Controlled Phase Transition in Titania Nanoparticles – Effect of Calcination Temperature

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ABSTRACT

Titania (TiO₂) nanoparticles (NPs) have attracted worldwide attraction because of their high refractive index, high dielectric constant, excellent photocatalytic abilities, high photoelectric conversion efficiency. These advantages of titania have led its applications in solar cells as a window layer and other optoelectronic devices. Titania NPs are synthesized via sol-gel method using TiCl₄ as precursor. NPs are prepared at low temperature of 60°C. Presence of (020), (202), (321), (402), (322), (040), (400) and (513) diffraction peaks correspond to brookite phase of titania under as-synthesized conditions.

NPs are calcined in temperature range of 100 to 1000°C. XRD results indicate that brookite to anatase phase transformation starts at 300°C. In the calcination temperature range of 300-400°C phase transformation from brookite to anatase completes. Increasing the calcination temperature to 500-800°C results in formation of rutile phase of titania. Further increase in calcination temperature results in phase stability of rutile phase. SEM results indicate the formation of spherical NPs with diameter ~20-50nm. Comparison of structural and dielectric properties indicates that dielectric constant and tangent loss are strongly affected by the formation of different phases of titania. Highest dielectric constant of 225 (log f = 6.0) is observed for nanoparticles calcined at 400°C. Titania nanoparticles show high transmission in the visible and infrared region with band gap in the range of 2.98eV-3.05eV with variation in phases of titania.

1. INTRODUCTION

Nanotechnology is the manipulation of matter at nanometer scale. It is the technique in which physical principles are used to make structures at nanometer scale, having at least one dimension ranging from 1 to 100 nm. In 1959 Feynman presented the idea of nano regime in American Physical Society annual meeting, by saying historic words “There’s Plenty of Room at the Bottom”. Since then a lot of scientist and engineers are working and exploiting the interesting facts of nanoscale structures, and in recent years the main research interest is working on nanoscale, where all the
research has shifted from micro scale to nanoscale (Carneiro et al. 2009, Moser et al. 2013).

At nanometer scale materials' physical, chemical and biological properties change when the size is reduced to 100 nm and below. These properties arise from the quantum mechanical nature of the nano structured materials. When the matter is pushed to nanometer scale, with decrease in the size, the surface area is increased which accounts for an increase in the surface free energy. This arises due to the fact that with decrease in the size there occurs a change in interatomic spacing. This change in interatomic spacing also leads to the lowering of melting point (Sakai et al. 2013, Wu et al. 2012).

Among various materials studied at nanoscale titania (TiO$_2$) is a promising candidate owing to its high refractive index, high dielectric constant and low absorption capability. Among various crystallized polymorphs of titania three important crystallographic structures are: 1) Rutile with tetragonal crystal structure; 2) Anatase with tetragonal structure; 3) Brookite with orthorhombic structure (Riaz and Naseem 2015).

As a stable semiconducting material titania has been used in various optoelectronic devices. Brookite, anatase and rutile has optical band gaps of ~3.3eV, 3.4eV and 3.0eV, respectively (Landmann et al. 2012). The basic building block of titania is composed of Ti atom which is surrounded by six oxygen atoms with elongated Ti-O bond (Ulrike 2003).

Phase transition between different phases of titania is the topic of research as the synthesis and calcination conditions dictate the phases present in titania. We here report sol-gel synthesis of titania nanoparticles. The particles are studied under as-synthesized conditions as well as after annealing in the temperature range of 100-1000°C. However, results of as-synthesized and annealed at 400°C and 1000°C are reported in this paper.

2. EXPERIMENTAL DETAILS

Titania nanoparticles were synthesized using sol-gel method. Titanium tetrachloride was used as precursor. Deionized (DI) water and ethanol were used as solvents. Titanium tetrachloride was dissolved in DI water and ethanol. Reaction was exothermic and was carried out in water bath. Detailed sol-gel synthesis was reported earlier (Riaz and Naseem 2015). Titania sol was heat treated at 60°C to obtain titania nanoparticles.

