

Electrical properties of green synthesized TiO₂ nanoparticles

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ABSTRACT

Titanium dioxide (TiO₂) nano particles are successfully synthesized by the green synthesis with simple solvothermal method using a domestic microwave oven, for the first time, the prepared samples were annealed at 400 °C for 3 hr to improve the ordering. Grain sizes and nano particles structure are confirmed by carrying out X-ray powder diffraction measurements. The photoconductivity measurement exhibits the positive photoconductive nature of the systems studied. AC and DC electrical measurements are done on pelletised samples at various temperatures ranging from 308 K- 368 K. The electrical parameters increase with the increase in temperature. Results of the present study reveal that the space charge contribution plays a significant role in the charge transport process and polarizability in the nano particles studied. The present study indicates the possible occurrence of nano-confined states in the TiO₂ nano particles studied.

INTRODUCTION

The nano structured metal oxides have received increasing consideration due to their unique physical and chemical properties and in particular, the functional metal oxides have emerged as strong candidates for variety of applications [1]. Among them, enormous efforts have been devoted to the research of Titanium dioxide (TiO₂) material, which has led to many promising applications such as dye sensitized solar cells, photo catalysis, self-cleaning material, photonic crystals, gas sensing devices, and biomaterials [2-7]. Titanium dioxide (TiO₂) is considered very close to an ideal semiconductor for photocatalysis because of its high stability, low cost and safety toward both humans and the environment. However, photonic or photoelectrochemical applications of TiO₂ using solar light are generally hampered by the wide-bandgap semiconductor (3.2 eV) that allows only for a use of approx. 7% of the solar light. Therefore, a large body of research works target band-gap engineering of TiO₂ in order to access also the visible light range, in particular for photocatalytic applications [8]. Synthesis of TiO₂ nanostructures may be achieved by various routes including sol-gel methods, template-assisted methods, hydro/solvothermal approaches, and by electrochemical methods. Advantages of these methods manifest themselves through product quality, environmentally acceptable processing and the manipulation of process conditions to control product characteristics. Significantly, Solvothermal treatment is useful because it can control the grain size, the particle morphology, the crystalline phases, and the surface chemistry by regulating the sol composition, the reaction temperature, pressures, solvents, additives, and aging time [9-11]. Recently, an eco friendly green mediated synthesis method of nano material is a fast growing research in the limb of nanotechnology. The biosynthesis method employing plant extracts have drawn attention as a simple and viable alternative to chemical procedures

physical methods [12]. Therefore, it is necessary to adopt proficient modified methods to enhance the photocatalytic performance of TiO₂. In the present work, TiO₂ nanoparticle have been prepared by using some green synthesis with simple solvothermal methods and characterize the prepared samples, for the first time. There is no report available on the electrical properties of TiO₂ nano particles.

MATERIALS AND METHODS

2.1 Preparation of plant extracts

Fresh plant leaves of *Anisomeles Malabarica* were collected from Thirumalai Engineering College campus, Kilambi, Kancheepuram. The collected plant leaves under experimentation were washed thrice with tap water and double distilled water and kept in the room temperature for air dry. After drying the known amount of leaf samples were grained into fine powder.

2.2 Preparation leaves extract *Anisomeles Malabarica*

The powdered *anisomeles malabarica* leaves (3g) were dissolved in distilled water (25 ml) with ethanol (25 ml) and stirred magnetically at room temperature for 1 hr and then filtered.

2.3 Green synthesis of TiO₂ nano Particle

Analytical Reagent (AR) grade titanium tetra isopropoxide (TTIP) and urea in 1:3 molecular ratio was mixed and dissolved in mixed solvent of ethanol and water (1:1) with continuous stirring at 30 mints until homogeneous solutions were obtained. Then the finely leaf extract of *anisomeles malabarica* (25ml) was added to precursor solutions and kept in a domestic microwave oven. 2.45 GHz microwave irradiation was carried out till the solvent was evaporated completely. The semi-colloidal precipitate formed was cooled and washed several times with distilled water and then with acetone to remove the organic impurities present, if any. The sample was then dried in open atmosphere and collected as yield. Finally, the resulting fine powder was annealed at 400 °C done for 2 hr to improve the ordering. Characterization studies were made on the annealed samples. The mass of the product nano particles was measured accurately and used for the estimation of yield percentage. The yield percentage was obtained by using the relation

$$\text{Yield percentage} = \frac{\text{Mass of the product}}{\text{Sum of the masses of the reactants}} \times 100.$$

The reactions were found to be within 14 min and highly yielding.

