

Study of Aluminium Doping in Titanium Dioxide Nanoparticles

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Abstract-I-V measurements were carried out to study the effect of aluminium doping in titanium dioxide nanoparticles on electrical conductivity. Various Al doping concentrations were used, namely 0.0 at% (undoped), 1.0 at% and 2.0 at%. These nanoparticles were synthesized by simple sol-gel method and calcined at 500° C. The crystalline structure and size of the particles were determined by X-ray diffraction (XRD) measurements. The results from XRD show that anatase phase of TiO₂ is formed in each case. Moreover, as we increase the doping concentration the size of nanoparticles decreases. This is so because ionic radius of aluminium is less than that of titanium. In addition, as the doping increases there is a shift in the diffraction peaks towards higher angle of diffraction due to lower values of lattice dimensions. I-V measurements clearly indicate an enhancement in conductivity due to Al doping. SEM images show that porosity of the sample increases with doping concentration, a desirable property for dye-sensitized solar cells.

Keywords: Doped Nanoparticles, Aluminium, Titanium Dioxide, Sol-Gel, DSSC.

I. INTRODUCTION

The demand of energy consumption is increasing every year. Fossil fuels being the main resource for energy production are used to fulfil this demand. Burning these fossil fuels cause emission of harmful gases like carbon dioxide (CO₂). This emission of harmful gases in the atmosphere is the main reason for global warming. Global warming is considered to be the real and growing threat for humankind, climate and environment. Global warming can be controlled by reducing the usage of fossil fuels in power and electricity generation. In the recent decades people started being concerned about environment. Therefore in the 21st century, demand of renewable energy resources is continuously increasing as it is considered to be one of the solutions to reduce environmental pollution. Renewable energy is environment-friendly as it does not emit harmful gases. Usage of solar energy is one of the most promising energy alternatives to reduce the emission of harmful gases. Solar energy being abundant, a lot of research work is focused on its

utilization in day to day applications such as energy storage devices and solar cells.

Metal oxide nanoparticles have attracted a great deal of attention due to numerous applications such as energy storage devices, photo catalysts and solar cells. Having characteristics of a semiconductor, titanium dioxide (TiO₂) nanoparticles have been used in photovoltaic cells especially in dye-sensitized solar cells (DSSC).¹⁻³ TiO₂ nanoparticles have found application in dye-sensitized solar cells because of their mesoporous nature and a large surface area, which allows sufficient dye adsorption and efficient light harvesting. Hence, the performance of such cells depends on the nature of porous structure and average particle size. Advantages of DSSC over other thin film solar cells are low production cost and simple manufacturing procedure. However, the cell's efficiency is lower than other thin film solar cells. Successful aluminium doping in TiO₂ is expected to increase the electrical conductivity and hence efficiency of DSSC.⁴

In the present work synthesis of undoped and Al doped TiO₂ nanoparticles has been carried out by using sol-gel technique.⁵⁻⁸ Various molar % of aluminium were used. Particle size and phase were determined by using XRD. I-V measurements were also taken to study the effect of doping on conductivity. The morphology of the prepared samples was determined by SEM.

II. EXPERIMENTAL DETAILS

In a typical experiment, aqueous solution of aluminium nitrate (Al(NO₃)₃·9H₂O) was taken and was made acidic by adding a small amount of acetic acid. This solution was stirred for about 15 minutes. Solution of titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄) in ethanol was added dropwise with constant stirring. The mixture was further stirred continuously for 3 hours. It was then kept for aging for 3 days at room temperature. The off-white gels were obtained for different concentrations of aluminium viz. 0.0, 1.0 and 2.0 at%. These gels were dried at 80° C for 10 hours. The crystals so formed were ground and calcined at 500° C for 2 hours.

The phase, structure and average grain size of the as-prepared samples were determined by powder X-ray diffraction (XRD) (SchimadzuLabX- 6100 at Garware College, Pune) with an incident wavelength of $\lambda = 1.54 \text{ \AA}$. The surface morphology of the as-prepared samples was investigated using the scanning electron microscopy (SEM) and EDAX measurements using a JEOL, JSM 5600 microscope at the Physics Department, SPPU, Pune. The I-V characteristics were carried out at the Physics Department, SPPU, Pune.