These nanoparticles were studied under as-synthesized and calcined conditions. However, results of few samples under optimized conditions have been reported in this paper i.e. as synthesized and after calcination at 400°C and 1000°C. Bruker B8 Advance X-ray diffractometer and 6500B Precision Impedance Analyzer were used to study structural and dielectric properties. Optical analysis was carried out using JA Wollam M-2000 Variable Angle Spectroscopic Ellipsometer.
3. RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern for titania nanoparticles under as-synthesized conditions. Presence of diffraction peaks, under as-synthesized conditions, corresponding to planes (020), (220), (202), (321), (402), (322), (040), (004), (513) indicated the structure of brookite phase (JCPDS card no. 76-1934).

Brookite nanoparticles are obtained under the conditions when $\text{[TiO}_6^6\text{]}$ octahedron is enclosed by three octahedrons. Presence of OH$^-$ ions are crucial for the formation of brookite phase. Under as-synthesized conditions, less oxygen ions are removed from octahedral sites as a result of which brookite phase appears (Riaz and Naseem 2015). Phase transition from brookite to anatase phase was observed as these nanoparticles were calcined at 400˚C (Fig.2) while transition to rutile phase was observed as these particles were calcined at 1000˚C (Fig. 3).

![Fig. 1 XRD patterns for TiO$_2$ nanoparticles under as-synthesized conditions](image)
Fig. 2 XRD patterns for TiO$_2$ nanoparticles calcined at 400°C (*Anatase)

Fig. 3 XRD patterns for TiO$_2$ nanoparticles calcined at 1000°C (*Rutile)
Crystallite size \( t \) (Cullity 1956) and dislocation density \( \delta \) (Kumar et al. 2011) were calculated using Eqs. 1-2

\[
\theta = \frac{0.9\lambda}{B \cos \theta} \tag{1}
\]

\[
\delta = \frac{1}{t^2} \tag{2}
\]

Where, \( \theta \) is the diffraction angle, \( \lambda \) is the wavelength \((1.5406\text{Å})\) and \( B \) is Full Width at Half Maximum. Crystallite size (Table 1) decreased as calcination temperature was increased to 400˚C. However, increase in crystallite size was observed with increase in calcination temperature to 1000˚C. Lattice parameters for titania nanoparticles are close to those reported in literature (Ulrike 2003, Landmann et al. 2012, Riaz and Naseem 2015).

Table 1 Structural parameters for titania nanoparticles

<table>
<thead>
<tr>
<th>Temperature (˚C)</th>
<th>Crystallite size (nm)</th>
<th>Dislocation density ( \left(10^{15} \text{lines/m}^2\right) )</th>
<th>Lattice parameters</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td>25.56</td>
<td>1.530658</td>
<td>a=9.2Å, b=5.5Å, c=5.16Å</td>
<td>Brookite (Orthorhomic)</td>
</tr>
<tr>
<td>400</td>
<td>18.25</td>
<td>3.002439</td>
<td>a=3.8Å, c=9.51Å</td>
<td>Anatase (Tetragonal)</td>
</tr>
<tr>
<td>1000</td>
<td>23.45</td>
<td>1.818504</td>
<td>a=4.6Å, c=2.94Å</td>
<td>Rutile (Tetragonal)</td>
</tr>
</tbody>
</table>

Dielectric constant \( \varepsilon \) and tangent loss \( \tan \delta \) were determined using Eqs. 3 and 4 (Barsoukov and Macdonald 2005).

\[
\varepsilon = \frac{Cd}{\varepsilon_o A} \tag{3}
\]

\[
\tan \delta = \frac{1}{2\pi\varepsilon_o \varepsilon \rho f} \tag{4}
\]

Where, \( C \) is the capacitance, \( \varepsilon_o \) is the permittivity of free space, \( A \) is the area, \( f \) is the frequency and \( \rho \) is the resistivity. In low frequency region, decrease in dielectric constant (Fig. 4) is ascribed to diverse polarization. Polarizations that add to dielectric constant at low frequencies are: 1) space charge polarization, 2) ion displacement polarization, 3) electron displacement polarization. On the other hand, in high frequency region only electron displacement polarization takes place (Riaz et al. 2015, Barsoukov and Macdonald 2005). Further, in polycrystalline aggregate both grain and grain boundaries affect the dielectric constant. Role of the grains dominates at high frequencies. Grain boundaries are themselves functional in low frequency region thus producing dispersion in dielectric constant at low frequencies. The relaxation peaks
observed in tangent loss data is ascribed to resonance effect. This effect arises when frequency of externally applied field becomes equal to jumping frequency of ions (Riaz et al. 2015).