3. Characterization

The X-ray diffraction analysis was done using RICH SEIFER with monochromatic nickel filtered CuK_α (λ=1.5461 Å) radiation to identify the structural and phase composition. The grain sizes were determined by using the Scherrer formula [13]. The TiO₂ nano particles were pelletised using a hydraulic press (with a pressure of about 4 tons) and used for the electrical measurements. The flat surfaces of the cylindrical pellet were coated with good quality graphite to obtain a good conductive surface layer. A traveling microscope (Least count = 0.001 cm) was used to measure the dimensions of the pellets. The dielectric measurements were carried out for the pellet of TiO₂ nano particles at different temperatures in the present study using the conventional parallel plate capacitor method using HIOKI 3532-50 LCR HITESTER instrument from 50 Hz to 5 MHz at different temperatures (308 K- 368 K). The measurements of dark current and photo current were made using a picoammeter (Keithley 485).

RESULTS AND DISCUSSION

The samples prepared in the present study are of yellowish green in colour. The yield percentage and grain size obtained in the present study are provided in the Table.1. Moreover, the yield percentage is observed to be significantly high and the results obtained indicate that the microwave assisted solvothermal method with green synthesis is a considerable one for the preparation of TiO₂ nano particles.

The powder XRD pattern of the green synthesized of TiO₂ nanoparticles are shown in Fig. 1. The peak positions and their relative intensities in sample are consistent with the standard powder diffraction pattern of TiO₂. The peaks are observed in the diffractogram around at 2θ = 24.95°, 37.44°, 47.70°, 53.60° and 62.41° corresponding planes (1 0 1)

(1 1 2) (2 0 0) (1 0 5) and (2 0 4) respectively. These 2θ values could be well indexed to anatase with tetragonal crystal structure (JCPDS no. 21-1272). The products are pure in phases with the calculated lattice constants, $a = b = 3.77 \text{ \AA}$ and $c = 9.53 \text{ \AA}$. These parameters are in good agreement with the values given in literature [14]. The presence of sharp diffraction peaks in the XRD confirms that the products are highly crystalline. The broadening of the peaks was attributed to the nanoscale size of the nanocrystals. Using half maxima width and the position of the diffraction peaks, the grain size of TiO_2 nanoparticles can be precisely estimated from the powder XRD spectrum. The size of crystallite TiO_2 nanoparticle samples was calculated using the Debye-Scherrer formula [13]. The broadening of TiO_2 peaks is due to the small particle size. The crystallite size of the TiO_2 nanoparticle calculated by applying the Scherrer's equation yielded a value of about 18 nm.

Table 1. Reaction time, yield percentage, and grain size

Sample Name	TiO₂
Reaction Time (min)	16
Yield Percentage %	35
Grain Size (nm)	18.6

