

Synthesis and electrical properties of TiO₂ nanoparticles using a wet chemical technique

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Abstract: TiO₂ nanoparticles were synthesized using a wet chemical technique. The as prepared nanopowder was used for further characterization. The prepared TiO₂ nanoparticles were characterized for phase composition, using X-ray diffractometry. The particle size and morphology were studied using Scanning electron microscope and transmission electron microscopy. The dielectric properties of TiO₂ nanoparticles were studied in the different frequency range of 50Hz-5MHz at different temperatures. The frequency dependence of the dielectric constant and dielectric loss is found to decrease with an increase in the frequency at different temperatures. Further, the electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the TiO₂ nanoparticles were calculated.

Keywords: TiO₂, Wet chemical, SEM, TEM, Dielectric Studies

1. Introduction

The oxide nanoparticles synthesized by several methods appear more and more useful, because these nanoparticles have good electrical, optical and magnetic properties that are different from their bulk counterparts[1]. Titania nanoparticles have received great interest for applications in optical devices, sensors, and photocatalysis[2,3]. There are several factors in determining the important properties such as the particle size, crystallinity and morphology that affect in the performance of TiO₂ in applications[4-6]. Major research efforts have recently focussed on the fabrication and characterisation of nano-sized dielectric materials, because the current technology requires very small sized particles to miniaturise microwave devices and components. Particularly, TiO₂ has been utilised in wide applications such as gas- and temperature-sensing devices[7,8], photocatalytic devices[9] and photoelectric devices[10]. Recently, TiO₂ has attracted attention for use in fabricating capacitors in microelectronic devices due to its unusually high dielectric constant. Although the dielectric properties of bulk TiO₂ having micron-sized grains have been well reported[11], those of TiO₂ having nano-sized grains have received less attention because of the difficulties in fabrication. Changes in the dielectric

properties were attributed to changes in the particle size, shape, and boundaries[12, 13]. The modified dielectric properties were used in devices, such as capacitors, electronic memories, and optical filters. The high dielectric permittivity and the low loss factors over a wide frequency range are always of great interest[14]. In the present investigation, we report the synthesis and characterization of TiO₂ nanoparticles by the wet chemical synthesis technique. The as-prepared TiO₂ nanoparticles are characterized by X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The scope of the present work is to study the dielectric properties of TiO₂ nanoparticles as a function of the frequency and the temperatures.

2. Experimental Procedure

TiO₂ nanoparticles were prepared using H₂O₂ solution added to 10 ml of 1 mol/l ethanol solution of titanium tetra isopropoxide (TTIP). Ethanol was added to the brown coloured solution obtained, and the total volume of the solution was adjusted to 100 ml. The solution was then heated at 60°C for 1hr in a closed vessel. The solution was calcined at 600°C for 3hr to obtain white titanium oxide powder.

3. Results and Discussion

3.1. Powder X-Ray Diffraction Analysis

In order to determine the size and to study the structural properties of the synthesized nanoparticles of TiO₂, the powder XRD analysis was performed. From Fig. 1, it can be clearly observed that the diffraction peaks appear in the pattern corresponding to the anatase phase with good crystalline nature. The average particle size of TiO₂ nanoparticles has been found to be 13 nm.

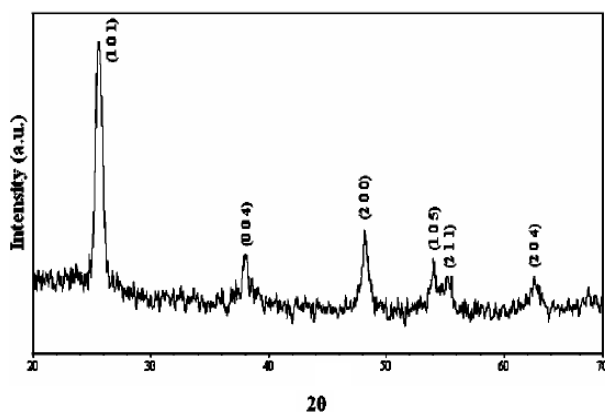


Fig 1. XRD spectrum of TiO₂ nanoparticles

3.2. Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of TiO₂. Fig. 2 shows the SEM images of the as-prepared TiO₂ nanoparticles. The TiO₂ nanoparticles formed were highly agglomerated. The spherical shaped particles with clumped distributions are visible through the SEM analysis.

