

Chromium doping in titania for making dye-sensitized solar cell with improved efficiency and stability

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Dye-sensitized solar cell was fabricated by modifying photo anode with chromium doping in titanium dioxide prepared by sol-gel technique. Photo-anode was treated with TiCl_4 and pre-sensitization with deoxycholic acid (DCA) for enhancement in its short circuit current (J_{sc}) and open circuit voltage (V_{oc}). Quasi solid state electrolyte was used for improving its stability. The observations reveal that Cr-doped TiO_2 inhibits the phase transformation, increase the surface area and decrease the crystallite size as is evidenced by its X-ray diffraction (XRD)/Raman spectrum. Under open solar radiation of 100 mW/cm^2 (1 SUN) in ambient condition, J_{sc} gets enhanced from 2.31 mA to 4.11 mA and V_{oc} from 0.42 V to 0.58 V due to modification in photo-anode. The overall efficiency (η) enhanced by 200%.

Keywords: Sol gel technique, chromium doping, curcumine, sensitization, chemical treatment, conversion efficiency, quasi solid state electrolyte.

Introduction

Solar energy harvesting using dye-sensitized solar cells (DSSC) is simple, cost-effective and environmental-friendly approach to produce electrical energy^{1,2}. Fabrication of inorganic solar cells is difficult, costly and un-ecofriendly. Organic solar cells based on dye-sensitized using titania based dye-sensitized organic semiconductor films is low-cost, easy and ecofriendly alternatives to commercially available solar cells. In present research work quasi solid state electrolyte were used to overcome with the leakage problem of liquid electrolyte. Quasi solid state electrolyte enhances stability of device³.

Quasi solid state electrolyte lowers conversion efficiency of cell as it does not allow that much free flow of electron as in liquid electrolyte.

Modification in photo-anode by doping of titania can be carried out by insertion of dopant into the lattice of TiO_2 by sol-gel methods⁴, hydrothermal/co-precipitation synthesis⁵, flame pyrolysis⁶, solid state synthesis⁷, physical vapor deposition and ion implantation⁸ etc.

Geetha *et al.* prepared TiO_2 nanoparticles by acid modified sol-gel method and doped it by varying different mole%

of chromium⁹. DSSC based on curcumine dye as sensitizer has been reported by Sreekala *et al.*¹⁰. They used different types of solvents for better sensitization. The cell fabricated with this dye shows J_{sc} 3.039 mA/cm^2 , V_{oc} 0.51 V, FF 0.44 and 1.42% conversion efficiency (at illumination intensity of 48 mW/cm^2). However, the drawback in this cell is the use of liquid electrolyte that reduces the stability of device.

In present communication we fabricated DSSC using solid state ionic polymeric electrolyte (I^-/I_3^-) to enhance stability. DSSC fabricated with such quasi solid polymeric electrolyte in ionic complex system retained its PV characteristics for longer time in comparison to cell based on liquid electrolyte. We have also studied the selective and combined influence of CDCA and TiCl_4 treatment on photo-anode after modification in terms of conversion efficiency of the cell.

Experimental

Materials:

Titanium(IV) butoxide was purchased from Fluka (CAS 5693-70-4) and used to prepare sol-gel based nc-titaniapaste. $\text{Cr}(\text{NO}_3)_3$ and glacial acetic acid were procured from CDH.

Hydrogen hexachloroplatinate (H_2PtCl_6) was purchased from Fluka USA (CAS 16941-12-1) diluted in methanol for making counter electrode by thermal bath evaporation. Pre-sensitizer Cheno Deoxycholic acid (CDCA) was procured from Acros USA (CAS 474-25-9). Etching solution for surface treatment titanium tetrachloride (TiCl_4) was procured from CDH, New Delhi (CAS-7550-45-0) having purity of 99.95%.

Device fabrication:

Preparation of photo-anode (working electrode):

Fluorine doped tin oxide (FTO) was used as conducting substrate and cleaning of substrate carried out using acidic and alcoholic media followed with Ultrasonic Cleaning Bath (Model: Sonicator SG-3042) and Plasma Cleaner (Model: Harrick Plasma PDC-002) for 5 min prior to the preparation of screen printable film.

