

Influence of Surfactants on TiO₂ Nanoparticles Grown by Sol-Gel Technique

Davoud Dastan and N. B. Chaure

Abstract—TiO₂ nanoparticles were prepared at room temperature by sol-gel method. In the current work, different surfactants such as Acetic Acid (AA), Oleic Acid (OA), and Oley amine (OM) were used for the preparation of TiO₂ nanoparticles. TiO₂ powder was collected by centrifuging precipitation obtained during gel formation. The powder was thoroughly cleaned few times in ethanol and annealed at 550o C and 950o C at specific time. I-V measurement is used to investigate the electrical properties of TiO₂ pallets. In order to elucidate the influence of using these surfactants, the structural and optical properties of powder were investigated by means of X-ray diffraction (XRD), U-v visible, and Photoluminescence (PL). It was found that annealing could improve the crystallization of TiO₂ powders and accelerated the phase transformation from anatase to rutile phase but surfactants do not change the particle size and energy band gap of titania.

Index Terms—TiO₂ Powder, sol-gel, surfactants, annealing, electrical, optical, and structural properties.

I. INTRODUCTION

Researchers have tried to find an insulator with a higher dielectric constant, large band gap, significant conduction band offset and high breakdown strength. Titanium is the ninth most abundant element in the Earth's crust [1]. Titanium dioxide (TiO₂) has high thermal and chemical stability and high transmittance in the visible spectral range [2]. Moreover, it is nontoxic, and applicable for biological coatings, optical devices, and photo electrochemical conversion, environmental photocatalytic processes such as prevention of strains, sterilization and removal of pollutants from air and water [1], sensors, preparation of solar energy cells, fabricating thin dielectrics in dynamic random access memory (DRAM) storage capacitors and as a gate dielectric of FETs [2].

TiO₂ could be formed in three possible crystallographic phases such as anatase, rutile, and brookite. Among these, anatase has excellent chemical and physical properties for environmental purification and is thermodynamically more stable than rutile phase. Furthermore, titania possess high available surface areas, which are beneficial for aqueous photocatalytic reactions [3]. The photocatalytic activity can increase dramatically, when the particle size of TiO₂ decreases. The most popular commercial form of TiO₂ is called P-25. It contains almost 80% anatase and 20% rutile [4]. Different techniques are used for the preparation of TiO₂

nanoparticles, including sol-gel, different forms of sputtering from metallic and ceramic targets, electron beam evaporation, pulsed laser deposition and chemical vapour deposition. The sol-gel process is a low cost and easy processing method for the preparation of titania powder [2]. In this work, we studied the effect of surfactants on structural, optical, electrical properties of different phases of TiO₂ nanoparticles.

II. EXPERIMENTAL DETAILS

A. Materials

Titanium Isopropoxide (TIP, C₁₂H₂₈O₄Ti), as a source of TiO₂, Acetic Acid, CH₃COOH, Oleic Acid, C₁₈H₃₄O₂, Oley amine, C₁₈H₃₇N Absolute ethanol, C₂H₅OH, Bi-distilled water, Acetone, C₃H₆O. These materials were purchased from Sigma Aldrich. The chemical composition of ethanol, TIP, AA, OM, and OA were 20 ml, 0.82 ml, 16 μ, 32μ, and 16 μ.

B. Preparation of TiO₂ Nanoparticles

Acetic Acid was added drop wise in absolute ethanol under vigorous stirring and a transparent solution was obtained. Subsequently, TIP was added drop wise to the solution to form the uniform solutions. The molar ratio of TIP/Ethanol/AA was kept 1:9:0.1 during the synthesis part. The same ratio was maintained using OA, whereas (1:9:0.2) ratio was kept in case of using OM as a surfactant [5]. The sol was further subjected to stirring for 24 h, and then the gel particles were separated by centrifugation under 12000 rpm followed by intermittent washing with ethanol thrice. The resulted precipitate was dried at room temperature. The collected nano-TiO₂ powders were annealed at various temperatures, 550°C and 950°C. To investigate electrical properties, the pallets of as deposited and sintered powder were made under pressure of 80 kg/cm² for 60 seconds after binding with Poly Vinyl Alcohol (PVA). The structural, optical and electrical properties of prepared powder and pallets were investigated by X-Ray Diffraction (XRD, D8, and Advanced Bruker Diffractometer), Photoluminescence (Jasco PL Spectroscopy), UV Visible (Jasco UV/Vis spectrophotometer), and I-V measurement (Potentiostat Biologic SP-300).