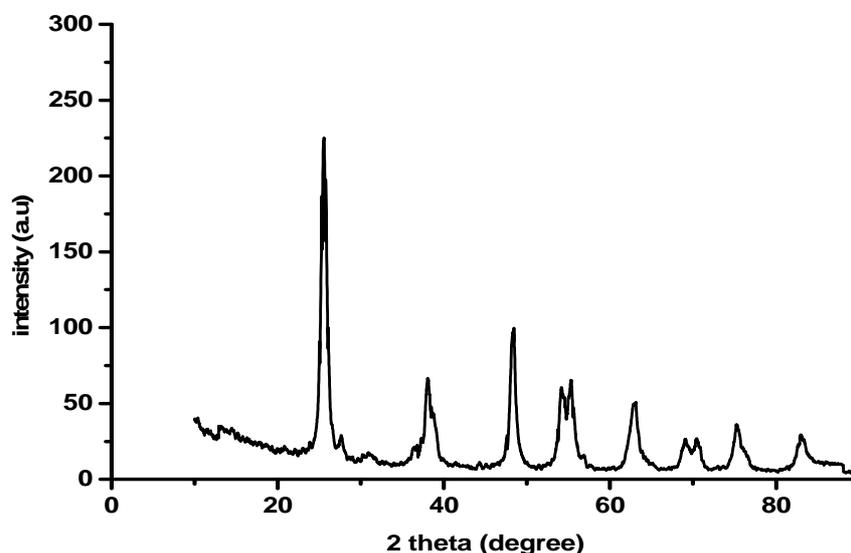


Fig. 1. The PXRD pattern for TiO_2 nano particles

The frequency variation studies are carried out to understand the electrical homogeneity of the material by identifying the relaxation mechanism as well as the nature of electrical conduction. These studies also help to find out the dielectric parameters of the material. Dielectric properties are associated with electro-optic property of the materials. Microelectronics industry needs low dielectric constant (ϵ_r) materials as an interlayer dielectric [15-16]. The electrical parameters, viz. σ_{dc} , ϵ_r , $\tan\delta$ and σ_{ac} observed in the present study are shown in Figs. 2-10. The ϵ_r values obtained for the TiO_2 (2.702 for Hz) are very small when compared to that observed for bulk crystals of the same (8.325 for Hz) [17]. The ϵ_r value observed in the present study (at 308 K with a frequency of 1 kHz) is only 13.028 which is high when compared to that reported for the bulk crystal.

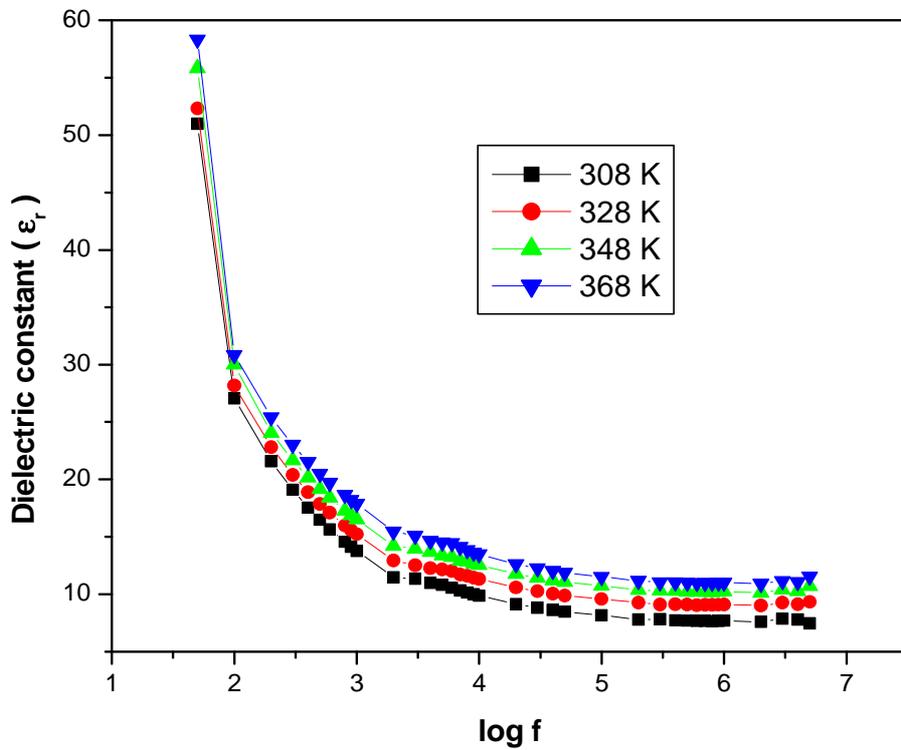


Fig. 2. Variation of dielectric constant with log frequency at different temperatures for TiO₂ nano particles (pelletised)

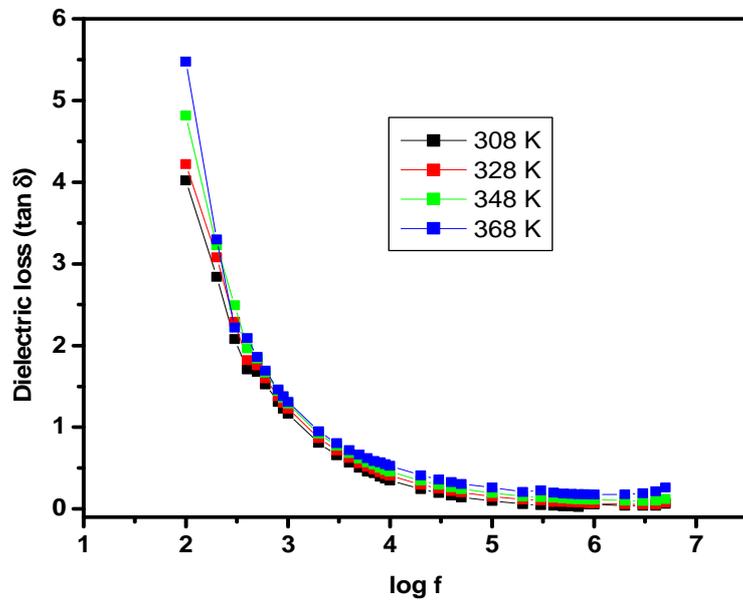


Fig. 3. Variation of dielectric loss with log frequency at different temperatures for TiO₂ nano particles (pelletised)