III. RESULTS AND DISCUSSION

A. XRD Spectra:

Fig. 1(a-c) shows the X-ray diffraction patterns of x at% Al doped TiO_2 nanoparticles with $x = 0, 1$ and 2 . These nanoparticles are labeled as undoped TiO_2 , 1% Al: TiO_2 and 2% Al: TiO_2 . All diffraction patterns match well with that of JCPDS data no. 841286 indicating the formation of body centered tetragonal anatase phase of TiO_2 in each case. As expected there is no change in phase, thus proper doping of Al in TiO_2 has taken place. Moreover, the finite width of the diffraction peaks clearly indicates the formation of nanoparticles. No extraneous peaks appear in the spectra which clearly indicate the formation of pure anatase phase. Rutile and Brookite phases of TiO_2 are completely absent. Particle size was determined by using Debye Sherrer formula and is found to decrease from about 31 nm for undoped TiO_2 (0% Al: TiO_2) to 24 nm for 2% Al: TiO_2 (Table 1). All the diffraction patterns are stacked together and shown in figure 1(d) to highlight the similarities and differences between them. It can be clearly seen from figure 1(d) that the relative intensities of diffraction peaks decrease with an increase in the doping concentration.

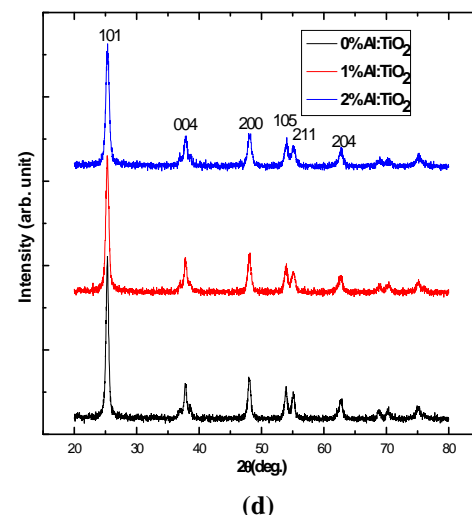
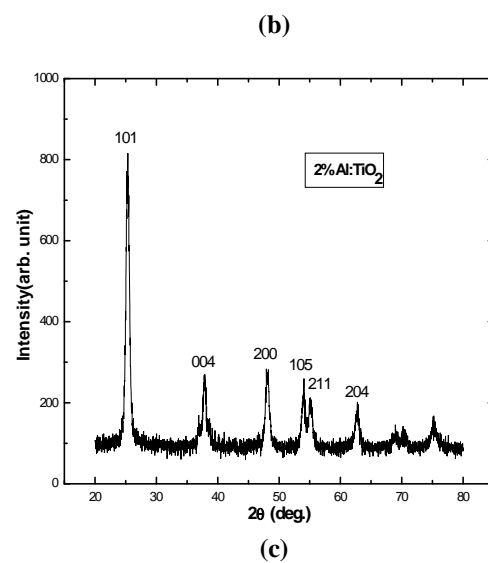
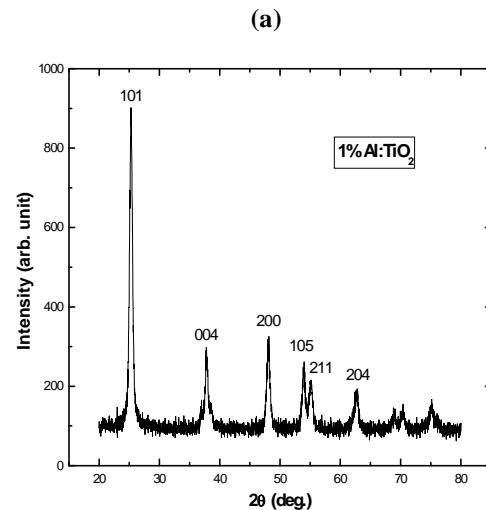
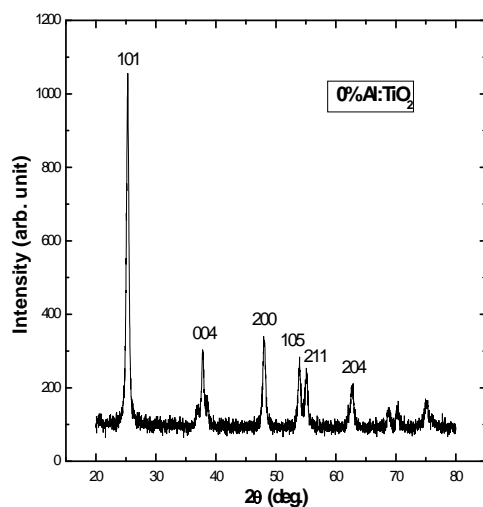