14 ml of titanium butoxide mixed with 40 ml of methanol with constant stirring at room temperature for preparation of sol-gel nc-TiO_2 . The prepared TiO_2 gel was then dried at 80°C for 10 h. The solid material obtained now crushed into fine particles and calcinated at 450°C for 2 h at a rate of 3°C per minute. Crushed fine particle dissolved in 1-butanol by continuous stirring for 24 h so that screen printable paste is prepared. This paste was used in screen printing using screen of 100 mesh to develop photo-anode. Chromium doping in titania by sol-gel technique was carried out by two solution steps:

Solution 1 contains 1.2005 g of $\text{Cr}(\text{NO}_3)_3$ is dissolved in 60 ml of DI water followed by addition of 5 ml glacial acetic acid at room temperature.

Solution 2 contains 14 ml of titanium butoxide mixed with 40 ml of methanol with constant stirring at room temperature.

Solution 1 added to solution 2 drop by drop within 60 min with homogeneous mixing by stirring it next 2 h. The obtained solution is now kept for 48 h to settle. The prepared $\text{Cr}:\text{TiO}_2$ gel was then dried at 80°C for 10 h. The solid material obtained in this way is now crushed into fine particles and calcinated at 450°C for 2 h at a rate of 3°C per minute. Now chromium doped titania is dissolved in 1-butanol by continuous stirring for 24 h so that screen printable paste is prepared. This paste was then used in screen printing using screen of 100 mesh to develop photo-anode. Chromium

doped titania film developed by screen printing was again sintered at 450°C .

1 mM solution of Cheno Deoxy Cholic acid (CDCA) in methanol is used as pre-sensitizer for working electrode. Sintered photo-anode immersed into CDCA solution and left for overnight. Finally, it is taken out and dried at room temperature.

1 mM solution of aqueous hydrochloric acid (HCl) solution was used to prepare etching solution. Further, two drops of titanium chloride (TiCl_4) were added to this acidic HCl solution. Now, sintered photo-anode was immersed into this solution for two hours and dried at room temperature.

Curcumin dye solution in acetone is used as sensitizer for preparing five types of photo-anodes i.e. (i) titania sensitized with curcumine, (ii) chromium doped titania sensitized with curcumine, (iii) deoxycholic acid treated chromium doped titania sensitized with curcumine, (iv) TiCl_4 treated Cr-doped titania sensitized with curcumine. Chromium doped titania electrode treated with TiCl_4 and then with CDCA and finally sensitized with curcumin dye.

In the process of sensitization with curcumin dye all five types of photo-anode were immersed into 0.5 mM solution of curcumin dye in acetone and left for overnight. After this, the photo electrodes were taken out and rinsed with acetone solvent to remove excess of dye, so that excess dye should not hinders the effective charge transfer process.

Fabrication of counter electrode:

Chloroplatinic acid hexahydrate (H_2PtCl_6) solution in methanol 10% v/v was evaporated on conducting FTO substrate by using hot water bath. Temperature of substrate is maintained at 70°C to evaporate diluted chloroplatinic acid hexahydrate solution on FTO substrate with the help of glass rod. Now chloroplatinic acid hexahydrate coated FTO substrate is sintered in muffle furnace (Make: Bio Technic India, Model: PTT1\$) at 450°C for 1 h.

Preparation of polymeric electrolyte:

A polymeric electrolyte consisting of iodide/triiodide redox was prepared by the procedure reported elsewhere³. In the process, a mixture of gamma butyro lactone (GBL) and n-methyl pyrrolidone (NMP) was taken and KI (0.5 M) and I_2 (0.1 M) was added into it. Further, a thin sheet of polyvinyl butraldehyde (PVB) was immersed into it for 2 h and then

taken out for the use as electrolyte.

Assembling of DSSC:

Quasi solid state electrolyte polymeric ionic complex system sandwiched between working electrode and counter electrode to fabricate DSSC as shown in Fig. 1.

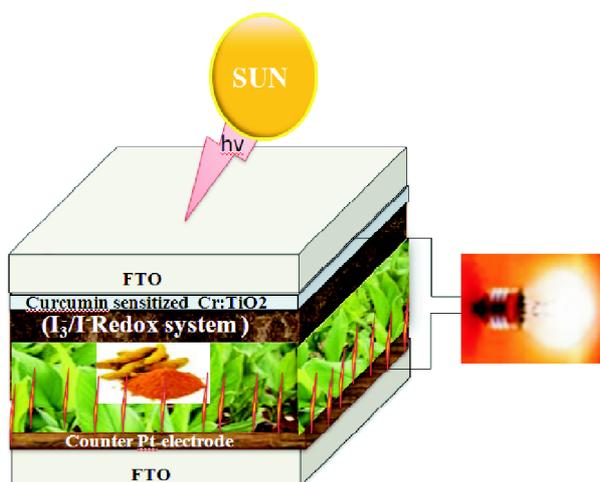


Fig. 1. Schematic device structure.