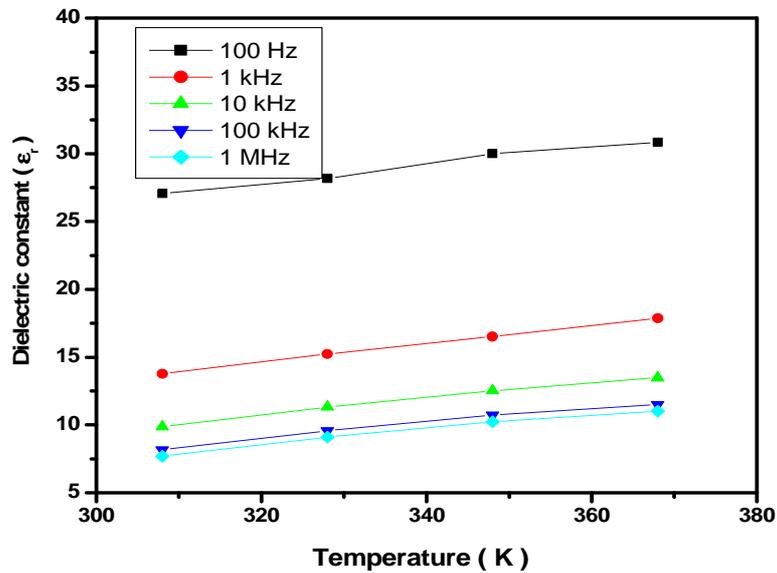


Fig. 4. Temperature dependence of dielectric constant for TiO₂ nano particles (pelletised)

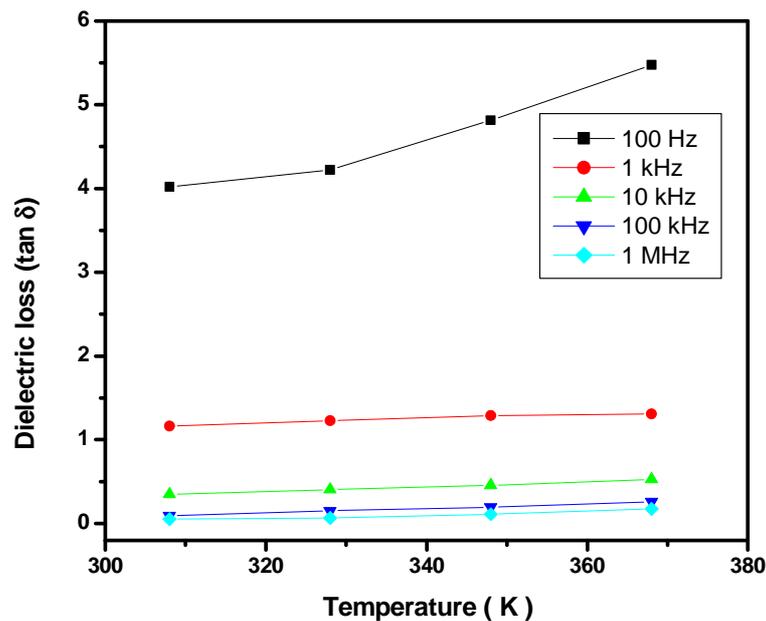


Fig. 5. Temperature dependence of dielectric loss for TiO₂ nano particles (pelletised)

In semiconductors a fundamental optical absorption process may occur if the photon energy is larger than the bandgap thus creating an electron and a hole. This electron hole (e-h) pair can move independently of one another resulting in electrical conductivity. The separation of the electron and the hole usually is large enough so that there is no coulombic attraction between them. Such description of non-interacting electrons and holes corresponds to the so called single particle presentation. If the absorption occurs at point ($k = 0$) and with a photon energy slightly below the bandgap, electrons and holes do interact via coulomb potential and form quasiparticle that corresponds to a hydrogen-like bound state of an e-h pair which is referred to as an exciton.

