absorption band between 3400 and 3200 cm$^{-1}$ indicates stretching vibration of hydroxyl group (O–H) [8–11]. The band at 2928 cm$^{-1}$ is assigned to the C–H stretching [9, 12] of the sample P25 and the peak slightly shifts by increasing intensity to 2926 cm$^{-1}$ and 2921 cm$^{-1}$ respectively in case of 20 mg and 40 mg samples, and the band at 1433 cm$^{-1}$ of P25 is shifted to 1424 cm$^{-1}$ and 1420 cm$^{-1}$ for the 20 and 40 mg respectively.

The C–O band stretching appears at the peak 1091 cm$^{-1}$ is shifted to 1084 cm$^{-1}$ and 1071 cm$^{-1}$ respectively with increased peak intensity. The peaks at 1559 cm$^{-1}$,1433 cm$^{-1}$,1375 cm$^{-1}$,1562 cm$^{-1}$,1424 cm$^{-1}$,1372 cm$^{-1}$,1571 cm$^{-1}$,1426 cm$^{-1}$,1370 cm$^{-1}$ corresponds the Ti–O–C groups of P25, 20 mg and 40 mg respectively [12]. The observed FT-IR results shifting in peak positions and variation in the peak intensity confirms the change in chemical bonds and hence forms the TiO$_2$ nanorods.

Figure 1. FTIR spectra of (a) P25 (b) 20 mg TiO$_2$ nanorods (c) 40 mg TiO$_2$ nanorods.
3.2. Surface morphology

Figure 2 shows the FESEM images of P25, 20 mg and 40 mg TiO$_2$ nanorods. Figure 2(a) confirmed the presence of TiO$_2$ nanoparticles and figure 2(b) reveal the formation of small rod like structure at 20 mg and figure 2(c) confirmed the formation of TiO$_2$ nanorods perfectly.

During the synthesis process, NaOH and HCl play the major role in changing the morphology. Due to the addition of NaOH and HCl the Ti–O–Ti bonds are broken and form an intermediate product like Ti–O–Na and Ti–OH bond and the process leads to formation of layered structure and after that Ti–O–Na and Ti–OH bonds treated with water (pH 7) which leads to the formation of TiO$_2$ nanorods [13, 14].

3.3. X-ray diffractometer (XRD) analysis

The XRD pattern of the samples P25 and TiO$_2$ nanorods are as shown in figure 3. The XRD spectra exhibits the characteristic peaks with corresponding (hkl) index values for P25 at $2\theta = 15.69^\circ$ [202], 22.64°, 25.23° [101], 35.15° [004], 43.21° [111], and 53.11° [211]. The major peaks intensity was varied and the peaks shifts for 20 mg to $2\theta = 14.96^\circ$, 20.91°, 24.88°, 34.59°, 42.83° and for 40 mg to $2\theta = 14.74^\circ$, 4.07°, 34.76° and 42.83°.

There is also a broad peak at around $2\theta = 13^\circ$ in P25, its decrease intensity or vanish for 20 mg and 40 mg is attributed to the initiation of phase transformation of TiO$_2$ nanoparticles into TiO$_2$ nanorods. The diffraction peak at $2\theta = 25.23^\circ$ is confirmed the anatase phase [15] of the pure P25 and corresponding diffraction anatase phase gets stronger and intense in both the 20 and 40 mg TiO$_2$ nanorods. The variations in the peak positions were clearly observed and the peak intensity increased significantly with increasing the weight ratio and disappearance or vanish of a broad peak at $2\theta = 13^\circ$ in P25 for 20 mg and 40 mg which attributed to the initiation of phase transformation of TiO$_2$ nanoparticles into TiO$_2$ nanorods. The observed results clearly indicate that the crystallinity was increased significantly in the nanorods.

3.4. Thermal analysis

The TGA/DTA techniques are widely used to evaluate the thermal stability of materials and the TG/DT graphs of P25, TiO$_2$ nanorods at 20 mg and 40 mg were shown in figure 4. The three major weight loss regions are observed in TG curves [16, 17]. The first stage was observed at 30–100 °C which is attributed to the removal of water or moisture content due to the braking of carbon-hydrogen bonds in the sample. The second stage was observed between 110–230 °C which is corresponding to the loss of dopants and any acid content from the sample. The major weight loss was observed in the third stage around the 550–575 °C which is related to the destruction in the backbone of polymer chain and losses the originality of the sample.
From the figure 4 it is noticed that the Thermogravimetric temperature of the samples P25, 20 mg and 40 mg of TiO$_2$ nanorods have increased up to 557 to 567 and 575 °C respectively with correspondingly increase in the decomposition temperature 319, 327 and 329 °C for P25, 20 mg and 40 mg of TiO$_2$ nanorods respectively, which indicates the increased thermal stability of TiO$_2$ nanorods.

