

Simple way to make Anatase TiO₂ films on FTO glass for promising solar cells

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Abstract

TiO₂ is a wide bandgap semiconductor material used as the photo anode in dye sensitized solar cells (DSSC). The fabrication of TiO₂ on conductive glass substrates plays an important role in the solar cell efficiency, since the thickness of the TiO₂ coating affects the transmission, photoconductive properties and the efficiency of solar cells. The uncorrected transmission in our fabricated films is as high as 80 %, and the bandgap obtained is similar to that of bulk anatase TiO₂, confirming that sol-gel prepared films in this work can be used effectively for DSSC.

Key words: TiO₂; structural; Optical properties

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1. Introduction

Titanium dioxide (TiO_2) or titania has been a subject of interest for decades due to its chemical properties, such as stability and non-toxicity, as well as its physical properties such as high transmittance in the visible spectral region, wide bandgap, high refractive index and permittivity. Although, titania shows photocatalytic activity only under UV light irradiation, because of its wide bandgap ~ 3.0 eV for rutile and ~ 3.2 eV for anatase, it has been proven a good window material in photovoltaic applications. In fact, TiO_2 is extensively used in the applications of dye sensitized solar cells (DSSC) [1]. The anatase phase has been preferred for its photocatalytic properties and widely used in solar cell applications, primarily owing to its wider bandgap [2]. One most important requirement of widegap materials for the application of solar cells is to have maximum possible transmission. The optical properties and the electronic transport properties of TiO_2 thin films depend on the fabrication process and the phase of the material.

The sol gel technique has extensively been used together with doctor blade method to produce nanoparticle structures of wide bandgap materials. Some of the advantages of such methods include the ability to deposit pre-determined structures by varying experimental conditions, homogeneity, low temperature preparation and low production cost [3]. It is noteworthy that thin films and nano- and poly-crystalline samples deposited by sol gel method can have different characteristics of compositional distribution and phase stability. The solubility range of as-prepared thin films appears significantly wider than that in the crystalline phases, because thin-film growth processes are substantially affected by kinetic parameters. Other low-cost wet chemical techniques have also been successfully used in depositing wide

bandgap materials such as ZnO [4]. Straumal et al [4] used a dip coating method to deposit a nanocrystalline thin film in a mixture of liquid organic acids at 150°C. Annealing at higher temperature (550°C) has lead to grain growth. Thus in order to understand and to explore the fabrication process of nanocrystallineTiO₂ on fluorine- doped tin oxide (FTO) conducting glass for the applications in solar cells, we have investigated different properties which are presented in this paper. A simple low-cost and an efficient method for the deposition of anatase TiO₂ thin films were used in this work.

2. Experimental

The TiO₂ nanoparticles were prepared by a sol–gel method [5]. TiO₂ nonporous thin films on fluorine doped tin oxide (FTO) glass were fabricated using the doctor blade method. The structural characterization of the prepared thin films was carried out using a Bruker AXS D8 advanced high resolution X-ray diffractometer (HRXRD) (wavelength $\lambda=1.542 \text{ \AA}$). The morphology of powder and thin films was observed using a Hitachi SU-70, high resolution scanning electron microscope (HR-SEM). The transmission spectrum was measured using a Shimadzu UV-3101 PC spectrometer for optical characterization. The dielectric measurements were carried using a Wayne Kerr 6440A in the frequency range 20Hz-3MHz with Precision Component Analyzer. The sample set up was connected as a parallel plate capacitor.

3. Results and discussions

Fig.1 (a) shows the X-ray diffraction patterns of TiO₂ nanoparticles and TiO₂ coated on FTO glass. All the XRD peaks of TiO₂ clearly indicate the unique phase of anatase. The microstructure of the prepared anatase TiO₂ nanoparticles is shown in Fig.1(b). The HR-SEM

image clearly shows the nanocrystallinity of the samples. The cross-section and the plane view microstructure of TiO₂ coated on FTO glass is as shown in Fig. 1(c) and (d). The TiO₂ coating on FTO glass can be clearly seen in Fig.1(c). The plane view of the FTO/TiO₂ image (Fig.1(d)) shows the uniform distribution of the TiO₂ coating on the FTO glass.