The binding energy of the exciton is strongly influenced by the presence of other electrons in the solid which screen the hole. In a continuum approximation the screening can be described by the dielectric constant of the material. The binding energies of the exciton are generally very small (large excitonic radius), i.e. they are on the scale of a few meV [18]. The excitonic states in solids are experimentally observable only at low temperatures because of the dissociation of the exciton into free carriers by the available thermal energy at room temperature. In contrast, in case of molecules the e-h pair is localized at the molecule resulting in a strong coulomb interaction. Thus, there is very little screening which leads to a strong excitonic absorption.

It is seen from the plot that the dielectric constant has high values in the low frequency regions for the TiO₂ nanoparticles and then it decreases with increasing frequency. In high frequency region both dielectric constant and dielectric loss are fairly remaining constant. The high dielectric constant at low frequency is due to the existence of different types of polarization mechanisms like electronic, ionic, orientation and space-charge polarization [19-21]. At lower frequencies at which all four types of polarizations contribute, the rapid increase in dielectric constant is mainly due to space charge and dipolar polarizations, which are strongly temperature dependent [22-23]. In the case of space charge polarizations, which is due to accumulation of charge at the grain boundary, an increase in polarization results as more and more charges accumulate at the grain boundary with the increase in temperature. From the Figs. 2 -5, it is found that the values of dielectric constant and dielectric loss increase with the increase in temperature and decrease with the increase of frequency. This may be due to the term contributing to dielectric constant from ion-dipole interactions being compensated by the thermal energy leading to the relaxation polarization. The low value observed for ϵ_r indicates that the polarization mechanism in the nanocrystals considered is mainly due to the space charge polarization. Due to the application of an electric field, the space charges are moved and dipole moments are created which are called as space-charge polarization. In addition to this, these dipole moments are rotated by the field applied resulting in rotation polarization which is also contributing to the high values. At high frequencies, the very low dielectric loss exhibited may be associated to the purity of the nanomaterial. So, it can be understood that there seems the occurrence of nano-confined states in the case of TiO₂ nanocrystals considered in the present study which may substantially contribute to the electrical properties. Thus, the space charge contribution plays an important role in charge transport process and polarizability in the case of TiO₂ nanocrystals considered in the present study. The general trend is that dielectric losses increase with increasing temperatures as shown in Figs. 4-5. To clearly state about this semi-conduction behavior which appears with increasing processing temperatures.

The electrical resistivity of nanocrystalline material is higher than that of both conventional coarse grained polycrystalline material and alloys. The magnitude of electrical resistivity and hence the conductivity in composites can be changed by altering the size of the electrically conducting component. The hopping (exchange) of the charge carriers in the lattice sites (which is responsible for electrical conduction) is thermally activated by increasing temperature. As a result, dielectric polarization increases causing an increase in dielectric constant and dielectric loss. Electrical conductivity depends on thermal treatment of materials. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies predominantly determine this region. The energy needed to form the defect is much larger than the energy needed for its drift. The σ_{ac} values in the temperature region studied are found to increase with increase in temperature for TiO₂ nano particles as shown in Figs. 6-7. The σ_{ac} and σ_{ac} values observed in the present study are very small (i.e. the resistivities are very large). When the crystal (grain) size is smaller than the electron mean free path, grain boundary scattering dominates and hence electrical resistivity is increased. From the graph, the value of *ac* activation energy for ionic migration was estimated as shown in Fig. 8. The variation of *dc* conductivity with temperature is shown in Fig. 9. From the graph, it is observed that conductivity increases as the temperature increases. The *dc* activation energy is found to be 0.0437 eV (Fig. 10). This indicates that TiO₂ nanocrystals may be considered as a low ϵ_r value dielectric material which is gaining more importance nowadays in the microelectronics industry.