3.5. Differential scanning calorimetry (DSC)

The melting temperature ($T_m$) of the samples was determined by DSC technique. DSC curves of P25, 20 mg and 40 mg were shown in figure 5. The thermal stability and melting temperature of the TiO$_2$ nanorods were examined between room temperature and 700 °C. It is observed that the melting temperature was increased with increase in the ratio of TiO$_2$ nanorods and it is responsible for enhancing the crystallinity.

The DSC curves exhibit two exothermic peaks in the temperature range from 135 to 148 °C and 528 to 549 °C. The exothermic peaks at 135 °C, 141 °C and 148 °C of P25, 20 mg and 40 mg respectively are assigned to the adsorption of water or removal of moisture content from the TiO$_2$ nanorods [17]. The increase in the melting temperature at the exothermic peaks at 528 °C, 542 °C and 549 °C are attributed to the phase transformation of the TiO$_2$ nanoparticles into TiO$_2$ nanorods [17] as a result the crystallinity of the TiO$_2$ nanorods was increased. These results are correlated with the XRD analysis.

3.6. UV–visible absorption spectra

UV-Visible absorption spectra of samples P25, 20 and 40 mg TiO$_2$ nanorods are shown in figure 6. The information about the band structure of compounds can be studied by optical absorption spectra. An electron excited from lower to higher energy state by absorbing a photon of energy of electron inter-/intrastrand transition or exciting transition. The main absorption wavelength of TiO$_2$ nanorods corresponds to the intrinsic absorption of anatase phase of TiO$_2$. The absorption shows red shift towards higher wavelength from 272 nm to 276 nm and 279 nm for P25, 20 mg and 40 mg of TiO$_2$ nanorods respectively, it reveal the fact that the valence band shifts toward the conduction band resulting into narrowband gap. Hence the energy required for the electrons to transit from the valence band to conduction band (optical excitation) decreases due to the red shift in the absorption [18]. The obtained results suggest that, after the formation of TiO$_2$ nanorods the optical response was expanded and hence improves in the photo catalytic properties of TiO$_2$ nanorods [19].
3.7. Optical band gap energy

The optical band gaps of samples calculated using the relation between the absorption coefficient ($\alpha$) and incident photon energy ($h\nu$) by the following equation,

$$\alpha = \frac{A (h\nu - E_g)^n}{h\nu}$$

Figure 4. TGA D−T−1A−1 Thermograms of P25, 20 mg TiO2 nanorods and 40 mg TiO2 nanorods.
The direct optical band gap was simply a transfer of the electron from the top of the valence band to the bottom of the conduction band without any change in momentum. The relation between the absorption coefficient ($\alpha$) for a direct transition and the photon energy ($h\nu$) was given by Fahrenbruch and Bube

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$
The indirect band gap is a transition of electron from the valence to conduction band which is associated with a photon of the right magnitude of crystal momentum and the bottom of the conduction band does not correspond to zero crystal momentum in indirect band gap materials and the absorption coefficient dependence on the photon energy for indirect transitions \[20\]. The direct optical band gap values are extracted from the linear portion of \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) plots \[21\] as shown in figure 7. The optical band gaps were decreased from 5.3 eV, to 5.2 eV and 4.9 eV for P25, 20 mg and 40 mg TiO\(_2\) nanorods respectively.

3.8. Dielectric property

The dielectric permittivity of P25, TiO\(_2\) nanorods at 20 mg and 40 mg as a function of frequency at room temperature are studied and presented the dielectric constant \((\varepsilon')\) in figure 8 and dielectric loss \((\varepsilon'')\) in figure 9. The dielectric constant \((\varepsilon')\) of a material is related to the dipole polarizability, which arises from electric dipoles they can change the orientation of polarization subjected to the applied electric field. The \(\varepsilon'\) of P25, TiO\(_2\) nanorods at 20 and 40 mg is frequency dependent in lower frequency because of the dipoles are response significantly with applied electric field and the contribution of the space charge effect towards polarization may tend to increase at lower frequencies as a result the high dielectric constant. The \(\varepsilon'\) of P25, TiO\(_2\) nanorods at 20 and 40 mg is frequency independent at higher frequency region due to the dipoles are unable to respond with applied electric field and thus they behaviours like tightly bounded at high frequencies is reason to maintain the
constant and low dielectric constant \[22\]. The dielectric constant \(\varepsilon'\) and dielectric loss \(\varepsilon''\) were calculated using following relations,

\[
\varepsilon' = C_0 d/(\varepsilon_0 A) \text{ and } \varepsilon'' = \varepsilon' - \tan \delta
\]