Dielectric measurements at room temperature were performed for FTO/TiO₂ using a silver electrode at the top. Fig. 2 shows the variation of dielectric constant (ϵ') versus frequency. Generally, ϵ' , decreases with increasing frequency. The value of the dielectric constant is very high at lower frequencies and decreases with increasing frequency. The higher values of ϵ' at lower frequencies were due to the simultaneous presence of space charge, dipolar, ionic, and electronic polarizations. At lower frequencies the grain boundaries are more effective than grain electrical conduction. The decrease in the ϵ' with increasing frequency can be explained on the basis of the mechanism of polarization process as in ferrites [6], which is similar to that in the conduction process [7]. The inset of Fig.2 shows the variation of dielectric loss tangent ($\tan \delta$) and dielectric loss factor (ϵ'') with frequency for FTO/TiO₂ sample. The $\tan \delta$ and the ϵ'' decrease rapidly at lower frequencies and then slowly at higher frequencies. Kramer and Panova [8] explain that the increase of loss factor at higher frequency would be attributed to the phenomenon of domain wall relaxation. The occurrence of high value of loss factor at lower frequency is due to the different types of wall relaxation processes [9]. The maximum loss occurs at a frequency $\tau = 1/\omega$, which is proportional to the conductivity [10]. Our observed variation appears to have a similar behavior.

Fig. 3 shows the measured transmittance (T) spectra of three TiO₂ thin films in the spectral region with interference fringes. One spectrum has two adjacent maxima and minima marked T_M and T_m respectively. Assuming the TiO₂ samples to be homogeneous and uniform,

thin films with thickness d , deposited on transparent substrates, whose thickness was several orders of magnitude larger than d , is given by the basic equation for the interference fringes:

$$2nd = m\lambda \quad (1)$$

Here, n is the refractive index of TiO_2 and m takes the form of an integer for interference maxima and half integer for minima. Taking into account two adjacent maxima and a minimum (T_M and T_m), according to Swanepoel's method [11] following Aly et al [12], the thickness of the TiO_2 films (d), can be expressed as:

$$d = \frac{\lambda_1 \lambda_2}{2(n_1 \lambda_2 - n_2 \lambda_1)} \quad (2)$$

where n_1 and n_2 , are the refractive indices and λ_1 and λ_2 are the photon wavelengths of the adjacent maxima and minima as labeled in Fig.3. In these calculations, it was assumed that the refractive indices $n_1 = n_2 = n$. As described by Aly et al [12], the refractive index n in the spectral region of medium and weak absorption can be derived from the formula.

$$n = \sqrt{(N + \sqrt{N^2 - S^2})} \quad (3)$$

where $N = 2S \frac{T_M - T_m}{T_M T_m} + \frac{1 + S^2}{2}$

The refractive index of glass, s can be estimated from the equation (4)

$$S = \left(\frac{1}{\tau_s} \right) + \sqrt{\left(\frac{1}{\tau_s^2} - 1 \right)} \quad (4)$$

where τ_s is the measured glass transmittance [13]. The raw values of T_s and calculated S values that were used in the thickness calculation corresponding to λ_{max} are also given in Table 1.

The absorption coefficient (α) in the high-absorption region ($\alpha \geq 10^4 \text{ cm}^{-1}$), is given by the Tauc equation (equation 5).

$$\alpha(\lambda) = \frac{B(h\nu - E_g)^2}{h\nu} \quad (5)$$

where B , $h\nu$, and E_g are a parameter that depends on the transition probability, the photon energy and the optical bandgap respectively. The transmission data were used to derive α ($\alpha = - (1/d)\ln T$) and the Tauc plot ($(\alpha \cdot h\nu)^{1/2}$ vs $h\nu$) for the three spectra A,B,C in Fig.3 are plotted in Fig.4.