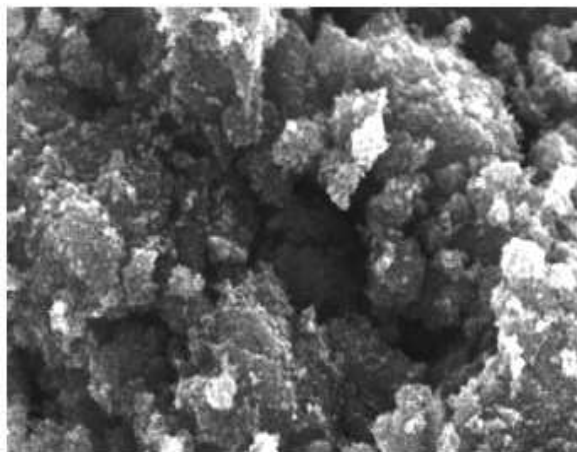


Fig 2. SEM Image of the TiO₂ nanoparticles

3.3. Transmission Electron Microscopy (TEM)

The transmission electron microscopic analysis was carried out to confirm the actual size of the particles, their

growth pattern and the distribution of the crystallites. It is evident from the micrographs that the average size of the particles as directly measured from the ruler of the image is ~13 nm. TEM image of the prepared TiO₂ nanoparticles as shown in Fig.3.

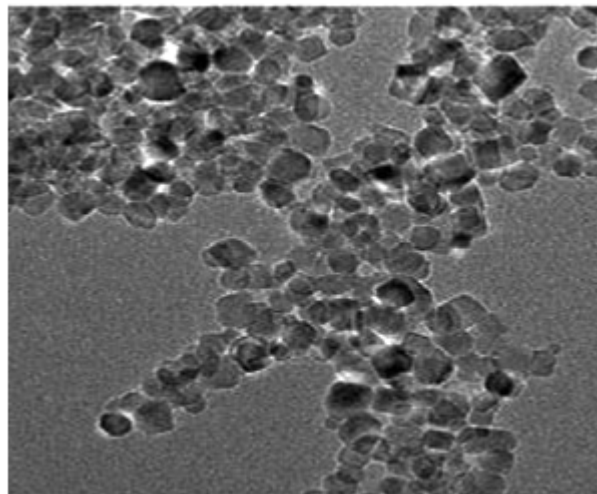


Fig 3. TEM image of TiO₂ nanoparticles

3.4. Dielectric Properties

The dielectric constant and the dielectric loss of the TiO₂ nanoparticles were studied at different temperatures using the HIOKI 3532 LCR HITESTER instrument in the frequency region of 50 Hz to 5 MHz. The dielectric constant was measured as a function of the frequency at different temperatures as shown in Fig.4, while the corresponding dielectric losses are depicted in Fig.5. Fig. 4 shows the plot of the dielectric constant (ϵ_r) versus applied frequency. It is observed (Fig.4) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. This also indicates that the value of the dielectric constant increases with an increase in the temperatures. The net polarization present in the material is due to ionic, electronic, dipolar and space charge polarizations[15]. The large value of the dielectric constant is due to the fact that TiO₂ acts as a nanodipole under electric fields. The small-sized particles necessitate a large number of particles per unit volume, resulting in an increase of the dipole moment per unit volume, and a high dielectric constant. The dielectric loss studied as a function of frequency at different temperatures is shown in Fig.5. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency at almost all temperatures, but appears to achieve saturation in the higher frequency range at all the temperatures. In the low frequency region, high energy loss is observed, which may be due to the dielectric polarization, space-charge and rotation-direction

polarization occurring in the low frequency range.