It is observed that the dielectric constant \(\varepsilon'\) and dielectric loss \(\varepsilon''\) of P25, TiO\(_2\) nanorods at 20 and 40 mg are decreased suddenly with increase in the frequency which may be because the dipole polarization failed to change the direction of orientation with applied field or the polarization of dipoles decrease when dipole rotation cannot follow electric field changes at high frequencies that results in the decrease the dielectric constant. The dielectric constant \(\varepsilon'\) and dielectric loss \(\varepsilon''\) increased at low frequencies due to the accumulation of charges between the sample and electrode as a result there is an increase in charge carrier density due to the increased dissociation of ion aggregation and hence the occurrence of the relaxation phenomenon which results in the increase of dielectric parameters at low frequency and contribute to increase the ionic conductivity \[23\].

3.9. Current-voltage (I-V) characteristics

I-V characteristics of the samples were examined at room temperature by using two probes Keithley workstation instrument as shown in figure 10. I-V characteristics of the samples reveal the ohmic behaviour i.e., the current increases linearly with the increase in the applied voltage in the range \(-5\) V to \(+5\) V. The current of the TiO\(_2\) nanorods is increase in the field of induced polarization of the applied bias voltage which is attributed to enhance
electrical conductivity [24]. By improving the interface and electrode contacts it is possible to obtain the good electrical characteristics with high stability which helps in high quality device applications of the TiO2 nanorods. Due to the formation of TiO2 nanorods the recombination of charge will decrease and increases the charge transfer rate, due to the path provided by straighten nanorods to flow easily. As a result the increase in the electron density and hence increases the conductivity.

4. Conclusion

The TiO2 nanorods were prepared by hydrothermal method and investigated the structure, morphology, thermal, optical and conductive properties. The phase transformation from nanoparticles to nanorods of TiO2 due to changes in the chemical structure or bonds was confirmed by the FTIR analysis. The surface morphology was studied by FESEM and noticed the formation of fine TiO2 nanorods. The increased peak intensity is evident to enhanced crystallinity as observed in XRD analysis. Thermal studies were carried out by TGA/DTA analysis and the results confirmed the increasing thermal stability of the TiO2 nanorods and the DSC analysis reveal the increased melting temperature from 528 °C to 542 and 549 °C for P25, TiO2 nanorods of 20 mg and 40 mg respectively. UV-Vis. spectroscopy exhibits the redshift in the wavelength by decreasing the energy band gaps from 5.3eV, to 5.2 and 4.9eV for P25, TiO2 nanorods of 20 mg and 40 mg respectively. The dielectric properties increased in low frequency and decreases with increased frequency. I-V characteristic shows that the linear increase in current with applied voltage. Finally, the obtained results are proved that the sensitive characteristics of the TiO2 nanorods are better than P25 for potential applications. Hence the hydrothermally synthesized TiO2 nanorods may overcome by P25 nanoparticles.

ORCID iDs

N Santhosh Kumar https://orcid.org/0000-0001-9375-7413
S K Naveen Kumar https://orcid.org/0000-0002-6560-9066