Optical bandgaps E_g extrapolated using Tauc plot (Fig.4) for three samples considered are ~ 3.2 eV, which corresponds to an indirect transition and of almost the same as that of the bulk TiO_2 at room temperature. Usually, nanocrystalline anatase TiO_2 thin films show larger bandgap values than that of the bulks, presumably due to axial strain effects and furthermore, to the difference in the density of carriers [14]. A more accurate value for the bandgap may be achieved by including the loss factors due to scattering of light and considering more accurate refractive indices for maxima and minima. The films are of similar thickness, suggesting the method of deposition to produce consistently uniform thin films. However, as shown in Table 1, the refractive indices of the three samples at maxima are 2.14 (955 nm), 2.15 (963 nm) and 2.23 (945 nm), which are typical of TiO_2 at near infra-red wavelengths.

Conclusions:

Stable anatase TiO₂ nanoparticles were synthesized by using a low-temperature sol-gel method. Nanoporous thin films on fluorine doped tin oxide (FTO) glass were made by a conventional doctor blade method. XRD and HR-SEM analyses confirmed that the films were uniform and of anatase phase TiO₂ nanostructures (with ~30 nm particle size). The dielectric constant of TiO₂, was found to be very high at lower frequencies, and it decreases with increasing frequency. Optical transmission studies further confirm the bandgap of TiO₂ film to be similar to that of bulks. The transmission of our films could achieve as high as 80%. Optical constants derived from the transmission spectra are also typical of bulk TiO₂ at near infra-red wavelengths. TiO₂ films made by this simple method indeed can be used as a part of future solar cells.

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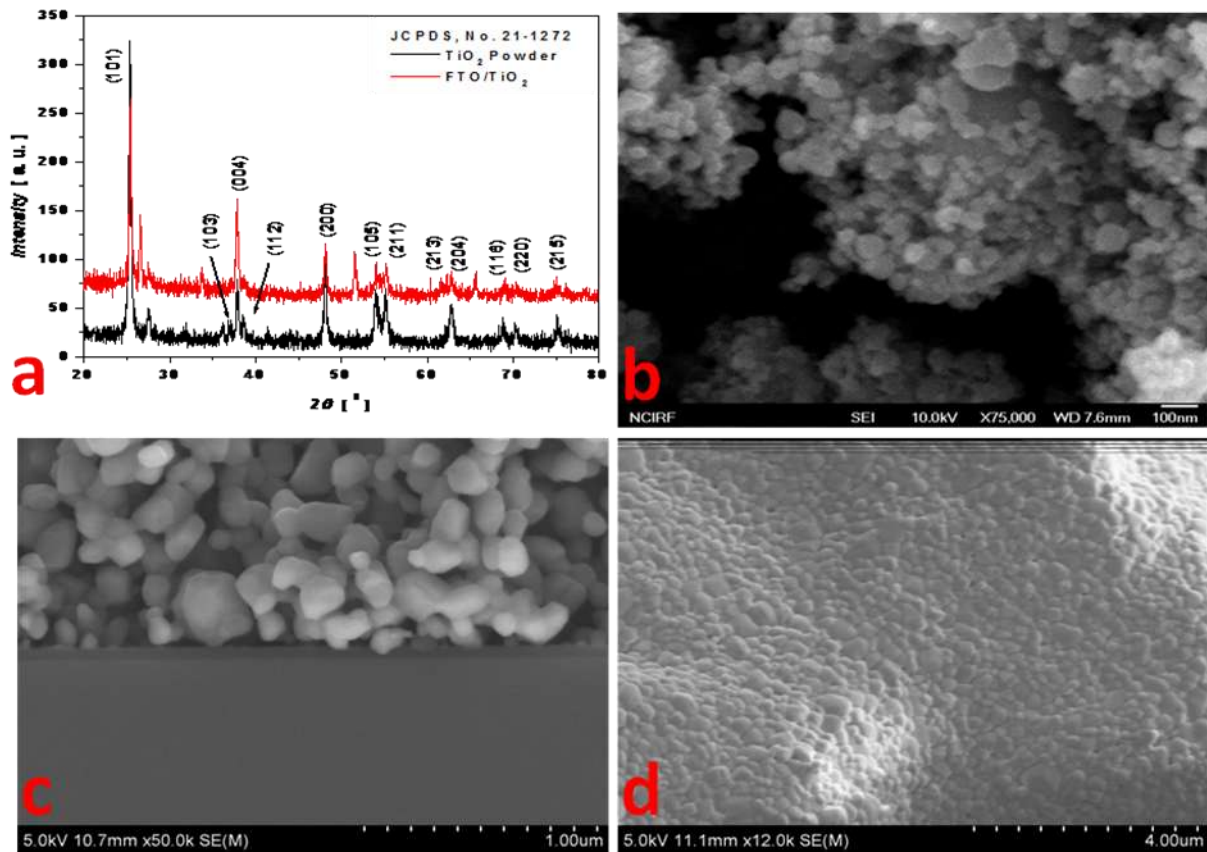


