Novel sol gel method of synthesis of pure and Aluminium doped TiO₂ nano particles useful for dye sensitized solar cell applications

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Abstract - *Pure and doped TiO₂ nano particles are prepared using acid tailored novel sol - gel method using different doping concentration of metal Aluminium and successfully used for making modified photo anode by doctor blade method in dye sensitized solar cells (DSSCs). The samples were characterized using powder XRD, UV-Vis and current- voltage curves. We report this versatile and easy novel method for preparation of pure and doped TiO₂ nanoparticles with increased performance of DSSCs. Ruthenium dye as photo sensitizer along with electrolyte enhanced the performance of DSSCs with the tuned actions of oxidation and reduction reactions.*

XRD results show that all samples prepared by this method having particle size in the range of 11 nm to 23.9 nm. Sample with 0.03 mole % Al doping having particle size of 17.2 nm is optimized for making photoanode with 9.7 % efficiency.

Key Words: *Sol gel1, photosensitizer2, redox couple3, oxidation4, reduction5.*

1.   INTRODUCTION

There is wide range of product applications of TiO₂ nanoparticles. Dye sensitized solar cells (DSSCs) have attracted a great attention due to their low cost, easy fabrication and stability. DSSCs devices based on ruthenium dyes such as N719 [cis-bis (isothiocyanato) bis (2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) bis-tetrabutyl ammonium], or natural dyes as photo sensitizer along with a suitable redox couple exhibits relatively a high photovoltaic performance and good stability. Researchers have tried to control the morphology of TiO₂ photo-electrodes by different methods. In this method enhancement is observed in the performance of cell which would provide enormous economic advantages [1-3]. This multi junction system used for separation, recombination and transport of electronic charges completely based on the mesoporosity

and nano crystallinity of the pure and doped TiO₂ thin film. It was usually found that different routes often produce different results [4-6]. So it is necessary for us to investigate in detail the methods which may have important effect upon the particle size. This feature of DSSCs help in large amount of dye adsorption. On the basis of available experimental data, the basic cause for the photo voltage is the change in the electron concentration that results from photo induced charge injection from the dye. Five samples are prepared using this novel method have particle size of 11nm in pure anatase form and the doped TiO₂ particles size varies from 12.9 to 23.9 nm. Thin film samples were tested under different conditions for photovoltaic performance. XRD analysis, UV-Vis spectroscopy and voltage-current characteristics are used in this typical method for the characterization of the thin films. To increase light harvesting of DSSCs, surface plasmon resonance effect of metal nanoparticles has been incorporated in photoanode. These metal nanoparticles will localize the incident light and extend optical path length in DSSCs for the improved performance [7-9].

2.   EXPERIMENTAL

2.1   Materials

This novel method can be divided into three basic steps. (i) Pure and doped TiO₂ nanoparticle preparation (ii) Paste preparation (iii) deposition. Chemical reagents for the preparation of pure and doped TiO₂ nanoparticles were used in this method are titanium tatra isopropoxide (TTIP) (Sigma-Aldrich), ethanol (Merck) and hydrochloric acid (HCl) (Merck) Al₂NO₃, deionized water glacial acetic acid anhydrous ethanol. Paste of TiO₂ nanoparticles for photo electrode were prepared using chemical reagents like distilled water, acetyl acetone (A.R.), triton (X-100) and polyethylene glycol (PEG). Florine doped SnO₂ (FTO) were cleaned with methanol and acetone and then ultrasonic treatment was given for 20 min before using for film deposition. Ruthenium N719 (solaronix) as sensitizer and idolyte as redox couple were used.

2.2 Preparation of TiO₂ nano powder

In this typical method TiO_2 nanoparticles are prepared using TTIP as raw material. First take 20 ml ethanol in a beaker and slowly add 0.5ml conc. HCl acid. Manually stir this solution for half an hour. Now add 2.5 ml TTIP to this solution and stir it for two hours using magnetic stirrer in a sufficiently large beaker. Now keep this solution for drying in hot air oven for 12 hours at 100^0 C. Obtained solids now ground well in agate mortar for 15 min then kept for calcination in muffle furnace at 450^0 C for 1 hour.

2.3 Preparation of doped TiO₂ nano powder

In a typical method Al_2NO_3 (0.01, 0.03, 0.05 mole %) were dissolved in 60ml of deionized water at room temperature followed by adding 5 ml of glacial acetic acid to obtain solution A.14 ml titanium isopropoxide was dissolved in 40 ml of anhydrous ethanol with constant stirring to form solution B. Then solution B was added drop wise into solution A within 60 min. under vigorous stirring. Subsequently the obtained solution was stirred continuously for 2 hours and aged for 24 hours at room temp. As prepared TiO_2 gels were dried for 10 hours at 80^0C. The obtained solids were ground and finally calcined at 450^0C for 2 h (Heating rate=3^0C/min.)

