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Spectroscopic and acoustic studies on synthesized nanoTiO_2-PEG complex

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Abstract:
Polymer nanomaterial composites are of importance as they find application in a variety of nanophotonic designs. Nano titania is an important material and finds use in nanophotovoltaics, paints etc. Titania nanopowder produced by reactive thermal plasma synthesis was dispersed successfully in PEG(Polyethyleneglycol) polymer matrix and characterized by FTIR. Acoustic studies were done on nanotitania-PEG complex and acoustic parameters were calculated. Thin film of nanotitania-PEG complex was prepared by dipcoating and characterized by microRAMAN and UV-Vis spectroscopy.

Key words:
NanoTiO_2 powder, PEG, Thinfilm, Acoustic studies, Spectroscopic studies.

Introduction:

Nanocrystalline TiO_2 has gained a great popularity in the semiconductor photoelectrochemical field, the reason being its special chemical (photocorrosion and chemical corrosion stability, photocatalytic potential) and optical (optical stability, high sensitivity for UV-Visible light) properties. In recent years, significant attention has been given to nanocrystalline TiO_2 due to its application in many fields such as photoelectro catalysis[1,2], solar cells[3,4], gas sensing[5], electrochromic devices[6,7], air and water purification systems[8,9] etc. The effects of different nanomaterial complexes, as with polymers, are important due to their influence on specific surface area, porosity and morphology and related functions [10,11]. Polyethyleneglycol(PEG) being a flexible water soluble polymer finds application as surfactant, dispersant and as solvent in pharmaceutic and cosmetic industry. PEG is a polymer composed of hydrophilic ethyleneoxide units with hydroxyl groups at each end with good wetting properties. This makes PEG an ideal matrix for dispersion of colloidal TiO_2 nanopowder. Complexation with PEG prevents agglomeration of TiO_2 nanoparticles and increases their stability.

In the present work, we have prepared nanoTiO_2-PEG complex by dispersing TiO_2 nanopowder in PEG matrix. TiO_2 nanopowder prepared by reactive thermal plasma synthesis was studied by SEM and EDX to determine the size and morphology of the TiO_2 nanoparticles. This TiO_2 nanopowder was used to prepare nanoTiO_2-PEG complex by dispersion by sonication. The nanoTiO_2-PEG complex so prepared was characterized by FTIR. Acoustic studies were performed to confirm TiO_2 penetration in the polymer matrix. Thin film of nanoTiO_2-PEG complex was prepared by dipcoating method. MicroRAMAN and UV-Vis studies were done on the nanoTiO_2-PEG thin film.

Materials and Methods:

Preparation of nanoTiO2-PEG complex and thin film:

Polyethyleneglycol(PEG) (AR Grade) was obtained from Alfa Aesar. TiO_2 nanopowder prepared by reactive thermal plasma synthesis [12] was used. 1.5g of PEG200 was dissolved in 100ml of toluene. 30mg of TiO_2 nanopowder was added to this PEG solution yielding a 2% by weight TiO_2:PEG mixture in toluene. This mixture was sonicated for 20mins. Glass slubstrates of length

4.5cm, width 2.5cm and thickness 0.12cm were dip coated in this solution. The solution was stirred for 8hrs over a magnetic stirrer ensuring proper dispersion and uniform deposition of nanoTiO_2-PEG complex on the immersed substrate. The dipcoated glass substrates were annealed at 200^{o}c for 30mins.

TiO_2, nanoTiO_2-PEG complex and Thin film characterization:

Scanning electron microscopy (SEM), X-ray Diffraction (XRD) and Energy dispersive Xray analysis (EDX) of the TiO_2 nanoparticle were done at SAIF, IITM. Acoustic studies on the nanoTiO_2-PEG complex were done using Digital ultrasonic velocity Meter (Ultrasonic instruments), SCSVMV University at ultrasonic frequency of 2MHz by Pulse-echo-overlap method. The viscosity of the nanoTiO_2-PEG complex was determined by Brookfield Viscometer, set at a speed of 75 rotations/min. FTIR studies were carried out using FTIR-ALPHA-T BRUKER (400-4000cm^{-1}) at SCSVMV University. KBr pellet of TiO_2 nano powder was used FTIR analysis. UV-Vis spectroscopy was done on SPECORD 200/PLUS Analytik jenaUV/Vis spectrometer.