Fig.1. (a) XRD patterns of TiO₂ nanoparticles, TiO₂ coated on FTO glass, HR-SEM images of (b) TiO₂ nanoparticles, (c) Cross-section view and (d) plane view of TiO₂ coated on FTO glass.

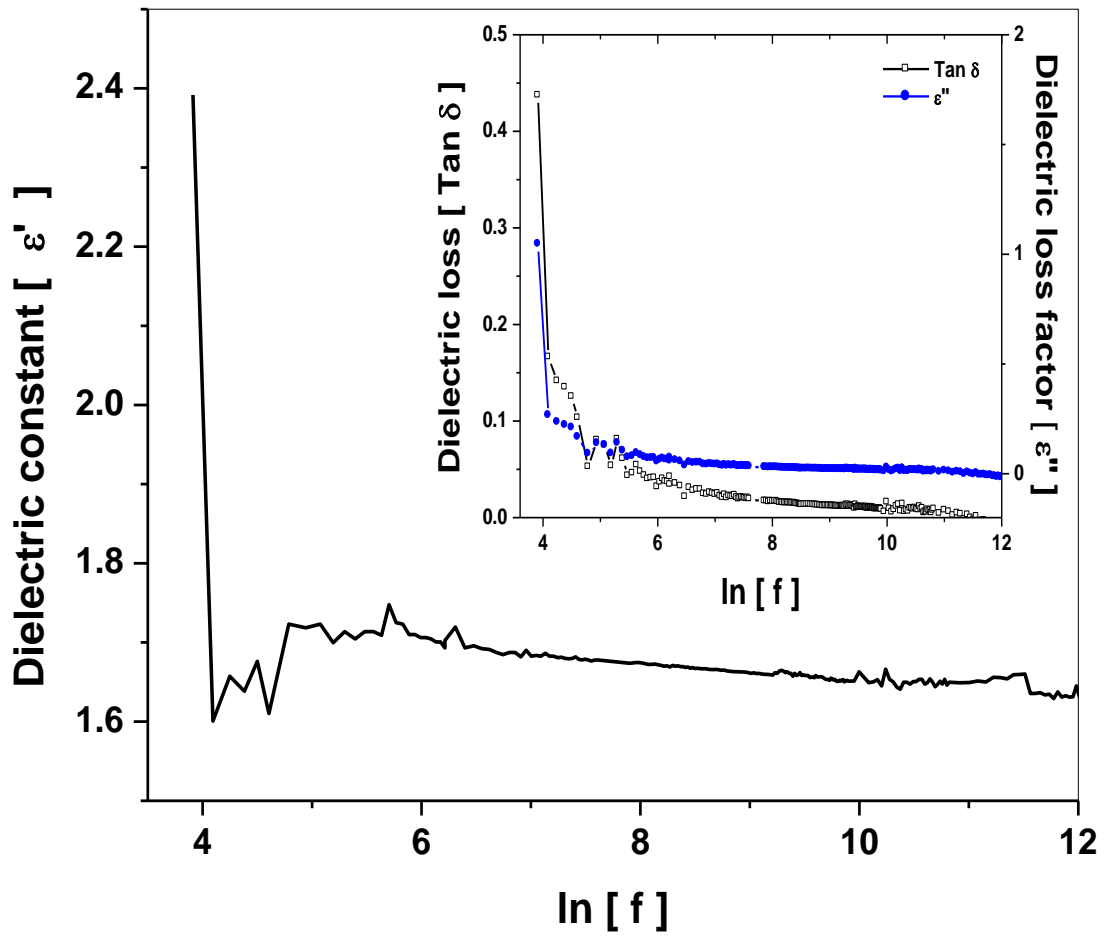