Figure 1: X-ray diffraction patterns of (a) undoped TiO_2 , (b) 1% Al: TiO_2 , (c) 2% Al: TiO_2 (d) XRD spectra of all the three samples

To study the effect of doping in detail we have expanded the most intense peak. A comparison of the most intense peak (101) of all the samples is shown in Figure 2. A vertical line passing through the peak position of the undoped TiO₂ sample serves as a reference line to compare the changes in the width β (FWHM) of the peaks as well as a shift in the diffraction angle due to doping. It is found that as the doping increases there is a systematic increase in the width of the diffraction peaks and a shift towards higher angles of diffraction. This is so because the ionic radius of aluminium (0.053 nm) is less than that of titanium (0.056 nm). As smaller Al ions are substituted in the TiO₂ lattice replacing larger Ti ions, lattice contraction takes place resulting in a decrease of the particle size with an increase in the aluminium doping concentration. Correspondingly there is a decrease in the values of the lattice dimensions.

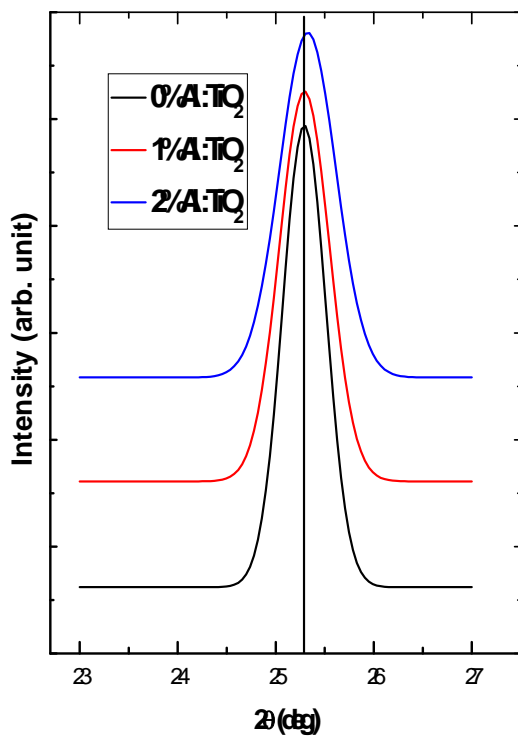


Figure 2: Comparison of the most intense diffraction peak (101) of all the samples

The positions of the most intense diffraction peak (101), values of FWHM (β), size of the nanoparticles and the d-spacing for 0, 1 and 2% Al:TiO₂ are reported in Table 1.

Table 1: Results from XRD spectra

Al:TiO ₂	Diffraction angle θ (deg.)	FWHM β (rad.)	Size of nanoparticles (nm)	d spacing (Å)
0% Al:TiO ₂	12.6454	0.00455	31.5665	3.51908
1% Al:TiO ₂	12.6462	0.00523	27.4727	3.51886
2% Al:TiO ₂	12.6630	0.00589	24.3983	3.51428

B. I-V Measurements:

From figure 3 it can be seen that, as the percentage of doping increases current increases from about 85 μ A for undoped TiO₂ (0% Al:TiO₂) to 195 μ A for 2% Al:TiO₂. This is about 2.3 times more, which is a large amount. Thus, conductivity will also increase proportionately. This increase is expected because Ti⁺⁴ ions are replaced by Al⁺³ ions causing availability of free electrons resulting in an increase in conductivity.