2.4 Preparation of DSSC

Pure and doped nano powder prepared using above methods dissolved in certain proportion of distilled water, acetyl acetone, triton (X-100) and polyethylene glycol. This mixture now stirred well for half an hour using magnetic stirrer. Using doctor blade technique for the deposition, a uniform layer of this paste is formed on the cleaned FTO. These pure and doped TiO_2 coated FTO is sintered at 450^0 C for half an hour using proportional integral derivative (PID) controlled heater at the temp. rise rate of 90C /min, then sample is held at 450^0 C for half an hour and finally sample is slowly cooled till room temp. with the rate of 10^0C /min for stable film formation. Another cleaned carbon coated FTO is used as counter electrode. 0.5 mM dye solution using ruthenium N 719 is prepared in ethanol [10-12]. For this 0.00297 gm of dye is dissolved in 5 ml ethanol and stirred for half an hour. Photo electrode is kept in this dye solution for 24 hours at room temperature. Sensitized photo electrode and carbon coated counter electrode were assembled using spacer and the then electrolyte is used into the working space via capillary action.

3. RESULTS AND DISCUSSION

3.1 Crystal phase and particle size

Fig.1(a) and 1(b) shows the XRD patterns of the samples prepared at annealing temperature of 450^0 C. Pure TiO_2 nanoparticles prepared by this method can be assigned to anatase crystal phase according to the standards available in JCPDS (pattern No.21-1272).Results shows that surface modified TiO_2 possess consistent peak positions and intensities with the standard anatase TiO_2. It has a main peak 25.2^0 corresponding to the [101] plane. The average grain size is calculated from the peak (101) present in the XRD pattern of anatase phase of TiO_2 using Scherrer's equation i.e.

$$D = \frac{k\,\lambda}{\beta\cos\varphi}$$ (eq.1)

where k is the constant for shape factor equal to 0.9, λ is the X ray wavelength, β is the full width at half maximum of the peak and ø is the diffraction angle[13]. Results shows that particle size of the pure TiO_2 sample with anatase phase is 11nm. The peak positions of pure TiO_2 (tatragonal) in anatase form are 25.4, 37.8, 48.2, 54.1 and 62.8 are in accordance with the reported value available in literature. Results show that Al doping in TiO_2 with 0.03 mole % has particle size comparable to the size of pure TiO_2 nanoparticles indicating a suitable concentration of Al.

Table-1: Particle size of undoped and doped TiO_2 (Tetragonal)

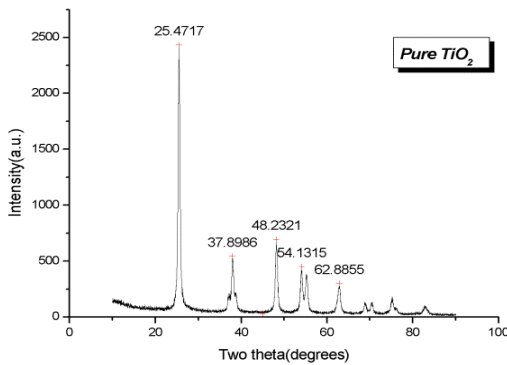| Sample	Mole % Al	Grain size(nm)
Pure TiO_2	0	11
Al doped TiO_2	0.01	12.9
Al doped TiO_2	0.03	11.2
Al doped TiO_2	0.05	19.5
Al doped TiO_2	0.07	23.9

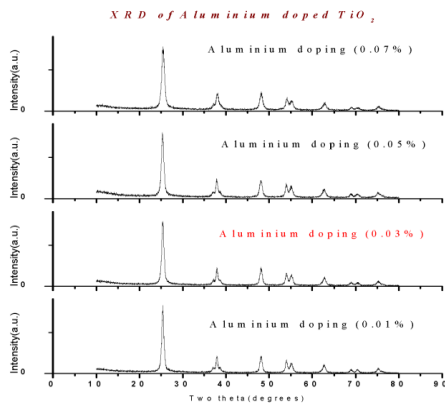**Fig.-1(a)**: XRD patterns of doped TiO$_2$

Fig.-1(b): XRD patterns of Al doped TiO$_2$

3.2 UV-Vis analysis

Electric method for energy band gap calculation using thermal excitation is not very useful as compared to the optical method which is very simple way of finding band gap. Energy band gap of pure and 0.03 mole % Al doped TiO$_2$ are 3.1eV and 2.8 eV respectively, which means there is a shift in the solar spectrum towards the lower wavelength region in case of doped TiO$_2$ due to which absorption is increased as compared to pure TiO$_2$. UV-Vis diffuse reflectance spectra of the Al doped TiO$_2$, based on Kubelka–Munk function [16,14],