Fig.2. Variation of dielectric constant (ϵ') of FTO/ TiO₂ and the inset shows the variation of dielectric loss ($\tan \delta$) and dielectric loss factor (ϵ'') of FTO/ TiO₂

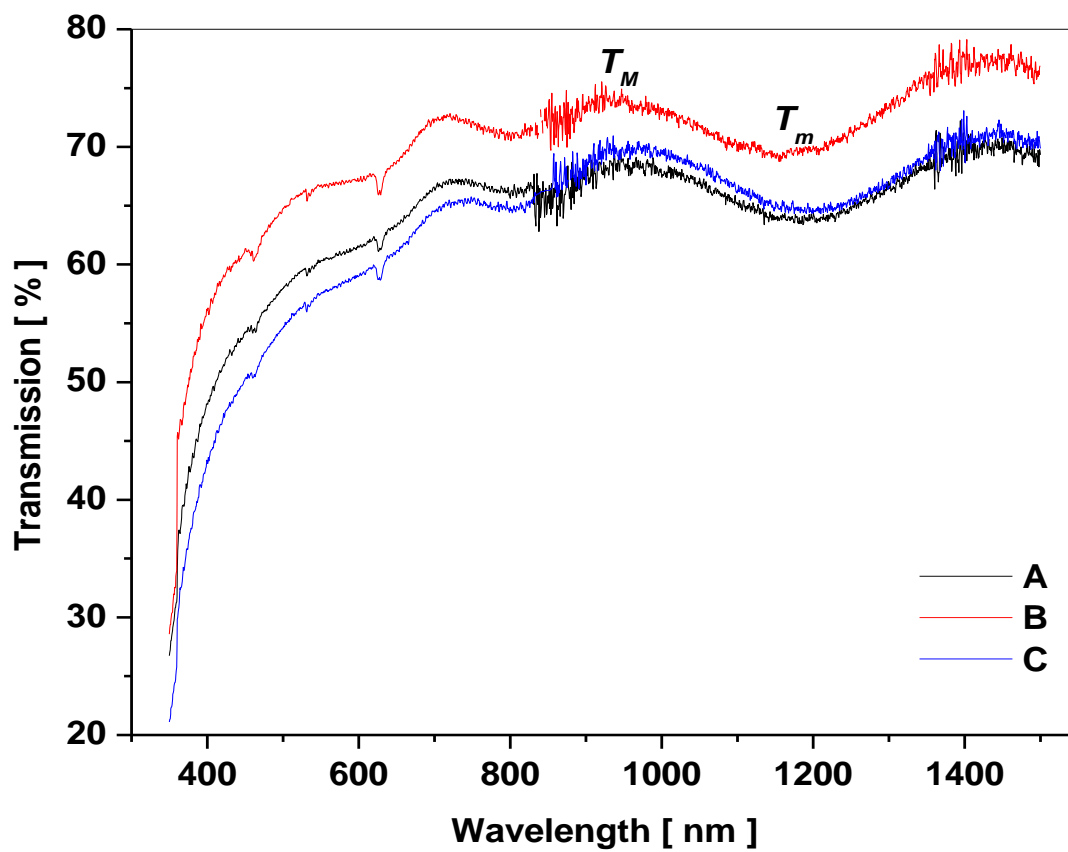


Fig.3. Transmission spectra of TiO₂ thin films deposited on FTO glass substrates.