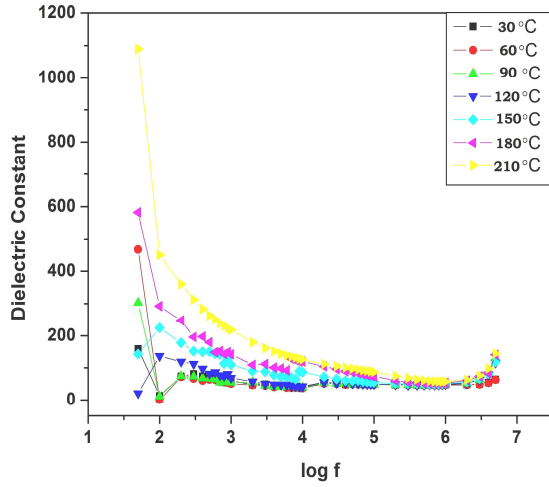


Fig 4. Dielectric constant of TiO_2 nanoparticles, as a function of frequency

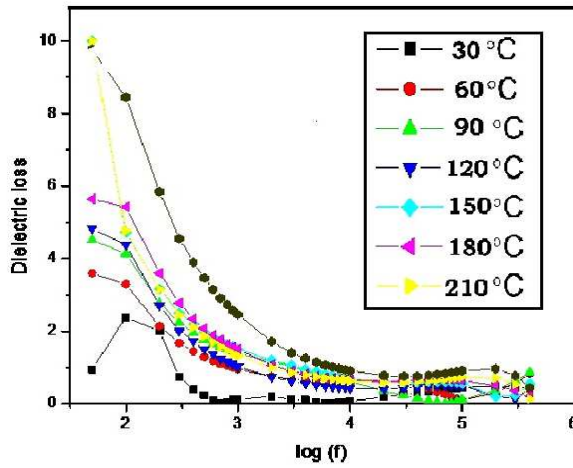


Fig 5. Dielectric loss of TiO_2 nanoparticles, as a function of frequency

In the proposed relation, only one parameter viz, the high frequency dielectric constant is required as input, to evaluate electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the TiO_2 nanoparticles. The theoretical calculations show that the high frequency dielectric constant is explicitly dependent on the valence electron Plasmon energy, an average energy gap referred to as the Penn gap and Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy[16]. The valence electron plasma energy, $\hbar\omega_p$, is calculated using the relation[17],

$$\hbar\omega_p = 28.8 \left(\frac{Z\rho}{M} \right)^{1/2} \quad (1)$$

According to the Penn model[18], the average energy gap for the TiO_2 nanoparticles is given by

$$E_P = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{1/2}} \quad (2)$$

where $\hbar\omega_p$ is the valence electron plasmon energy and the Fermi energy[16] given by

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (3)$$

Then we obtained the electronic polarizability α , using a relation[18, 19],

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_F^2} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (4)$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F} \right] + \frac{1}{3} \left[\frac{E_P}{4E_F} \right]^2 \quad (5)$$

The value of α obtained from equation (4) closely matches with that obtained using the Clausius-Mossotti relation,

$$\alpha = \frac{3}{4} \frac{M}{\pi N_a \rho} \left[\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \quad (6)$$

Considering that the polarizability is highly sensitive to the bandgap[20], the following empirical relationship is also used to calculate α ,

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (7)$$

where E_g is the bandgap value determined through the UV absorption spectrum. The high frequency dielectric constant of the materials is a very important parameter for calculating the physical or electronic properties of materials. All the above parameters as estimated are shown in Table 1.

Table 1. Electronic properties of the TiO_2 nanoparticles

Parameters	Value
Plasma energy ($\hbar\omega_p$)	18.73 eV
Penn gap (E_p)	3.21 eV
Fermi Energy (E_F)	14.52 eV
Electronic polarizability (using the Penn analysis)	6.88 x 10 ⁻²⁴ cm ³
Electronic polarizability (using the Clausius-Mossotti relation)	6.89 x 10 ⁻²⁴ cm ³
Electronic polarizability (using bandgap)	4.18 x 10 ⁻²⁴ cm ³

4. Conclusion

TiO₂ nanoparticles have been successfully synthesized using a wet chemical technique. The formation of the TiO₂ nanoparticles was confirmed by powder X-ray diffraction (XRD). The size and morphology of the samples were characterized using scanning and transmission electron microscopy (SEM and TEM). The spherical shaped particles were confirmed through the SEM analysis. The transmission electron microscopic analysis confirms the prepared TiO₂ nanoparticles with the particle size of around 13 nm. The dielectric constant and dielectric loss of the TiO₂ nanoparticles are measured in the frequency range of 50Hz-5MHz at different temperatures. The dielectric studies reveal that both the dielectric constant and dielectric loss decrease with an increase in the frequency. The dielectric characterization shows the low value of the dielectric constant at higher frequencies. Some of the electronic properties like the plasma energy, Penn gap, Fermi energy and electronic polarizability of the TiO₂ nanoparticles have been calculated.

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