III. RESULTS AND DISCUSSIONS

A. (Structural Properties)/X-Ray Diffraction

Fig. 1 shows the X-ray diffraction (XRD) patterns of titania nanoparticles prepared with different surfactants and calcinations temperatures, which is in good agreement with

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the standard JCPDF data of anatase and rutile phases of TiO_2 . The dominant peaks at 2θ of about 25.2, 37.9, 47.8, 53.8, and 55.0, which represent the Miller indices of (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) planes, respectively, correspond to the crystalline structure of the pure anatase phase of TiO_2 [6]. The characteristic peaks located at 27.5, 36.1, 39.1, 41.3, 44.1, 54.3, and 56.6 two-theta degree, representing the hkl Miller index (110), (101), (200), (111), (210), (211), and (220), respectively, correspond to pure rutile phase of titania. As-prepared samples do not show any peak corresponding to TiO_2 indicates the amorphous nature. The crystallite size can be determined from the classical Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where, D is the crystallite size, λ is the wavelength of the X-ray radiation ($\text{Cu K}\alpha = 0.15418 \text{ nm}$), K is the Scherrer constant (usually taken as 0.89) for spherical shape, and β is the full width at half-maximum height, θ is the Bragg diffraction angle.

The calculated results are summarized in Table I. It is observed the enhancement in grain size after annealing. The size of particle depends on the annealing temperature.

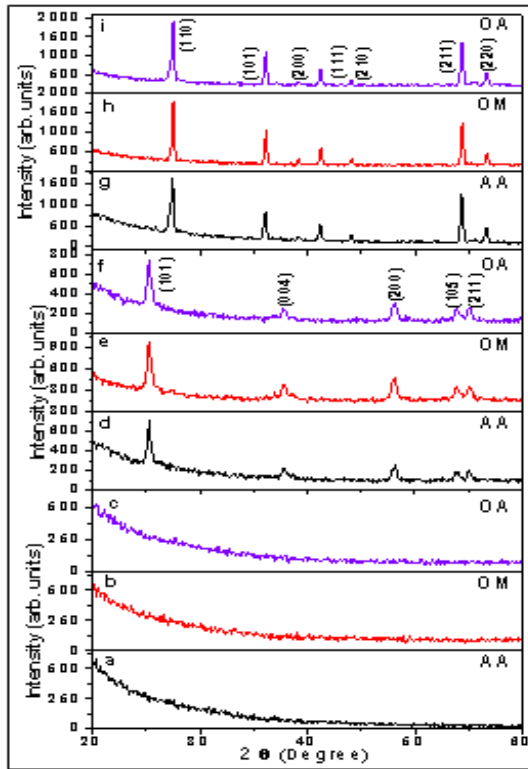


Fig. 1. XRD's from as synthesized (a, b, c), calcined at 550°C (d,e,f), and 950°C (g, h, i) TiO_2 samples.

The samples annealed at 950°C having higher particle size than those annealed at 550°C. This could be rechange of crystal structure of titania. Therefore, calcination is a common treatment that can be used to improve the crystallinity of TiO_2 particles [4]. Surfactants had no significant influence on the phase formation of the nanoparticles. The main reason could be attributed to the fact that the formation of crystal phases is mainly determined by the calcination temperature [7].

TABLE I: PARTICLE SIZES CALCULATED FROM XRD

Temperature Surfactants	Grain size at 550 (°C)	Grain Size at 950 (°C)
Acetic Acid	27.44 nm	40.50 nm
Oley amine	23.10 nm	42.60 nm
Oleic Acid	23.80 nm	37.50 nm

B. Optical Properties

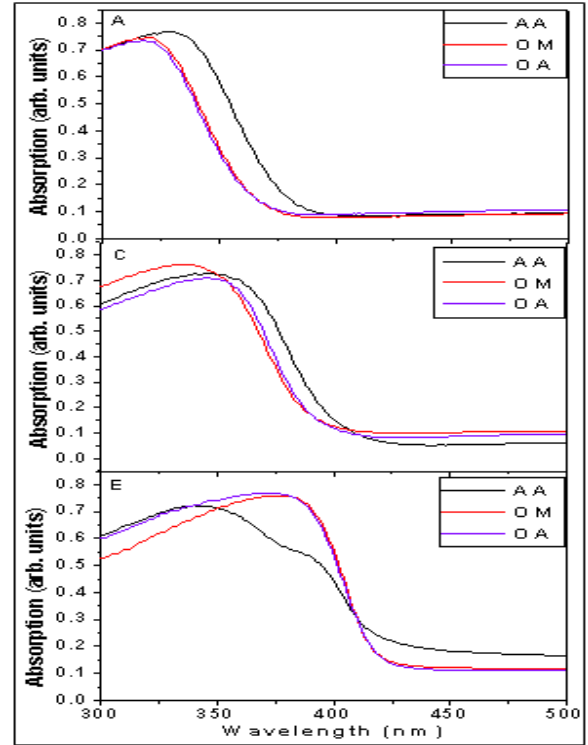


Fig. 2. UV Vis. Absorption spectra (A) as prepared, (C) 550°C, and (E) 950°C samples respectively.