Results and Discussion:

Microstructure and phase of TiO_2 nano particle

X-ray diffraction pattern of TiO_2 nanopowder is shown in Fig.1. Enlisted are the observed peaks and their corresponding (hkl) indices in Table 1. .

Fig 1. XRD Pattern of TiO_2 nano particle

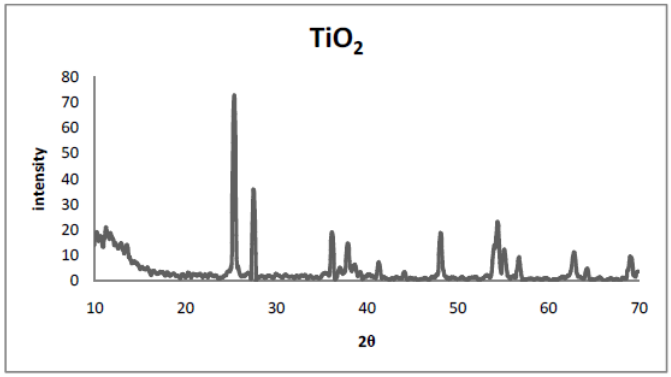
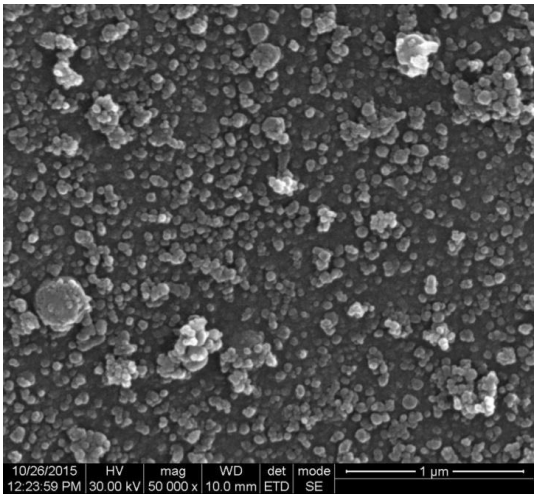


Table 1. XRD Pattern of TiO_2

Peaks	2ɵ (Degrees)	(h k l)
1	25.32	101
2	37.72	004
3	48	200
4	54.5	211
5	62.4	118

The prominent peak at 101 is characteristic of anatase TiO_2 with tetragonal structure[12]. The sharp peaks indicate that the TiO_2 nanopowder is crystalline in nature. This compares well with #JCPDS84-1286. The scanning electron microscopic image of the TiO_2 nano powder is shown in Fig2. The average size of the nanoparticles was to found be 39.1nm with specific surface area 153x10^6 m^{-1}.

Fig 2. SEM image of TiO_2 nano particle



EDX analysis confirms the purity of the TiO_2 sample with correct stoichiometric ratio of TiO_2. Figure 3 and Table 2 summarize results obtained in EDX analysis.