Dielectric constant and tangent loss of titania nanoparticles can be seen in table 2. It can be seen that dielectric constant increases from 150 (log $f = 6.0$) to 225 (log $f = 6.0$) as titania nanoparticles were calcined at 400˚C. This increase in dielectric constant and tangent loss is associated with phase transition from brookite to anatase phase i.e. structural transition from orthorhombic to tetragonal phase as was observed in Fig. 1. In addition, it was observed in Table 1 that crystallite size reduces from 25.56nm to 18.25nm as titania nanoparticles were calcined at 400˚C. The reduction in crystallite size increases number of grain boundaries. Electrons that travel through the more conducting grain boundaries, under the application of field, pile at the grain boundaries that offer more resistance (Riaz et al. 2015, Barsoukov and Macdonald 2005). Thus, dielectric constant increases. Decrease in dielectric constant at high calcination temperature is associated with increase in crystallite size and phase transition to rutile phase (Table1).

Table 2 Dielectric constant and tangent loss for Titania nanoparticles

<table>
<thead>
<tr>
<th>Calcination temperature (˚C)</th>
<th>Phase</th>
<th>Dielectric constant (log $f = 6.0$)</th>
<th>Tangent loss (log $f = 6.0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td>Brookite</td>
<td>150</td>
<td>0.0060</td>
</tr>
<tr>
<td>400</td>
<td>Anatase</td>
<td>225</td>
<td>0.0018</td>
</tr>
<tr>
<td>1000</td>
<td>Rutile</td>
<td>210</td>
<td>0.0020</td>
</tr>
</tbody>
</table>
Fig. 5 shows transmission curves for titania nanoparticles. It can be seen that titania nanoparticles exhibit high transmission in the visible and infrared region. Sharp increase in transmission at wavelength 375-425nm is indicative of direct band gap of titania nanoparticles. It can be seen that transmission of titania nanoparticles decreases as these nanoparticles were calcined at 400˚C. This decrease in transmission is associated with decrease in crystallite size (Table 1). Decrease in crystallite size results in increase in number of grain boundaries that act as scattering centres for incident photons thus resulting in decrease in transmission (Riaz and Naseem 2015). Increase in transmission with increase in calcination temperature is associated with increase in crystallite size. This leads to decrease in grain boundaries and hence less scattering from grain boundaries. $d^2$ vs. $E$ (eV) curve for titania nanoparticles can be seen in Fig. 6. Titania nanoparticles exhibit direct band of 3.05eV, 3.01eV and 2.98eV for nanoparticles under as-synthesized conditions and after calcination at 400˚C and 1000˚C. Band gap values are close to that reported in literature (Ulrike 2003, Landmann et al. 2012, Riaz and Naseem 2015).
4. CONCLUSIONS

Titania nanoparticles were prepared using sol-gel method with titanium tetrachloride as precursor. These nanoparticles were studied under as-synthesized conditions and after calcination. Brookite, anatase and rutile phases of titania were obtained under as-synthesized conditions and after calcination at 400°C and 1000°C, respectively.
Dielectric constant and tangent loss both demonstrated normal dispersion behavior. Comparison of structural and dielectric properties revealed that highest dielectric constant of 225 ($\log f = 6.0$) was observed for nanoparticles calcined at 400˚C. Titania nanoparticles showed high transmission in visible and infrared region with band gap of 3.05eV, 3.01eV and 2.98eV under as-synthesized conditions and after calcination at 400˚C and 1000˚C, respectively.

REFERENCES