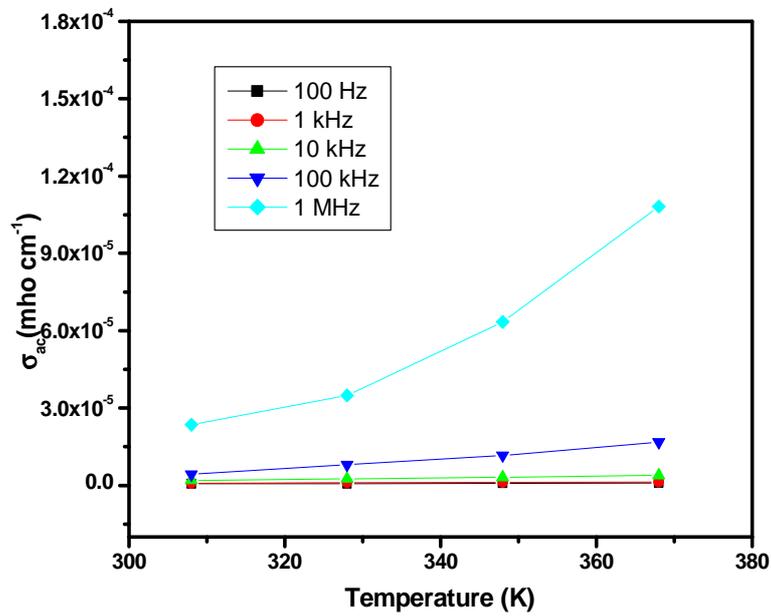


Fig. 6. The *ac* electrical conductivities for TiO₂ nano particles (pelletised)

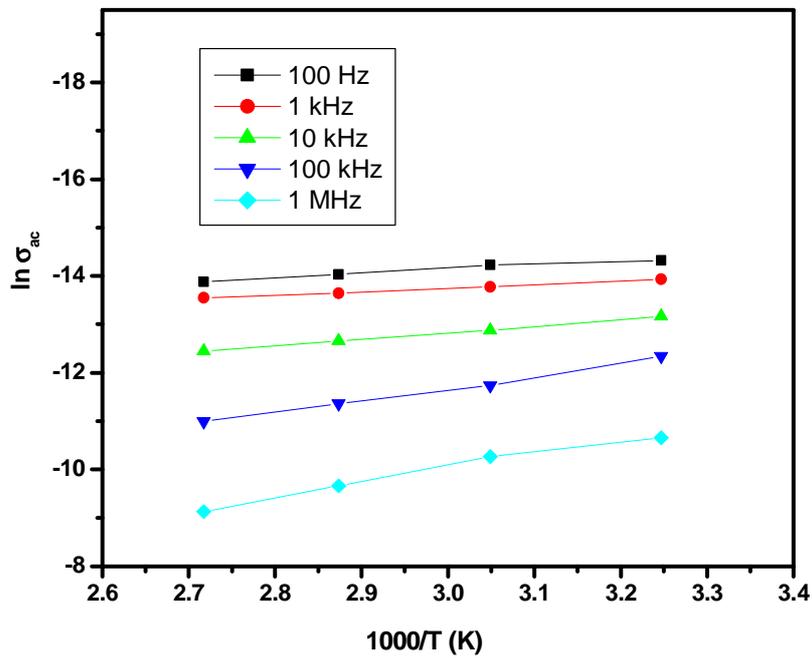


Fig. 7. Plot of $\ln(\sigma_{ac})$ versus $1000/T$ for TiO₂ nano particles (pelletised)

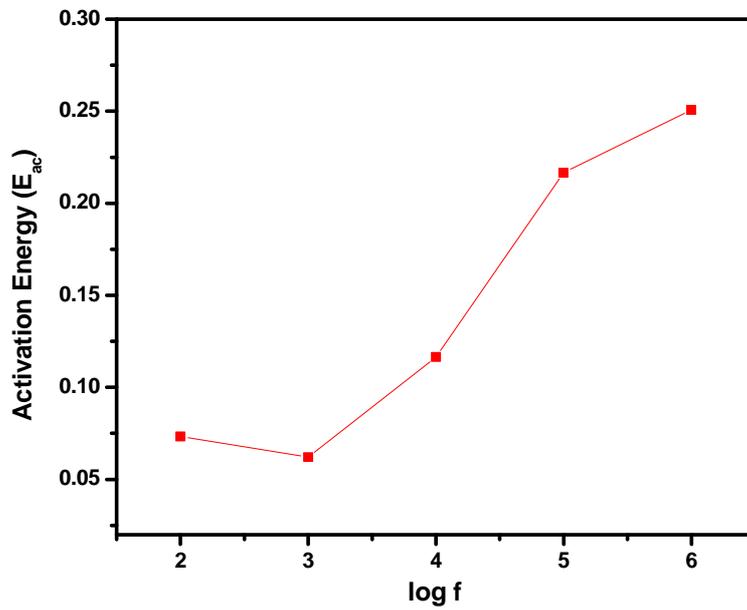


Fig. 8. Frequency dependence of *ac* activation energy for TiO₂ nano particles (pelletised)