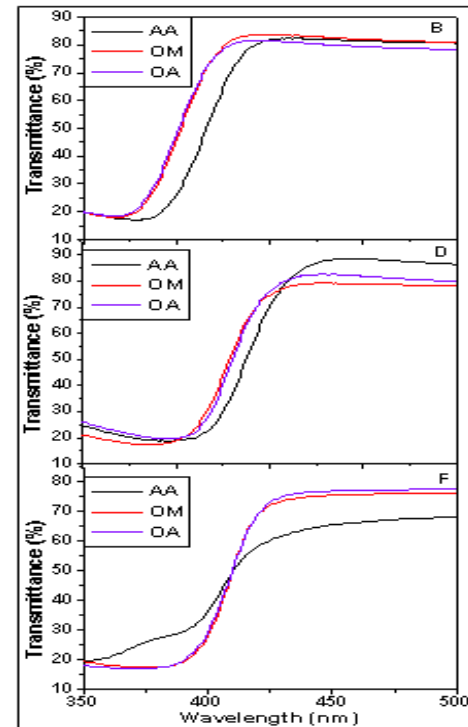


Fig. 3. UV Vis. Transmission spectra (B) as prepared, (D) 550°C, and (F) 950°C samples respectively.

The optical properties of the as-synthesized and annealed powder of titania are investigated using UV-Vis and photoluminescence spectrophotometer at room temperature.

Fig. 2 and 3 illustrate the absorption and transmission spectra's of TiO₂ powder prepared using different surfactants along the heat treatments respectively.

The band gap was the crossing point between the line extrapolated from the onset of the rising part and x-axis of the plot of absorbance as a function of wavelength (λ , nm) [6].

The optical results are summarized in the Table II. It is clear from the Table II that the band gap and transmittance (%) of titania powder decreases with increase in annealing temperature for each surfactant. The change in bandgap could be attributed to formation of big clusters. Grain size has a significant impact on the optical and electronic properties of nanoparticles. The UV-vis absorption band edge is a strong function of TiO₂ particle size, which can be attributed to the quantum size effect of semiconductors [7]. On the other hand, the effects of the quantum size on optical property were greater than that of the Coulomb and surface polarization and it causes the difference in energy band gap of titania [4].

TABLE II: OPTICAL PROPERTIES RESULTS

Temperature (°C)	Energy band gap Eg (eV)	Transmittance (%)
As prepared	Eg(AA) = 3.23	82.3
	Eg(OM) = 3.36	83.8
	Eg(OA) = 3.37	81.7
550°C	Eg(AA) = 3.04	88.6
	Eg(OM) = 3.12	82.6
	Eg(OA) = 3.11	79.2
950°C	Eg(AA) = 2.88	68.4
	Eg(OM) = 2.94	76.1
	Eg(OA) = 2.93	77.6

C. Photoluminescence Spectra

Fig. 4 shows the PL spectra of as-deposited and annealed TiO₂ powder, which were taken under an excitation wavelength 310 nm at room temperature. The two main emission peaks appear at about 385 and 473 nm wavelengths, which are equivalent to the energy band gap of 3.24 and 2.62 eV, respectively. The former is ascribed to the emission of band gap transition related to the anatase structure of TiO₂. The latter is emission signal originated from the charge-transfer transition from Ti³⁺ to oxygen anion in a TiO₆⁸⁻ complex [8], [9]. However, luminescence spectra in the near-band gap emission and free exciton emission at 3.03 eV i.e at 413 nm are reported for high quality rutile crystals at low temperature [10], [11]. The weak peak with small shoulder at 521 nm is possibly resulted from the surface states such as Ti⁴⁺-OH when excited with light having energies larger than the band gap of the samples [4]. The origin of small shoulders appears at 435 nm and 448 nm are due to oxygen vacancies. The as-synthesized samples have broad peaks with two small shoulders at 382 nm and 395nm, whereas the samples annealed at 550°C shows the only single peak at 395 nm. There is small hump at 395 nm for the sample annealed at 950°C with strong emission peak of rutile phase at 413 nm. Since PL emission was the result of the recombination of excited electrons and holes, the lower PL intensity of the modified sample indicated a lower recombination rate of excited electrons and holes [3].