Fig 3. EDX analysis of the TiO_2 nano particle

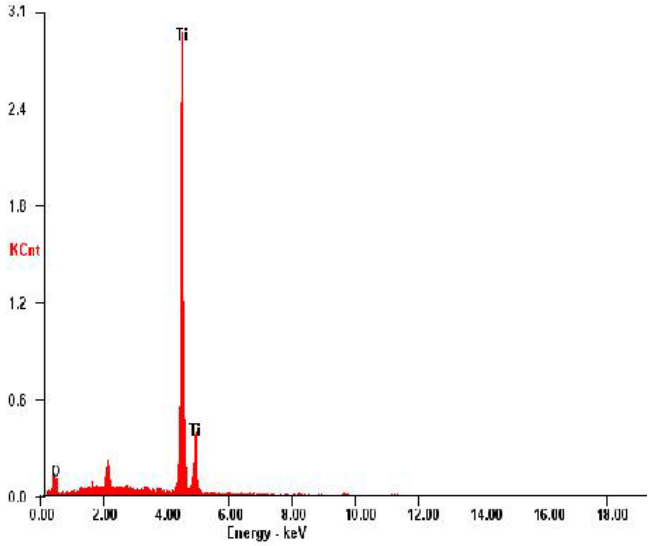


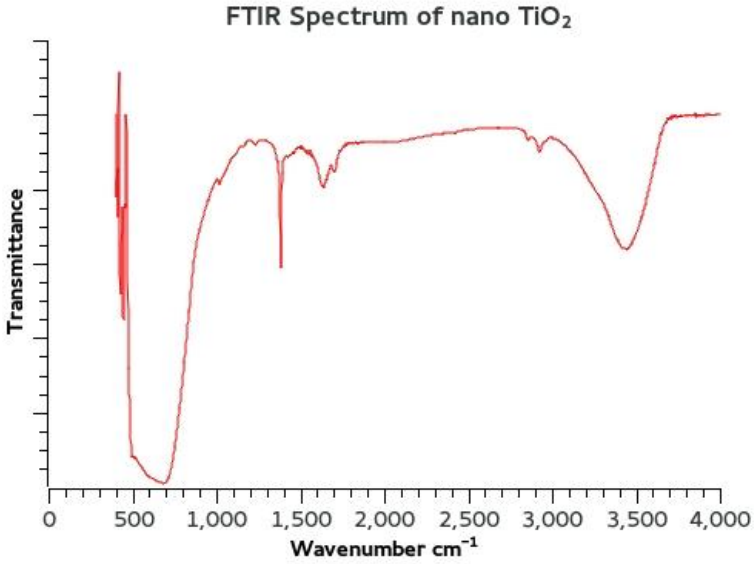
Table 2. EDX analysis of TiO_2 nanoparticle

Element	Wt%	At%
OK	15.84	36.04
TiK	84.16	63.96
Matrix	Correction	ZAF

FTIR Spectrum of nanoTiO_2

The FTIR spectrum of TiO_2 is shown in Fig 4. Prominent peaks characteristic of TiO_2 are observed at 1388 cm^{-1}, 1627 cm^{-1} and 3428 cm^{-1}. The broad band centered at 500-700 cm^{-1} is attributed to the vibration of the Ti–O-Ti bonds in the TiO_2 lattice. Peak at 1627 cm^{-1} and the broad peak appearing at 3428 cm^{-1} is assigned to stretching vibrations of hydroxyl groups and bending vibrations of the adsorbed molecular water species [12].

Fig 4. FTIR Spectrum of nanoTiO2



Acoustic studies on nanoTiO2-PEG complex

The ultrasonic parameters free volume V_f, adiabatic compressibility β, free lentgh L_f, internal pressure π_i, acoustic impedance Z, relaxation time τ, molar sound velocity R_v and Gibbs free energy can be calculated using the ultrasonic velocity, viscosity, density and effective molecular weight. Phenomena like particle-particle adhesion, mixing and degree of association can be inferred from these acoustic parameters.Ultrasonic velocity and viscosity measured for nanoTiO2-PEG200 complex are given in the following table

Table 3. Ultrasonic velocity and viscosity

Sample	Concentration in %	Density ρ(Kg/m^3)	Relative viscosity η(cp)	Ultrasonic Velocity U(m/s)
PEG200 + Toluene(306K)	2	856.589	1.008	1243.081
NanoTiO2-PEG complex+ Toluene(306K)	2	855.389	1.009	1240.951

Adiabatic compressibility is a measure of relative volume change of a fluid in response to change of pressure. It is also a measure of intermolecular association, repulsion or dissociation.