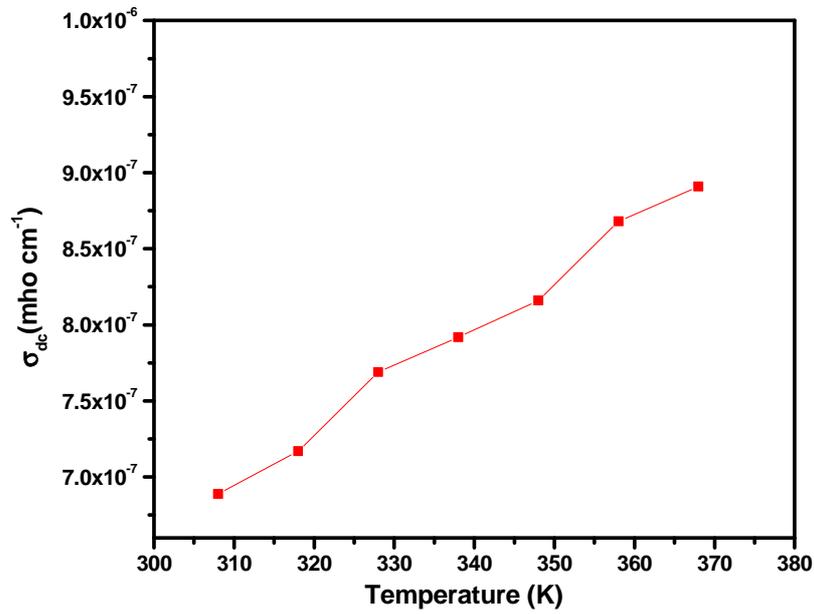


Fig. 9. The *dc* electrical conductivities for TiO₂ nano particles (pelletised)

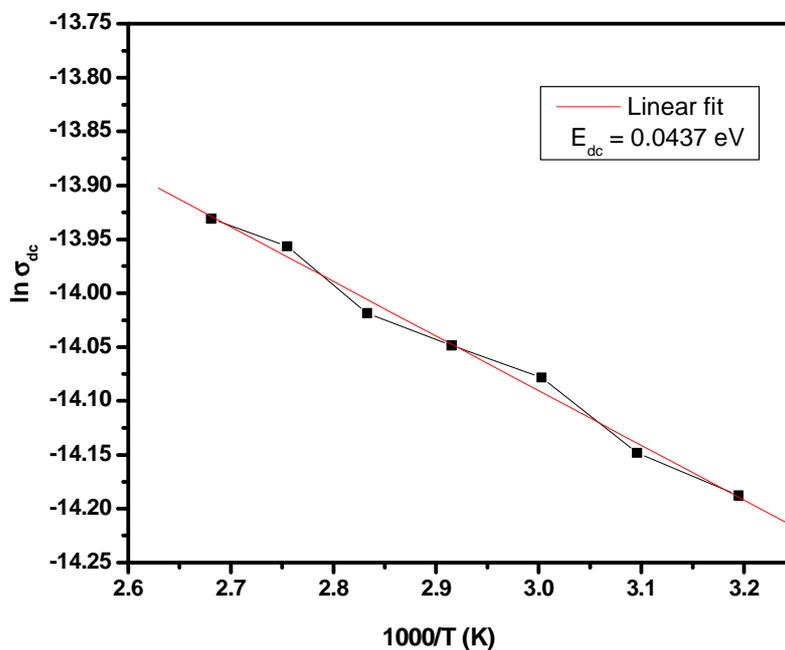


Fig. 10. Plot of $\ln(\sigma_{dc})$ versus $1000/T$ for TiO_2 nano particles (pelletised)

The dark current as well as the photocurrent measurements on the prepared sample was recorded using a Keithley 480 picoammeter. The applied field was varied from 130–3500 V/cm. The sample was covered with a black cloth to avoid exposure to any radiation and the corresponding values of the dark current were noted. To measure the photo current, the sample was illuminated with a halogen lamp (100W) containing iodine vapour by focusing a spot of light on the sample with the help of a convex lens. The applied field was increased from 130–3500 V/cm and the corresponding photo current was recorded.