Device characterization:

Absorption spectra analysis:

Absorption spectra of sensitized working electrodes were recorded after sensitization with curcumin dye in acetone solvent for ranging from 200 nm to 1100 nm using Photo-diode Array Spectrophotometer (Model: Specord S-300 analytic jena).

Absorption spectra of working electrode after pre treatments CDCA and surface etching treatments with TiCl_4 widened dye absorbance as shown in Fig. 2. Optical spectra of Cr-doped titania shows red shift from 640 nm to 800 nm due to d-d transition between doping level of Cr^{3+} ion and conduction band¹¹.

Raman spectra analysis:

Raman spectra of the TiO_2 and Cr- TiO_2 were recorded with Avalon Raman Spectrometer from 250 cm^{-1} to 3000 cm^{-1} .

As revealed from the Fig. 3, that, the characteristic peak E_g appears at 640 cm^{-1} and other active modes appears at 400 cm^{-1} and 530 cm^{-1} . The peak at 860 cm^{-1} clearly indicates doping of titania with chromium.

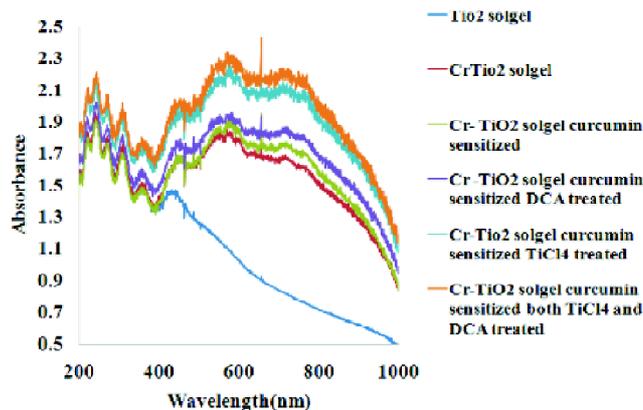


Fig. 2. UV-Vis absorption spectra of working electrode.

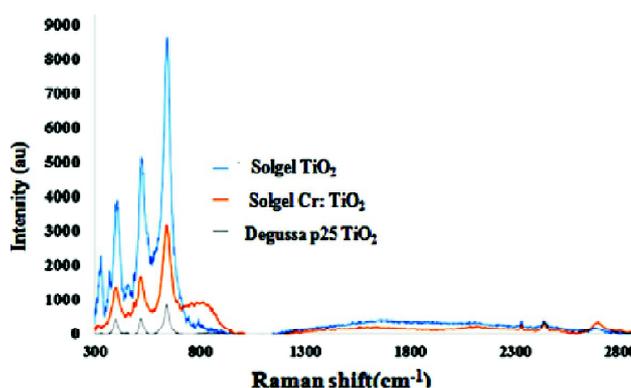


Fig. 3. Raman spectra of (a) Degussa p25 titania, (b) Cr-doped titania and (c) titania by sol-gel technique.

XRD analysis:

XRD spectra of the TiO_2 and Cr- TiO_2 were recorded using XRD (Make: PANalytical. XRD). Reflection from (101), (103), (200), (105), (211), (204), (116) and (220) planes, at 2θ values 25.34° , 37.9° , 48.24° , 53.9° , 55.0° , 62.9° , 68.7° and 70.1° , respectively correspond to anatase phase of TiO_2 (as per JCPDS card no. 84-1286). The average size of nc TiO_2 estimated using Sherrer equation for anatase diffraction peak.

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta}$$

Here, D_{hkl} denotes crystal size, λ denotes X-ray wavelength (0.154 nm), θ denotes the diffraction angle and β denotes full width at half maximum (FWHM) of the diffraction peak.

Crystal sizes estimated about 10.07 nm for TiO₂ prepared by sol-gel technique while chromium doped was about 9.83 nm.

It is clear that anatase crystalline phase of TiO₂ remain unchanged with incorporation of Cr into the TiO₂ lattice. However, Cr-doped TiO₂ nano-particles show reduced intensity with increased full-width half maximum of Bragg peak. Additionally, the decrease in particle size with Cr-doping results lowering of Fermi level in comparison to undoped nc-TiO₂¹².

