WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.084
Volume 10, Issue 2, 226-233. **Review Article** ISSN 2277– 7105

SYNTHESIS AND CHARACTERIZATIONS OF TITANIUM DIOXIDE NANOPARTICLES

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Article Received on
01 Dec. 2020,

Revised on 21 Dec. 2020,
Accepted on 10 Jan. 2021

DOI: 10.20959/wjpr20212-19587

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ABSTRACT

Nanostructured TiO_2 thin film has been prepared by simple spray pyrolysis technique. was employed to prepare. To prepare nanocrystalline TiO_2 thin film by using solution of AR grade Titanium chloride ($TiCl_3$, 0.05 M). The solution was sprayed on quartz substrate heated at 350^0C temperature to obtain the film. This thin film was annealed for a one hours at 600^0C. As prepared thin film was characterized by X-ray diffraction, Microstructure properties study was conducted using Transmission Electron Microscopy. The sensing performance of this thin film was tested for various gases such as LPG, H_2, CO_2, Ethanol, NH_3 and Cl_2 (500 ppm). Gas response, selectivity, response and recovery time of the sensor were measured and presented.

KEYWORDS: *Spray pyrolysis techniques, TiO_2 thin film, gas sensor, sensitivity, bandgap.*

1. INTRODUCTION

Gas sensor researches are focused on new studies to developed smaller and most efficient device, which are very important in the electronic industry and are pursued with increasing demand. There is great attention has been focused on the titanium dioxide (TiO_2) thin films over the last few years. Because TiO_2 is an excellent material in many applications such as in the field of sensors, antireflection coatings, solar cells, gas sensors.[1-13] There are many methods that can be used to prepare TiO_2 thin films with desired properties including sol-gel[14], sputtering[15], anodic oxidation[16], pulsed laser deposition (PLD)[17] and spray pyrolysis.[1-12] Of all the afore-mentioned thin film fabrication methods, spray pyrolysis is widely used because of its simplicity, cheap chemical deposition procedure, allowing the growth of rough-surface films at atmospheric pressure, on large area.

2. EXPERIMENTAL

2.1 Preparation of pure TiO_2 thin film

The spray pyrolysis technique was employed to prepare TiO_2 thin film. Aqueous solution of Titanium chloride was used as precursor ($TiCl_3 \cdot 6H_2O$, 99.9% pure, Merck made, Germany) with concentrations of 0.05 M, were prepared in double distilled water. The solution was sprayed onto quartz substrate heated at 350^0C to obtain the film. This thin film was fired for a one hour at 600^0C and termed as S.

2.2 Optimized parameters

The optimized parameters used for preparation of nanocrystalline TiO_2 thin film using spray pyrolysis techniques were presented in Table 1.

Table 1: Optimized parameters for preparation of nanocrystalline TiO_2 thin film.

Parameters	**Optimization**
Solution delivery	Syringe gun
Nozzle diameter	0.001mm
Compressed Air	2.5 Kg/cm^2
Solution flow rate	4.9 ml/min
Distance from nozzle to substrate	27 cm
Carrier gas	Air
Solvent	Double distilled water
Precursor	Titanium chloride ($TiCl_3$)
Concentration	0.05 M
Substrate	quartz
Deposition time	10 min.
Deposition temperature	350^0C
Firing temperature	600^0C
Annealing time	60 min

3. MATERIALS CHARACTERIZATIONS

The structural analysis of nanocrystalline TiO_2 thin films was carried out by XRD (Rigaku DMAX 2500) with CuKα radiation at a wavelength of 1.5418 Å. Electron diffraction patterns of nanocrystalline TiO_2 thin films were obtained using a Transmission Electron Microscopy [Philips, CM 200 (200 KV HT)]. A UV-Visible spectrophotometer (Shimadzu 2450 UV-VIS) was used to study the optical properties of nanocrystalline TiO_2 thin film.