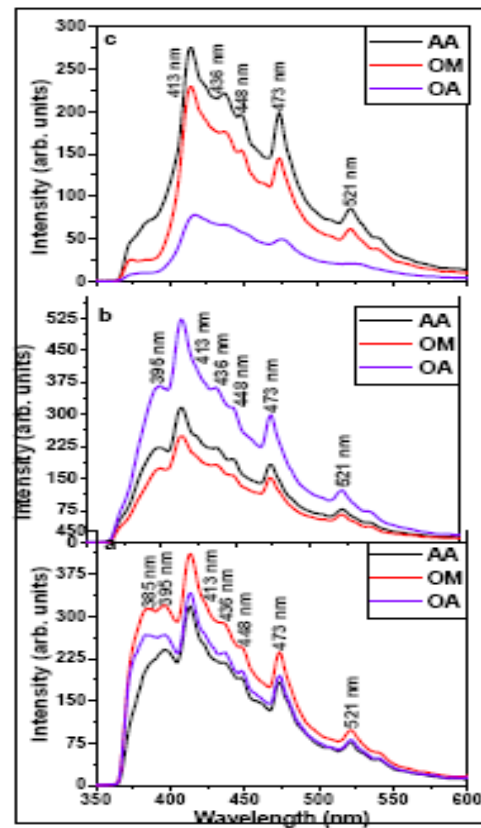


Fig. 4. Photoluminescence spectra at excitation wavelength 310 nm for As prepared (a), 550°C (b), and 950°C (c) samples.

D. Electrical Properties (I-V Characteristics)

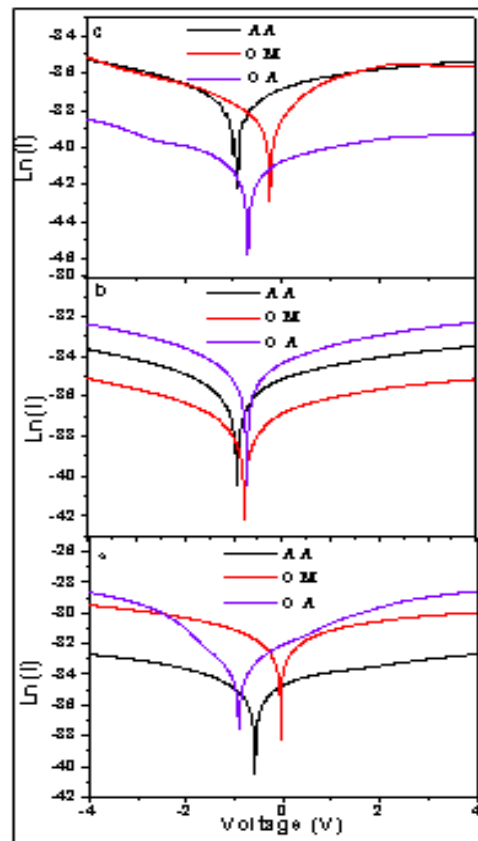


Fig. 5. I-V Characteristics of TiO₂ samples prepared using different surfactants and annealing temperature (a) as prepared, (b) 550°C, and (c) 950°C.

Fig. 5 presents a typical variation of leakage current as a function of voltage. The leakage current through the pallets TiO₂ powder can be modeled in terms of the MIS diode equation in the form:

$$n = \frac{q}{KT} \frac{dV}{d(\ln I)} \quad (3)$$

where q is electron charge, K is Boltzmann constant, and T is typically room temperature. The value of $\frac{dV}{d(\ln I)}$ is obtained from the inversion of slope of $\ln I$ vs V . It is clear from Table III that ideality factor decreases with increase in annealing temperature in case of using different surfactants and it could be attributed to the voltage dependence of the standard deviation of the distribution of barrier heights [2].

TABLE III: I-V RESULTS (IDEALITY FACTOR)

Temperature	Acetic Acid	Oley amine	Oleic Acid
As prepared	5.02	4.60	3.25
550°C	3.70	4.20	3.12
950°C	3.42	3.25	2.85

IV. CONCLUSION

In summary, we successfully used sol-gel method to prepare titanium powder. The results obtained from XRD showed the development of both pure anatase and rutile phases at 550°C and 950°C. The experimental results reveal that with increase in the annealing temperature, size of particles increases and energy band gap and ideality factors decrease. Additionally, change in ideality factor may be an indication of the distribution of barrier heights and the effect of recombination of carriers. The calcination not only improves the crystallization of TiO₂ powders but also accelerates the phase transformation from amorphous phase to anatase or rutile. The different peaks in PL spectra could be owing to the recombination of photoinduced electrons and holes, free or trapped excitons emission and the surface states and presence of anatase and rutile phases of TiO₂.

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