Performance engineering of dye sensitized solar cells (DSSC) using Ag modified titania as photoanode

Ranjith G. Nair¹,a, Mathan Kumar P.¹,b and S. K. Samdarshi²,c

¹Solar Energy Materials Research and Testing Laboratory (SMaRT Lab), Department of Physics, National Institute of Technology Silchar, Cachar, Assam-788010, India.
²Centre for Energy Engineering and Centre of Excellence in Green and Efficient Energy Technology (CoE-GEET), Central University of Jharkhand, Ranchi, 835205, India.

a rgnair2007@gmail.com, b mathannits92@gmail.com, c drkssamdarshi@rediffmail.com

Abstract. Present work reports the fabrication of silver (Ag) modified titania photoanode as an efficient photoanode for Dye Sensitized Solar Cell (DSSC). Pristine and Ag modified Titania nanomaterials were prepared using sol gel method. The structural analyses confirm the high crystallinity of the samples with crystallite size distribution in nanorange. TEM micrograph confirms that the synthesized nanomaterials are in uniform size. A red shift is observed in the UV DRS spectra compared to pristine Titania and which confirm the incorporation of Ag inside titania. A prototype DSSC was fabricated using the pristine and modified Titania as photoanode, Ruthenium dye as sensitizer, I-/I-3 as redox electrolyte and platinum counter electrode. The cell with Ag modified titania photoanode showed 15 times enhanced photoconversion efficiency (PCE) than the pristine one. This improved performance of the Ag modified DSSC can be ascribed to reduced recombination and improved charge carrier transport of electrons/ holes at the interfaces.

1. Introduction

Dye-sensitized solar cells (DSSCs) is a promising alternative to the traditional silicon photovoltaic technology due to its low cost, flexibility, and easy fabrication[1]. The maximum reported photoconversion efficiency of DSSC is 13%[2]. Stability, interfacial charge carrier transport and recombination of charge carriers are the major factors that limit DSSC for commercialization. The performance of the DSSC can be improved by increasing the light harvesting, reducing interfacial charge carrier recombination and increasing the charge carrier transport at the interfaces [3].

Multiple attempts were made over decades to solve the above issues through modified photoanodes[4], increased dye loading and tuning its absorption[5], replacing liquid to solid state electrolyte[6] and modifying the interfaces to favor the electron transport[7]. Recently it has been reported that, incorporation of noble metals such as gold, silver etc. in photoanode can improve the photoconversion efficiency through tuning the dye absorption coefficient due to Surface Plasmon Resonance (SPR), reducing interfacial recombination and improving charge carrier transport[8-11].

Based on the above present work investigates the synthesis and characterization of Ag modified titania as an effective photoanode for DSSC and its photovoltaic performance. Initially pristine and Ag modified Titania nanoparticles were synthesized and its physico-chemical characteristics were studied.
A prototype Dye Sensitized Solar Cells were fabricated using pristine and Ag modified Titania as photoanode. The photovoltaic performances of the fabricated DSSC were studied using I-V characteristics and compared. The open circuit voltage and the short circuit current are measured under light and dark conditions.

2. Experimental

2.1. Materials
The precursors used for the synthesis of Ag modified Titania were Titanium iso-propoxide with 95% purity from Sigma Aldrich [Ti (OCH (CH3)2)4], isopropyl alcohol [CH3)2(CHOH)] and Silver nitrate (AgNO3) from Merck. FTO glass substrates of 2.2mm thick with a surface resistivity of 7 Ω cm-2 with 80% transmission, Ruthenizer 535-bisTBA or N719 , Platisol T (a liquid paint containing a chemical platinum precursor) and Iodolyte AN-50 were obtained from Solaronix SA, Switzerland.

Pristine Titania was synthesized by mixing titanium iso-propoxide with propanol in 1:10 ratio at room temperature under constant stirring to form sol and kept 24 hrs to obtain gel. Ag modified Titania was prepared by adding 2.5 wt.% of AgNO3 solution in 1ml of water to the Titania sol at room temperature under constant stirring to form resultant sol. The substrates were cleaned with ethanol, acetone and sonication followed by washing with double distilled water. The pristine and Ag modified Titania thin films were prepared by gently dipping the substrates into the as prepared and Ag modified sol respectively. The films were then dried at 100°C for 10 min. This process is repeated to get the desired thickness. The prepared films were then annealed at 400°C for 1 hour.

The N719 dye solution was prepared by mixing 10mg of dry dye powder in 25mL of methanol. The prepared Ag modified photoanode was then cooled down and soaked into the dye solution for 2 days in a sealed beaker at room temperature for dye sensitization. The sensitized photoanode is washed with ethanol to remove the additional dye absorbed portions and it was dried at 60°C. The platinum counter electrode was prepared by gently painting the platinum precursor ink with a regular brush on FTO substrate. Later the platinum-coated conducting glass (counter electrode) is sandwiched with N719 dye-sensitized electrode (working electrode) with clips. A proper amount of redox electrolyte, Iodolyte AN-50(Solaronix SA, Switzerland) was injected in between the two glass plates and gently press the clips to allow the electrolyte to spread along the surface. Finally the device was sealed properly to avoid electrolyte leakage.

2.2. Characterization
The structural analyses of the prepared samples were studied using X ray diffraction (XRD) pattern, with a diffractometer (Rigaku Miniflux,Japan) using Cu Kα radiation (λ=1.5Ǻ) at 30 kV and 450W at a scan rate of about 0.05° 20 per second and scan range between 10-70o and Transmission Electron Microscope (TEM) recorded using Joel Jem- 1000CX II, Japan. The surface and elemental analyses of the samples were recorded using Scanning electron microscopy (SEM) employing scanning electron microscope (Joel 6390 LV,Japan) operated at an operating voltage of 15 kW and Energy dispersive X-ray analysis(EDAX) using the EDAX (Oxford instrument, UK) attached to the SEM system. The optical properties of the samples were studied using Shimadzu UV-2200, Japan UV-visible spectrophotometer with diffuse reflectance attachment for UV- Visible light response and BaSO4 was used as reference. The solar cell performance of the samples were studied using I-V characteristics with Potentiostat /Galvanostat (AUTOLAB 302N, Metrohm, Holland). The performance of the cell was tested under both dark and white light illumination (100 W/m2 at 1.5 AM).