$\beta = 1/(U^2\rho)$

β – Adiabatic compressibility,

U- Ultrasonic velocity,

ρ – Density.

Free length is the distance between surfaces of neighboring molecules. An increase in ultrasonic

velocity through a substance means a decrease in free length.

$L_f = K_T \ \beta^{1/2}$

L_f – free length,

K_T – Jacobson's constant,

β – Adiabatic compressibility.

Free volume $V_f = Mw\ U/k\ \eta$

Mw – molecular weight,

k – Temperature independent constant,

η – Viscosity.

Internal pressure a measure of resultant force of attraction and repulsion between molecules is given by

$\pi_i = bRT(k\eta/U)^{1/2}\ (\rho^{2/3}/Mw^{7/6})$

b = 2 for all liquids,

R = 8.314 SI units,

T- Temperature,

$k = 4.28 \times 10^9$ Temperature independent constant.

Relaxation time (τ) is the time required for a viscous substance to recover from the shearing stress after flow has stopped. Relaxation time and absorption coefficient are directly correlated. It is given by

$\tau = (4/3)\ \eta k_c$

$k_c = 1/U^2\ \rho$

The acoustic impedance Z is a measure of transmission and reflection at the boundary of two materials differing in acoustic impedance. It is given by:

$Z = \rho\ U$

Where Z - acoustic impedance,

ρ – Density,

U – Ultrasonic velocity.

Gibbs free energy of the system is a measure of the relative stability of the system under different conditions.

$\Delta G = 2.303kT\log\ [h/kT\tau]$

k – Boltzmann's constant,

h – Planck's constant

The acoustic parameters calculated for PEG200 and nanoTiO_2-PEG200 complex are compared in table 4

.

Table 4. Acoustic parameters

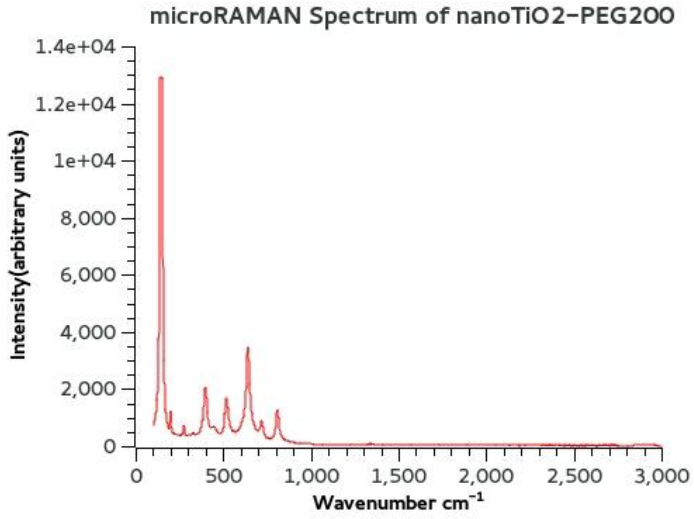
Acoustic Parameter	PEG200	TiO_2-PEG200	%Change	Nature of Change
Adiabatic compressibility $\beta(m^2/N)$	7.55489×10^{-10}	7.59149×10^{-10}	0.48	increase
Free length L(m)	5.73911×10^{-11}	5.75575×10^{-11}	0.28	increase
Free Volume $V_f(m^3/mol)$	1.39322×10^{-7}	1.38681×10^{-7}	0.46	decrease
Internal Pressure π_i (atm)	384249713.7	380641564.1	0.93	decrease
Relaxation Time τ(s)	1.0153×10^{-12}	1.0213×10^{-12}	0.59	increase
Specific Acoustic Impedance $Z(Kgm^{-2}s^{-1})$	1064810.132	1061495.835	0.31	decrease
Gibbs free energy ΔG (kJ/mol)	1.8706×10^{-21}	1.4944×10^{-21}	0.2	decrease