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \qquad\qquad (eq.2)$$

is observed in the wavelength range of 200–800nm. Here F(R) and R are the absorbance and the reflectance of the samples respectively. The absorption properties and the band gap of materials can be calculated by using absorption spectra. The optical band gap of the

nanoparticles was determined by using the Tauc relation [17,15],

$$\alpha h\nu = \beta(h\nu - E_g) \qquad\qquad (eq.3)$$

The value of n = 1/2, 3/2, 2 or 3 depending on the nature of the electronic transition responsible for absorption. Here n=2 is used for indirect band gap semiconductor [18, 16].Here α is Absorption coefficient, h is Planck's constant and ν is the photon frequency. The indirect band gap value reported corresponding to n=2 in literature for bulk anatase in estimated from 3.10 to 3.20 eV.Fig.2(a) and Fig.2(b) show the reflectance absorbance of pure and Al doped TiO$_2$ samples with respect to energy band gap. Sample doped with 0.03 mole % of Al showing a band gap reduction from 3.1eV to 2.83eV.The change in band gap with doping causes a spectral shift from UV region to visible (blue) region.
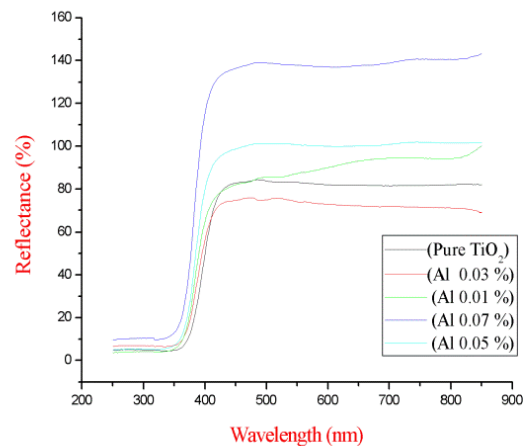

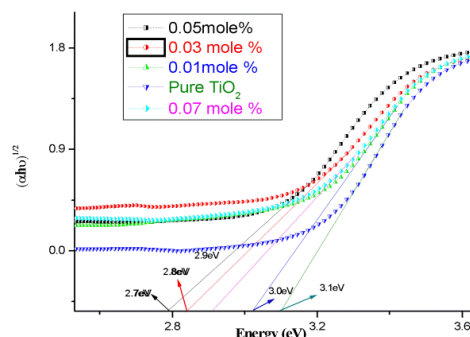**Fig-2(a):** Reflectance versus wavelength curves

Fig -2(b): Tauc plot of pure and doped TiO$_2$

3.3 Photovoltaic characteristics of DSSC

The photocurrent and voltage behavior of DSSCs with different size nanoparticles are characterized by using open circuit voltage (V_{oc}) and short circuit current (I_{sc}). The maximum voltage and maximum current were calculated using following equation at maximum power value [13-15].

$$P = IV \qquad \text{(eq.4)}$$

Furthermore the fill factor is given by

$$FF = \frac{Vmax \cdot Imax}{Voc \cdot Isc} \qquad \text{(eq.5)}$$

$$\text{Efficiency}(\eta) = \frac{Voc \cdot Isc \cdot FF}{Pin} *100 \qquad \text{(eq.6)}$$
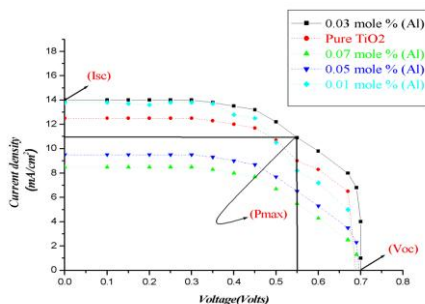

Fig- 3: Current-voltage characteristics of pure and Al

doped TiO_2 for DSSC

Table -2: Comparative study for the efficiency and fill factor of pure and doped DSSCs

Sample	V_{oc}, Volts	I_{sc}, mA/cm^2	V_{max}, Volts	I_{max}, mA/cm^2	P_{in}, mW/cm^2	Fill factor %	Efficiency, %
Pure TiO_2	0.63	12.3	0.5	9.0	100	0.58	7.7
0.01 %	0.65	13.8	0.5	9.6	100	0.53	8.9
0.03 %	0.69	14.1	0.5	10.09	100	0.52	9.7
0.05 %	0.63	9.5	0.5	6.4	100	0.57	5.9
0.07 %	0.67	8.4	0.5	5.5	100	0.49	5.6

Properties like conduction band position and trap /defect level distribution in nano TiO_2 can be tailored using metal doping. Doping affects values of V_{oc} as well as I_{sc} and researchers frequently discussed the mechanism responsible for this change. To date photo conversion efficiency (PCE) of DSSC using Donar-pi-Accepter organic dye is approximately 10.5% and using I_3^-/I^- redox electrolyte it is about 11.9% [19,20,21].

4. CONCLUSIONS

Pure and Al doped TiO_2 samples are prepared successfully for the photocurrent enhancement using novel acid tailored sol-gel method. XRD results shows that the particle size of TiO_2 is purely in anatase form and from UV–Vis analysis results confirm that the doped TiO_2 can reduce the energy band gap of TiO_2. Sample with 0.03 mol% of Al doping is optimized for the excellent solar conversion efficiency than pure TiO_2. Doped DSSC is the fascinating system from a scientific point of view which converts light energy into electrical energy in a very efficient way.

ACKNOWLEDGEMENT

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BIOGRAPHIES

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