The photo current and dark current are plotted as a function of the applied field which is shown in Fig. 11. Both the photocurrent and dark current of TiO_2 nano particles increase linearly with applied field. It is observed from the plot that the dark current is less than the photo current, hence it is concluded that TiO_2 nano particle exhibits positive photo conducting nature. The centers are probably cation (i.e Ti) vacancies and are thus negatively charged even after capturing holes. They may be a very small cross section for capturing electron and lifetime of photo excited electrons is essentially the same order as that for the release of holes from the trapping centers. The TiO_2 nano particle is found to be very photosensitive because oxygen anions equally share with Ti vacancies and influence the band gap energy.

In general positive photoconductivity is attributed to generation of mobile charge carriers caused by the absorption of photons [24]. Photoconductivity results if the effect of light is primarily either to increase the density of free carriers or if the effect of light is to decrease the resistance of barriers in the material. The action of light in this case is to decrease the height of the barrier, thus permitting greater charge carrier flow between different regions of the photoconductor [25]. Results obtained in the present study indicate the photo current is higher than that of dark current it is referred to as positive photoconductivity.

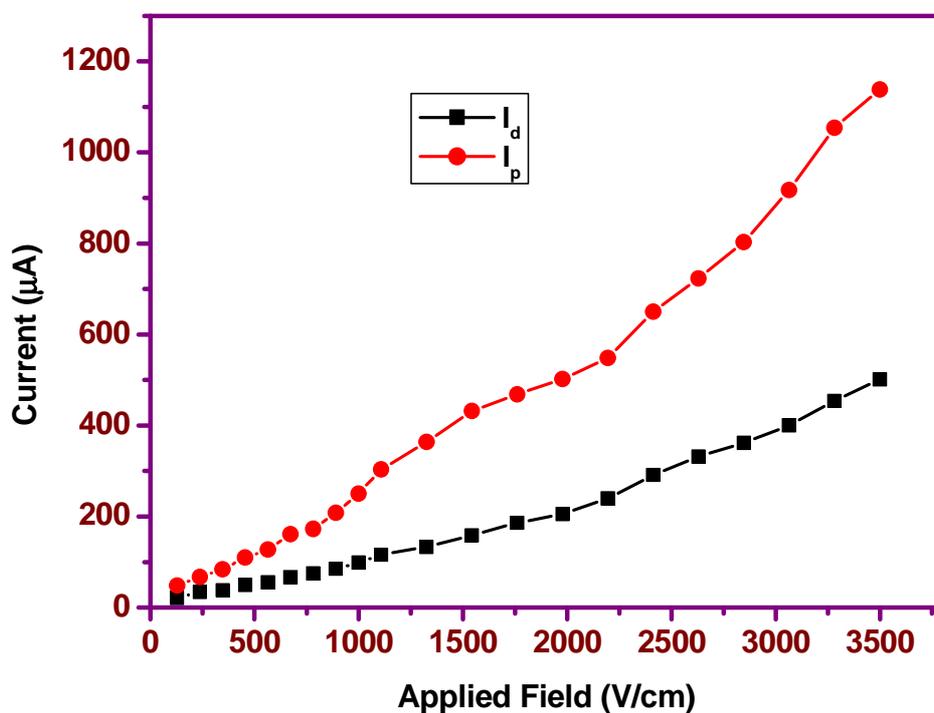


Fig. 11. Field dependent photoconductivity of TiO₂ nano particles (pelletised)

CONCLUSION

The TiO₂ nano particles were synthesized via a convenient microwave assisted solvothermal with green synthesis method using domestic microwave oven and characterized by PXRD, and electrical (both AC and DC) measurements. The yield percentage and grain size estimated indicate that the method used in the present study is a reasonable one for the preparation of TiO₂ nano particles. The positive photoconducting nature of the sample is confirmed by photoconductivity study. The dielectric parameters increase with the increase in temperature. The *ac/dc* conductivity studies are carried out and the activation energy is also determined. The present study indicates that the possible occurrence of nano-confined state in the TiO₂ nano particles studied. The low value of dielectric constant at higher frequencies is important for the fabrication of materials for ferroelectric, photonic and electronic devices.

Acknowledgements

Authors (P. Saravanan, A. Charles and M. Vimalan) would like to thank the management, Mr. T. Mohanraj (Principal i/c) and Dr. R. Sendhil Kumar (Administrative Officer), Thirumalai Engineering College, Kilambi, Kancheepuram, Tamil Nadu, India, for their encouragement, support, valuable suggestions and useful discussion.

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