References

[1] Rajaeiana B, Anna Heitza B, Tadeb M O and Liub S 2015 Improved separation and antifouling performance of PVA thin film nanocomposite membranes incorporated with carboxyalted TiO2 nanoparticles J. Membr. Sci. 485 48–59
[2] Omprakash S, Naveen Kumar S K and Holla R 2018 Titanium dioxide and zinc oxide as a dielectric material for application in TFT’s Materials Today: Proceedings. 5 10835–8
[3] Diasanayake M A K L, Sena era G K R, Sarangika H N M, Ekanayake P M P C, Thotavattage C A, Divarthi ne H K D W M N R and Kumari M K W 2016 TiO2 as a low cost, multi functional material Materials Today: Proceedings 35 S40–7
[4] Ali I, Suhail M, Alothman Z A and Alwarthan A 2018 Recent advances in syntheses, properties and applications of TiO2 nanostructures RSC Adv. 8 30125–47
[5] Mosaddeghi H, Rezaei B and Mosaddeghi H 2009 Applications of titanium dioxide nanoparticles Nano-Technology Environ. Conf. 1–4
[6] Lee D, Lee S, Yop K and Park S 2014 Effect of hydrothermal temperature on photocatalytic properties of TiO2 nanotubes Curr. Appl. Phys. 14 415–20
[7] Wong C L, Tan Y N and Mohamed A R 2011 A review on the formation of titania nanotube photocatalysts by hydrothermal treatment J. Environ. Manage. 92 1669–80
[8] Sivarani S D S, Kaviyarsu A, Ayeshamariam A, Ravi Kumar B, Pandiarajan S, Veeralakshi C, Jayachandran M and Maaza M 2018 Synthesis and characterization of ZnO–CuO nanocomposites powder by modified perfume spray pyrolysis method and its antimicrobial investigation Int. J. Nanomedic. 39 033001–1–033001-7
[9] Sagar R N, Ravindrachary V, Guruswamy B, Hegde S, Mahanthes B K and Kumari R P 2018 Effect of TiO2 nanoparticles doping on structural and electrical properties of PVA: NaBr polymer electrolyte AIP Conf. Proc. 1953 2–6
[10] Rajaeian B, Heitz A, Tade M O and Liub S 2018 Improved separation and antifouling performance of PVA thin film nanocomposite Membranes incorporated with carboxyalted TiO2 nanoparticles J. Membr. Sci. 485 48–59
[11] Shehab A M and Akil D S 2016 Structural and optical properties of TiO2 nanoparticles/PVA for different composites thin films Int. J. Nano-elec trom. Mater. 9 17–36
[12] Naskhudin I E P, Diantoro M, Kusumaatmaja A and Triyana K 2017 Preparation of PVA/TiO2 composites nanofibers by using electrospinning method for photocatalytic degradation IOP Conf. Ser. Mater. Sci. Eng. 202 1–6
[13] Ranjitha A, Muthukumarasamy N, Thambidurai M and Veluthappillai D 2015 Effect of reaction time on the formation of TiO2 nanotubes prepared by hydrothermal method Opt.—Int. J. Light Electron Opt. 126 2491–4
[14] Nian J and Teng H 2006 Hydrothermal synthesis of single-crystalline anatase TiO2 nanorods with nanotubes as the precursor J. Phys. Chem. B 110 4193–9
[15] Venkatachalam S, Hayashi H, Ebina T and Nanjo H 2013 Preparation and characterization of epitaxial growth of ZnO nanotip arrays by hydrothermal method J. Colloid Interface Sci. 395 64–7
[16] Yesappa L, Niranjana M, Ashokkumar S, Vijeth H, Raghu S and Devendrapra H 2018 Characterization, electrical conductivity and electrochemical performance of polyaniline–LiClO4–CuO nano composite for energy storage applications Polym. Plast. Technol. Eng. 58 1–13
[17] Hu M L, Fang M H, Tang C, Yang T, Huang Z H, Liu Y G, Wu X W and Min X 2013 The effects of atmosphere and calcined temperature on photocatalytic activity of TiO2 nanofibers prepared by electrospinning Nanoncal. Res. Lett. 8 1–9
[18] Zhang X, Zhou J, Gu Y and Fan D 2014 Visible-light photocatalytic activity of N-doped TiO$_2$ nanotube arrays on acephate degradation J. Nanomater. 16 1–6

[19] Li D, Pan N, Liao J, Cao X and Lin S 2013 Effects of surface modification of TiO$_2$ nanotube arrays on the performance of CdS quantum-dot-sensitized solar cells Int. J. Photoenergy 2013 129621

[20] Yesappa L, Niranjana M, Ashokkumar S P, Vijeth Chapi Sharanappa H, Raghu S and Devendrappa H 2017 Investigation of the structure, optical and electrical properties of lithium perchlorate doped polyaniline composite: aloe vera used as a bio-plasticizer J. Electron. Mater. 46 6965–76

[21] Yang S, Liu Y and Sun C 2006 Preparation of anatase TiO$_2$/Ti nanotube-like electrodes and their high photoelectrocatalytic activity for the degradation of PCP in aqueous solution Appl. Catalysis A : General 301 284–91

[22] Yesappa L, Niranjana M, Ashokkumar S P, Vijeth H, Ganesh S and Devendrappa H 2018 Electron beam irradiated polymer electrolyte film: morphology, dielectric and AC conductivity studies AIP Conf. Proc. 1953 050006-1–050006-4

[23] Wypych A, Bobowska I, Tracz M, Opasinska A, Kadlubowski S, Krzywania-Kaliszewska A, Grobelny J and Wojciechowski P 2014 Dielectric properties and characterisation of titanium dioxide obtained by different chemistry methods J. Nanomater. 124814 1–9

[24] Nirmala Jin Won Jeong R, Navamathavan Hak R and Yong Kim W 2011 Synthesis and electrical properties of TiO$_2$ nanoparticles embedded in polyamide-6 nanofibers via electrospinning Nano Micro Letters 3 56–61