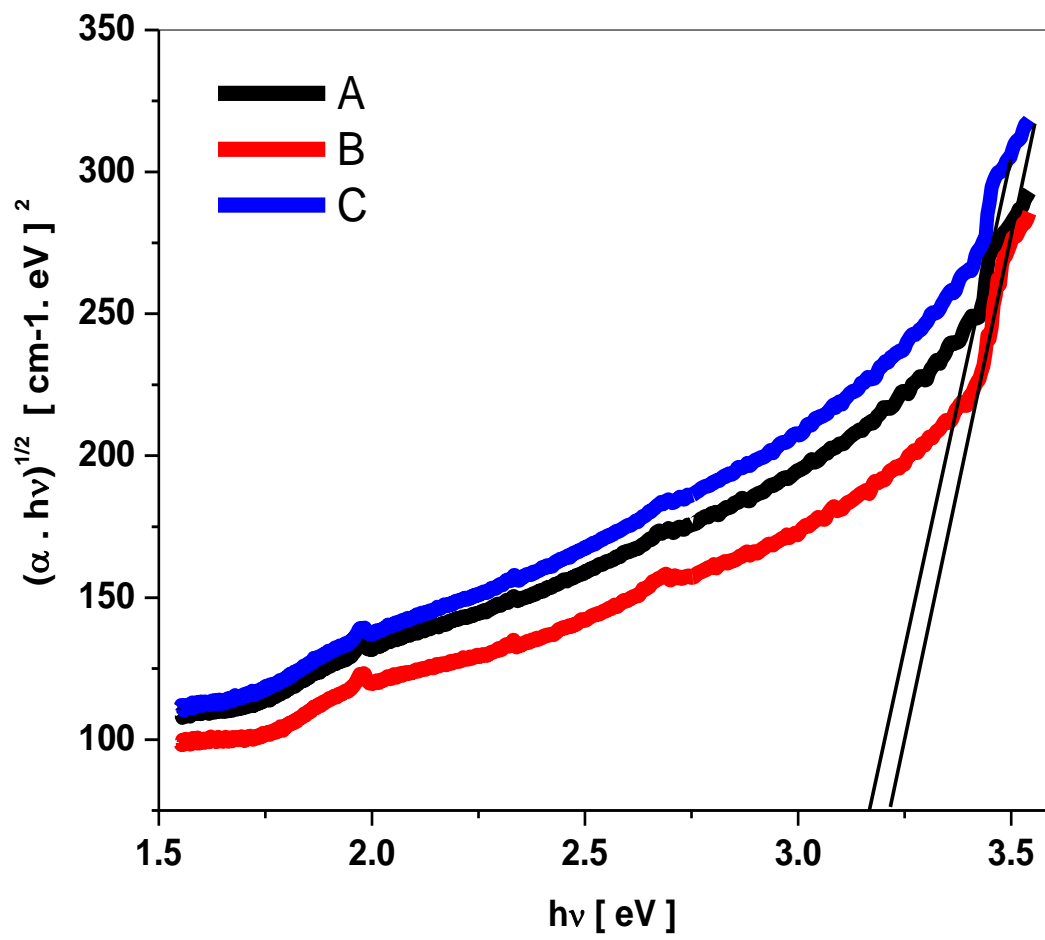


Fig.4. Tauc plots for samples A, B and C

Table 1: Values of λ_{max} , λ_{min} , τ_s , T_M , T_m , S , N , n and d , for TiO_2 thin films from transmission spectra of Figure 3.

Sample	λ_{max}	λ_{min}	τ_s	T_M	T_m	S	N	n	d (nm)
A	955	1202	0.8739	0.6863	0.6360	1.87	2.6794	2.14	540
B	963	1195	0.8645	0.7029	0.6425	1.92	2.8568	2.23	553
C	945	1184	0.8659	0.7354	0.6952	1.96	2.7290	2.15	544