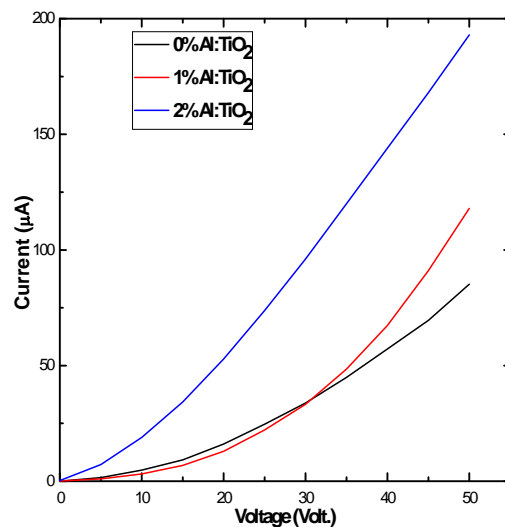


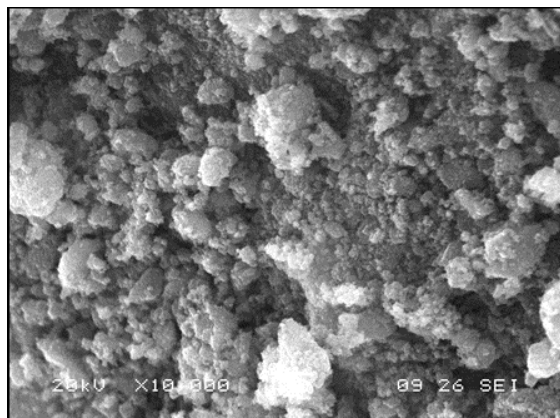
Figure 3: I-V measurements of 0, 1 and 2 % Al:TiO₂

As TiO₂ is semiconductor, the graph of I-V measurement is non-linear. However with an increase in aluminium doping concentration, a substantial decrease in the curvature is clearly visible in the 2% Al:TiO₂ data indicating an increase in the conducting nature of the particles.

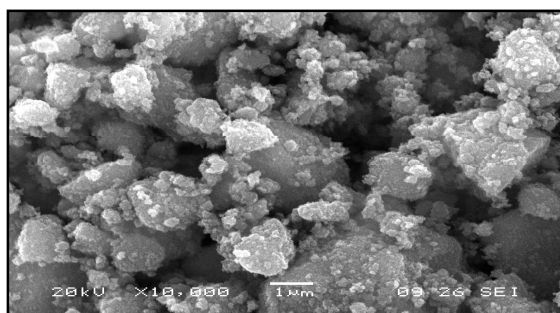
C. Scanning Electron Microscopy (SEM):

The morphology of synthesized undoped TiO₂ nanoparticles and 2% Al:TiO₂ nanoparticles is determined by SEM. From figure 4 we can see that 2% Al:TiO₂ nanoparticles are porous than the undoped TiO₂ nanoparticles. This

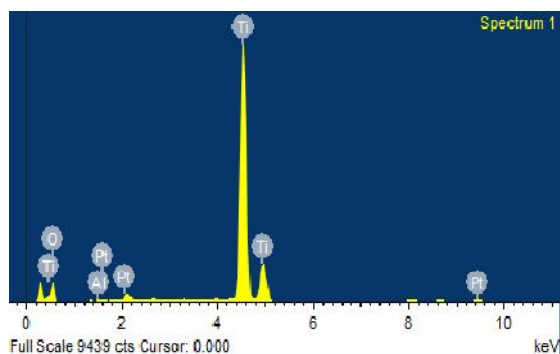
increased porosity results in larger surface contact area between the dye and TiO_2 which improves the electron transfer from dye to the front electrode. The EDS result of 2% Al: TiO_2 nanoparticles (Fig. 4c) confirms that the sample contains only titanium, aluminium and oxygen; no other impurity is present in the sample.



(a)



(b)



(c)

Figure 4: SEM images of (a) 0% Al: TiO_2 , (b) 2% Al: TiO_2 nanoparticles and (c) EDS of 2% Al: TiO_2 nanoparticles

IV. CONCLUSIONS

A lot of research work has been carried out to improve the efficiency of the dye-sensitized solar cell (DSSC). In the present work, we have proposed a simple and

convenient method to enhance the efficiency of DSSC by replacing TiO_2 nanoparticles with aluminium doped TiO_2 nanoparticles. The Al: TiO_2 nanoparticles synthesized by us have a single anatase phase. The structures are porous, a property desirable for the functioning of DSSC. Moreover, the results from I-V measurements show that conductivity increases substantially as doping concentration increases. Thus, dye-sensitized solar cells (DSSC) having higher efficiency can be manufactured by using Aluminium doped TiO_2 nanoparticles. Enhanced efficiency leads to higher energy production without polluting the environment.

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