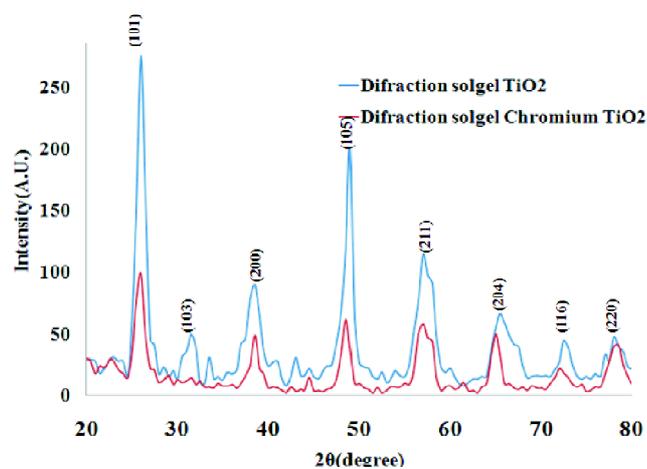


Fig. 4. XRD of (a) bare titania and (b) Cr-doped titania.

Energy mechanism analysis:

The energy flow diagram of the fabricated DSSC (Fig. 5) reveals that LUMO level of curcumin dye lies above the CB edge of nc-TiO₂ becomes more prominent after chromium doping due to reduction in the carrier density in the Ti 3d band, like an acceptor in the TiO₂ matrix resulting in a systematic reduction of the Fermi energy level¹³. This enhances an effective electron transfer from the excited state of curcumin dye to the CB of Cr-TiO₂ with respect to undoped TiO₂.

Electrical characteristics:

Current-Voltage characteristics of fabricated DSSC were carried out in ambient field condition having incident solar radiation of about 1000 W/m² using HP Semiconductor Parameter Analyser (Model: 41458).

DSSC having photo-anode only titania without any doping and treatment given low J_{sc} due to limited loading of dye

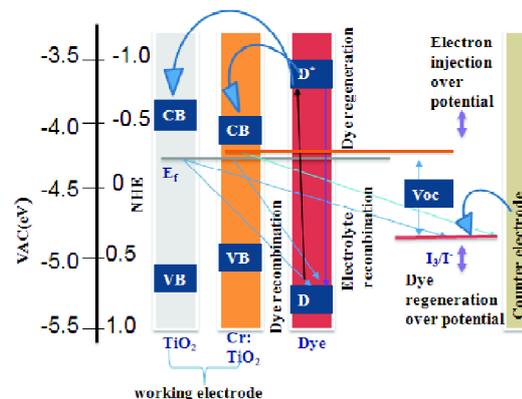


Fig. 5. Comparative energy flow mechanism of (a) bare titania and (b) Cr-doped titania photo-anode based fabricated DSSC.

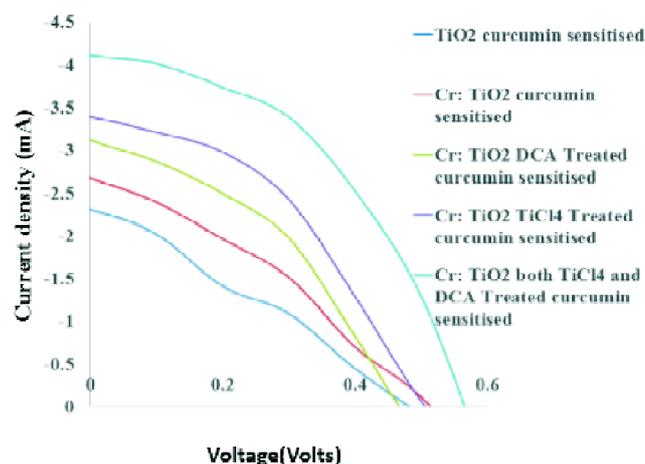


Fig. 6. V-I Characteristics of devices.

and efficiency of the cell was only 0.3%. When photo-anode prepared by doping chromium in titania by sol-gel process there was improvement in J_{sc} due to enrichment in electron and efficiency enhanced to 0.44%. When this photo-anode processed for pre-sensitization using Cheno deoxy cholic acid (CDCA) there was further enhancement in J_{sc} may be due to restriction in aggregation of dye molecules over the surface.