3. Results and Discussion
The XRD spectra of Ag modified Titania calcined at 400°C is shown in Figure 1. The spectra show that Ag modified Titania is in anatase phase with nanoscale crystallite distribution and which is in good agreement with the JCPDS (card no 73-1764) data.
A peak shift is observed in Ag modified Titania compared to pristine Titania and which can be ascribed to the incorporation of Ag inside the Titania matrix. The crystallite size of the samples were calculated using Scherrer’s equation[12]. The effective crystallite size of the samples were calculated without strain using Williamson Hall equation[13] The WH plot of Ag modified Titania shows the positive slope and which confirms the presence of tensile strain. The intercept values give the crystallite size without strain, which was found to be 18.10 nm for Ag modified Titania. The specific surface area was also calculated using the formula S= 6/pD, where p is the material density and D is the crystallite size obtained from Scherer’s equation. The values of the crystallite size, strain and specific surface area are given in Table 1.

| Sample     | Strain  | Crystallite size (nm) | Specific surface area (m²/g) | Bang Gap (eV) | EDS (Atom %) |
|------------|---------|-----------------------|------------------------------|--------------|--------------|
| Ag-TiO₂    | 0.0147  | 10.5                  | 18.18                        | 12.5         | 145.793      |
|            |         | Scherrer | WH  | TEM          |              |              |
|            | 18.18   | 12.5     | 2.7 | 5.48         | 94.52        |

Transmission Electron Microscope (TEM) analyses were carried out to understand the structure of the samples and shown in Figure-2a. The micrograph confirms that the crystallite size of the samples was in nanorange (~12.5nm) and which is in accordance with the XRD data.

Figure 1. XRD Spectra (a) and W-H Plot (b) of Ag modified Titania

Table 1. Physicochemical characteristics of the samples.

Figure 2. TEM (a) and SEM (b) images of Ag modified Titania

Surface and elemental analyses of the sample was carried out using Scanning Electron Microscopy and Energy Dispersive analyses respectively and shown in Figure-2b. The SEM micrographs of the sample reveals that the particles are highly agglomerated. The EDAK analyses of the sample confirm the Ag loading inside the Titania matrix and shown in Table 1.
UV-Visible spectroscopy of the samples is shown in figure 3. The spectrum shows the absorption edge of pristine Titania to be 385nm [14] and it is in agreement with the XRD results. A noticeable red shift is observed in the Ag modified Titania which can be attributed to the incorporation of Ag inside the Titania matrix[15]. The average band gap of the sample was calculated from the Tauc plot and the values are summarized in the Table 1.

![Figure 3. UV DRS Spectra (a) of Ag modified Titania along with Tauc's Plot (b)](image)

The current – voltage characterization of the fabricated solar cell was measured using 500W halogen lamp (Philips Halotone plus Line). The photovoltaic performance of the pristine and Ag doped cells were tested under both dark and white light illumination. The I-V characteristics of the fabricated cell are shown in Figure 4 and the values of Short circuit current, open circuit voltage, fill factor and efficiency are summarized in Table 2. The addition of Ag content greatly reduces the recombination and facilitates the photo generated electrons from the dye to the Titania due to the creation of electron-hole separation centers at the Ag / TiO2 interface and thus increases the Short circuit current Jsc. Whereas the significant improvement in the Open circuit voltage Voc is due to the shift of quasi-Fermi level of Ag-TiO2 to more negative level compared to the Pristine TiO2[11]. The photo conversion efficiency of the Ag/TiO2 cell is found to be 15 times more than the Pristine TiO2 cell.

![Figure 4. J-V characteristic of the fabricated cells](image)

| Table 2. Photovoltaic performance of Pristine and Ag Modified Titania |
|------------------------|---------|---------|---------|---------|---------|---------|
| Electrode       | Voc (V) | Jsc (mA) | Vmax (V) | Jmax (mA) | FF     | η (%)   |
| TiO2            | 0.277   | 1.374    | 0.147    | 0.957    | 0.371  | 0.028   |
| Ag/TiO2         | 0.490   | 10.600   | 0.302    | 7.040    | 0.409  | 0.421   |
4. Conclusion
Pristine and Ag modified titania photoanodes were prepared using a modified sol-gel method. The structural, surface, elemental and optical characterization of the samples were analyzed using XRD, TEM, SEM, EDS and UV-Vis spectroscopy. The structural analyses confirm the pristine anatase phase of the sample with nanoscale distribution. Surface analysis reveals that the particles are uniformly distributed with little agglomeration. Elemental analysis along with UV-visible spectra confirm the presence of Ag in the sample. A Dye Sensitized Solar Cells (DSSC) was fabricated using pristine and modified titania as photoanode, and its performance was tested under light and dark conditions. J-V characteristic of the Ag modified photoanode based DSSC shows an increased short circuit current, open circuit voltage, fill factor and photoconversion efficiency compared to pristine photoanode. The photo conversion efficiency of the Ag/TiO2 cell is found to be 15 times more than the pristine TiO2 cell. This improved performance is due to incorporation of Ag which reduces the interfacial recombination and enhances the transport of electron at the interfaces. The performance of the fabricated cell may be further improved by achieving surface plasmon resonance in the photoanode.

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