3.1 Structural properties: X-ray diffraction studies

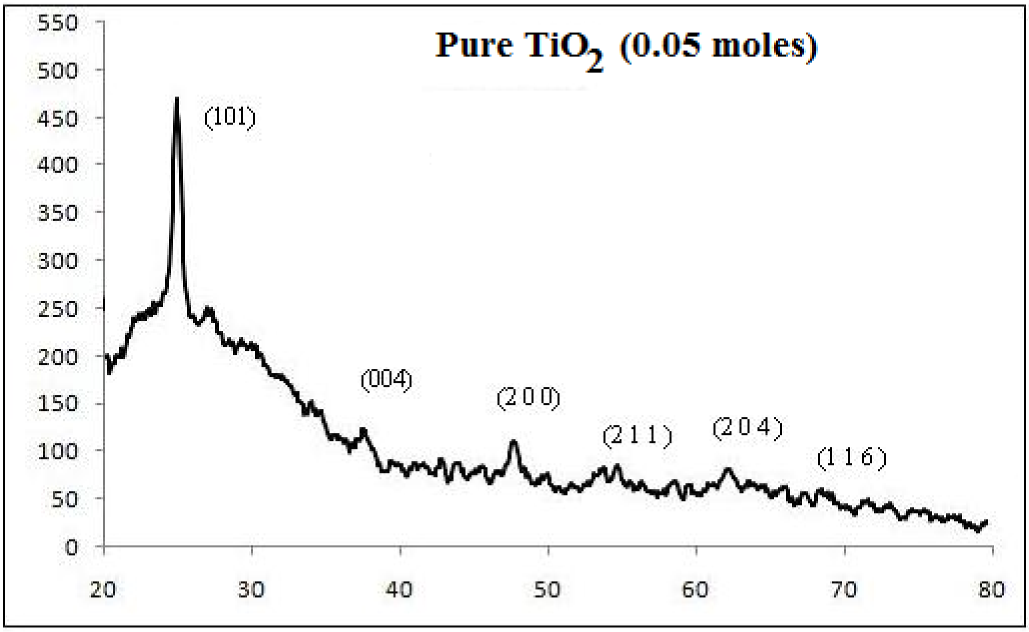

Figure 1: X-ray diffraction spectra of sample S.

Figure 1 shows XRD spectra of sample S. The observed "d" values of TiO_2 films confirmed that the deposited films are of TiO_2 anatase phase with tetragonal structure matched well with the ASTM data book.[18] In the XRD pattern, the (101) peak has the most distinct reflection. So, the mean crystalline size is calculated with the line broadening of the (101) reflection using well known Scherrer Eq. (1)

$$d = 0.9\, \lambda / \beta \cos\theta \qquad (1)$$

Where, d is crystallite size, β is the full width at half maxima in radians and λ the wavelength of X-ray (1.5418 Å). The crystallite size was observed to be 10.27 nm.

3.2 Microstructure and electron diffraction using TEM

Figure 2 show the Transmission Electron Micrograph [CM 200 Philips (200 kV HT)] of powder obtained by scratching the thin film sample S and powder was dispersed in ethanol. TEM uses Copper grid to hold the powder. The sample particles on the grid were scanned in all the zones before the picture was taken. Figure 2 shows that the grains are ellipsoidal in nature with an average grain size of 12 nm. XRD and TEM studies confirmed pure tetragonal structure of TiO_2 as evidenced from figure 1 and figure 2 respectively. XRD and TEM studies confirmed pure tetragonal structure of TiO_2 as evidenced from figure 1 and figure 2 respectively. Table 2 show the comparison of grain size from Transmission Electron Micrograph and X-ray Diffraction.

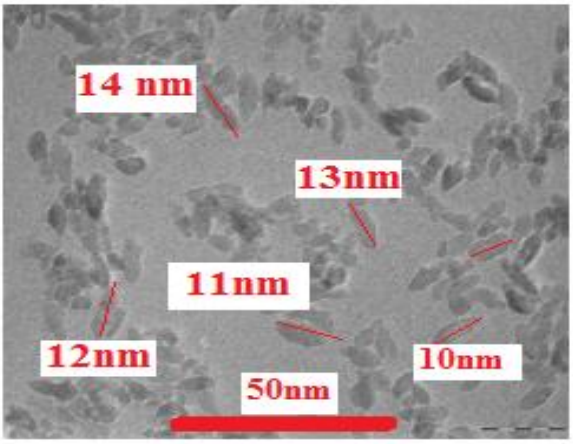

Figure 2: TEM image of sample S.

Table 2: Grain size calculated from XRD and TEM.

Sample	Grain size calculated from XRD(nm)	Grain size calculated from TEM (nm)
S	10.27	12.00

3.3 Optical absorption

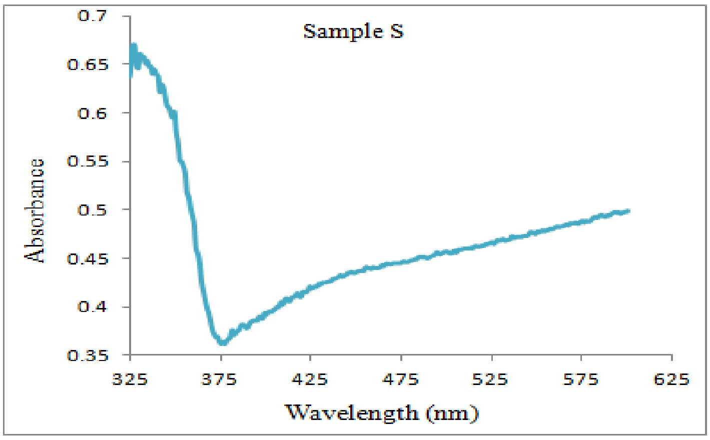

Figure 3: Absorption spectra of samples S.