Increase in adiabatic compressibility clearly indicates reduction in intrachain interactions of the polymer due to incorporation and association of nanoTiO_2 in the voids of the polymer. Increase in free length along with the decrease in ultrasonic velocity indicates association of nanoTiO_2 sterically with the polymer effecting structural arrangement. Decrease in free volume of the polymer matrix clearly confirms TiO_2 entrapment in the PEG matrix. Decrease in internal pressure indicates decrease in the cohesive force of the polymer matrix. Increase in relaxation time clearly proves addition of mass to the polymer by introduction of TiO_2. Also, the wave stays in the section of the polymer for longer duration indicating absorption of the ultrasound wave. Decrease in specific acoustic impedance is a pointer to damping effect of TiO_2 on the acoustic wave since it decreases the elastic nature of the polymer. Decrease in free energy indicates greater stability of the nanoTiO_2-PEG complex.

Micro RAMAN spectrum of nanoTiO_2-PEG thin film:

Raman spectrum of nanoTiO_2-PEG complex is shown in Fig. 5. Factor group analysis is routinely employed to analyse RAMAN spectra[13]. The peak at 275.8 cm^{-1} is attributed to PEG. The following five peaks observed at around 140.9, 199.6, 401.7, 517.6, and 640.5 cm^{-1} are assigned as Eg, Eg, B1g, (B1g/A1g), and Eg modes of anatase phase of TiO_2, respectively[13]. The minor peak at 447.7 cm^{-1} is attributed to presence of negligible quantity of rutile phase TiO_2.

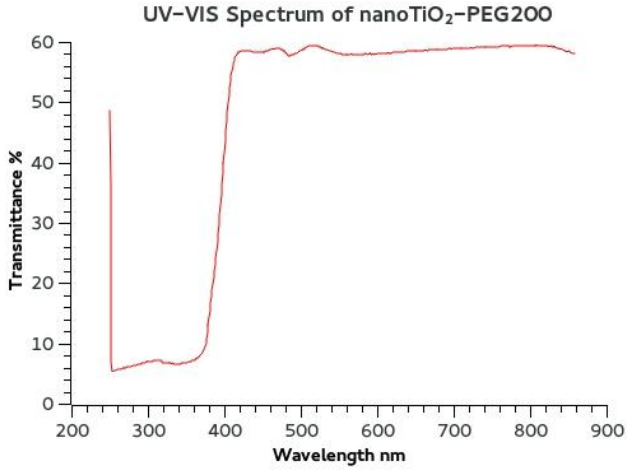
Fig 5. RAMAN spectrum of nanoTiO$_2$-PEG200 complex



UV-Vis Spectrum of nanoTiO$_2$-PEG200 thin film:

UV-Vis transmittance spectrum of nanoTiO$_2$-PEG200 complex is shown in Fig 5. It is observed that the thin film is highly transparent in the visible region from 400-800nm. It also appears that the thin film absorbs in the UV region from 390-250nm.

Fig 6.UV-Vis spectrum of nanoTiO$_2$-PEG200 complex



Conclusion

EDX, SEM and XRD of TiO_2 prepared by reactive thermal plasma method confirm the nano size(~39.1nm) of anatase phase TiO_2 with tetragonal structure. FTIR data further supports the fact that the TiO_2 nano particle is of anatase phase. Acoustic parameters calculated confirm the incorporation of TiO_2 nanoparticle in PEG matrix. RAMAN spectrum of thin film prepared from nanoTiO$_2$-PEG complex indicates sterically stable incorporation of TiO_2 nano particle in PEG matrix. TiO_2 nano particles are known to be transparent in the visible range and highly absorbent in the UV region. The UV-Vis spectrum of thin film of nanoTiO$_2$ dispersed in PEG matrix confirms retention of optical properties of TiO_2 nanoparticle in the nanomaterial-polymer complex. Thus, PEG can be employed as a good scaffold for dispersion of TiO_2 nanoparticle for optical applications without matrix interference.

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