This leads to better injection process and lesser recombination. Thus enhancement in efficiency of cell reached to 0.54% when TiCl₄ is used as etching solution for treatment of photo-anode. It shows further enhancement in J_{sc} due to

enhanced dye loading leading to enhanced efficiency upto 0.76%. Photo-anode treated with both etching and pre-sensitization compounded enhancement in J_{sc} and V_{oc} both. Fabricated DSSC enhanced by this process up to 1.0%. Thus, etching treatment with $TiCl_4$ imparts improvement in photo-current due to enhanced dye loading and at the same time pre-sensitization with DCA restricts aggregation of dye molecules. Overall improvement in the conversion efficiency of the cell is depicted in Table 1. The parameters evaluated in ambient field condition are V_{oc} , J_{sc} , FF and η . Standard equation used for evolution of conversion efficiency of the cell, are as follows:

$$\text{Fill factor (FF)} = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}$$

$$\text{Efficiency } \eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$

Results and discussion

Liquid electrolytes are frequently used in making DSSCs but major drawback is seen in durability due to problems of leakage. We have used polymeric electrolyte consisting of iodide/triiodide system to fabricate DSSC. This electrolyte imparts durability to the cells as it restricts leakage and also acts as a binder so that both the electrodes becomes rigid with time to maintain structure of device shown in Fig. 1. Study reveals that co-adsorption of photo-anode with CDCA improves electron injection due to restriction in formation of dye aggregates and imparts enhancement in J_{sc} from 2.67 mA to 3.11 mA. Additionally, surface roughness of photo-anode gets increased after etching treatment with $TiCl_4$ that generates more binding sites for dye molecules and therefore an increased J_{sc} from 3.11 mA to 3.39 mA is observed due to enhanced dye loading^{14–16}.

Photo-anode is treated with $TiCl_4$ followed by pre-sensitization with CDCA shows enhancement in both J_{sc} and V_{oc} .

Table 1. Photovoltaic parameters of device

Device configuration	V_{oc} (Volts)	J_{sc} (mA/cm ²)	Fill factor (FF)	Efficiency ($\eta\%$)
FTO/TiO ₂ /Dye (Untreated)	0.42	2.31	0.36	0.3
FTO/Cr-TiO ₂ /Dye (Untreated)	0.52	2.67	0.32	0.44
FTO/Cr-TiO ₂ /Dye (DCA treated)	0.50	3.11	0.38	0.54
FTO/Cr-TiO ₂ /Dye ($TiCl_4$ treated)	0.51	3.39	0.42	0.76
FTO/Cr-TiO ₂ /Dye ($TiCl_4$ and DCA treated)	0.53	4.11	0.44	1.0

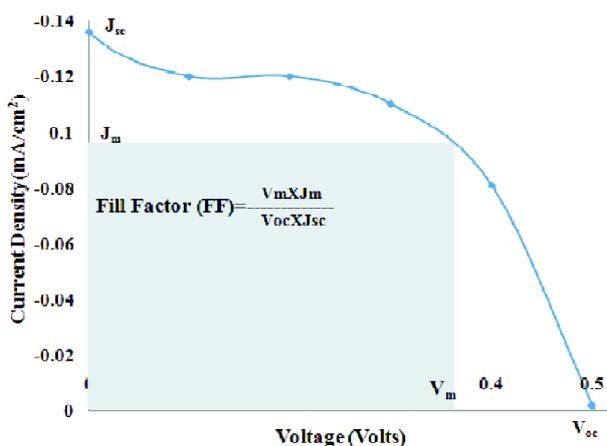


Fig. 7. Fill factor (FF).

J_{sc} enhanced from 3.39 mA to 4.11 mA and V_{oc} enhanced from 0.51 V to 0.53 V. The overall increase in conversion efficiency of DSSC is observed up to 1.0%. It does mean that modification in nc-TiO₂ by chromium doping followed by etching treatment with $TiCl_4$ and pre-sensitization treatment with CDCA plays very important roles to increase conversion efficiency of the cell. CDCA is a bile acid which imparts reduction in dye aggregation at the surface of photo-anode and $TiCl_4$ treatment provide large surface area along with binding sites.

Conclusion

Conversion efficiency of the cell is improved by modifying photo-anode with Cr-doping. Further, etching treatment with $TiCl_4$ followed by pre-sensitization with CDCA imparts

enhancement in J_{sc} and V_{oc} and overall conversion efficiency. In addition to this, the use of iodide/tri-iodide based ionic polymer matrix enable cell's stability by restricting its leakage. It is useful in development of efficient low cost dye-sensitized solar cells and modules with improved stability having commercial potential.

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