Figure 3 show the variation of absorbance with wavelength of nanocrystalline TiO_2 thin films in the range of 300-600 nm. The band gap energy of the samples was calculated from the absorption edges of the spectra.[19] The band gap was observed to be 3.28 ev.

4. SENSING PERFORMANCE OF TIO_2 THIN FILM

4.1 Gas sensing performance of thin film resistors

The thin film sensors mounted in static gas sensing system were tested on exposure of ethanol, carbon dioxide, LPG, ammonia, chlorine and hydrogen. Values of currents before and after exposure of gas were measured and gas responses at various operating temperatures were determined.

4.2 Measurement of gas response and selectivity

Gas response (S) is defined as the ratio of the change in conductance of the sensor on exposure to the target gas to the original conductance in air. The relation for S is as:

$S = (G_g - G_a) / G_a$

where, G_a and G_g are the conductance of sensor in air and in a target gas medium, respectively.

Selectivity or specificity is defined as the ability of a sensor to respond to a certain gas in the presence of other gases.

4.3 Variation of gas response with operating temperature for different gases

Figure 4 shows the variation of gas responses with operating temperature. It is clear from the figure 4 that the gas response increases with operating temperature, reaches to maximum [for LPG (S=397) at 250^0C for 500 ppm] and falls with further increase in operating temperature. Sensor S is most sensitive to LPG at 250^0C.

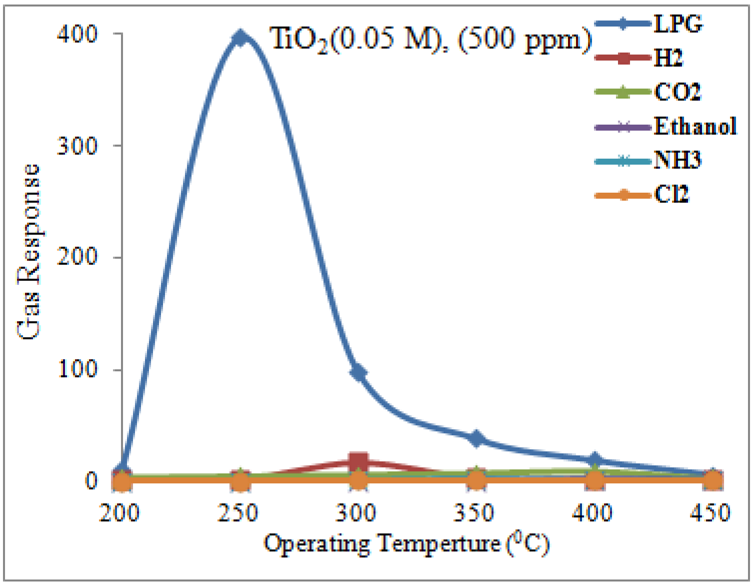

Figure 4: Variation of gas responses with operating temperature.

5. DISCUSSION

Gas sensing mechanism is generally explained in terms of conductance either by adsorption of atmospheric oxygen on the surface and/or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. In case of former, the atmospheric oxygen adsorbs on the surface by extracting an electron from conduction band, in the form of super-oxides or peroxides, which are mainly responsible for the detection of the test gases. At higher temperature, the adsorbed oxygen captures the electrons from conduction band as.

O_2(air) +2e$^-$ (cond. band)→ 2O$^-$ (film surface).

It would result in decreasing conductivity of the film. When LPG reacts with the adsorbed oxygen on the surface of the film, it gets oxidized to CO_2 and H_2O by following series of intermediate stages. This liberates free electrons in the conduction band. The final reaction takes place as.

$C_4H_{10(gas)} + 13O^-_{\text{(film surface)}} \rightarrow 4CO_{2(gas)} + 5H_2O_{(gas)} + 13e^-_{\text{(cond. band)}}$

This shows n-type conduction mechanism. Thus generated electrons contribute to a sudden increase in conductance of the thin film. Therefore, the higher response was obtained to 500 ppm LPG.

6. CONCLUSIONS

1. Simple spray pyrolysis technique was observed to useful for the preparation of nanostructure film of $TiO_{2.}$
2. The grain size calculated from XRD match well with the grain size observed from TEM.
3. Nanocrystalline TiO_2 thin films were observed to be sensitive to LPG at 250^{0}C.
4. Nanocrystalline nature was observed to be useful in gas sensing.

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