

Efficiency Enhancement of Dye-Sensitized Solar Cells using Silver nanowires

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Abstract: Development of highly efficient dye-sensitized solar cells (DSSCs) with good photovoltaic parameters is an active research area of current global interest. In this article, Ag-TiO₂ nanocomposite was used as the photoanode to fabricate dye sensitized solar cells. It was found that Ag-TiO₂ based solar cells have a significantly increased photocurrent density resulting in a improved conversion efficiency of 10.026% compared to pure TiO₂ based solar cells. The improved performance is attributed to two factors: (1) the increased light harvesting efficiency due to the plasmon enhanced optical absorption induced by Ag nanowires, and (2) the improved electron collection efficiency as a result of faster electron transport in the Ag-TiO₂ nanocomposite photoanode. We believe that simple approaches such as the present one to develop nanoparticle based DSSCs would open up enormous possibilities in effective harvesting of solar energy for commercial applications.

Keywords: Dye Sensitized solar cells; silver nanowires; surface plasmon resonance; photoanode.

I. INTRODUCTION

Development of efficient dye-sensitized solar cells (DSSCs) by simple methodologies offer immense scope and potential in the global strive towards harvesting solar energy. Most DSSCs employ TiO₂ as the porous material for anchoring light harvester (dye) molecules. In a DSSC, the photoexcited electrons of the dye are transferred to the conduction band of TiO₂, which are taken out through an external circuit using a working electrode (fluorine-doped tin oxide, FTO) and a counter electrode (platinum sputtered FTO), respectively, in the presence of an electrolyte. Recently, one dimensional nanomaterials, such as nanorods, nanotubes and nanofibers, have been proposed to replace the nanoparticles used in DSSCs because of their ability to improve the electron transport leading to enhanced electron collection efficiencies in DSSCs [1–4].

Another promising approach is to enhance optical absorption of the dyes by localized surface plasmons. Several groups have explored this approach using two dimensional thin films or nanoparticle of TiO₂. Yamada et al. [5] prepared Ag islands on top of thin film of TiO₂ by thermal evaporation and found an enhancement of the optical absorption of the dyes, which contributed to an increased photocurrent. Hägglund et al. [6] used nanofabricated gold ellipsoids on thin film TiO₂ in DSSCs and found that the dye charge carrier generation rate was elevated. Hupp et al. [7,8] examined the distance dependence of the plasmon-enhanced properties in DSSCs by varying the TiO₂ layer thickness forming the photoanode. It was reported that the plasmon-enhanced absorption of the dye was most pronounced in the sample with the thinnest layer of amorphous TiO₂ (2 nm). Chou et al. [9] investigated TiO₂/Au (or TiO₂/Ag) composite particles as a photoanode for DSSC and showed that their

performance always exceeded that of the conventional DSSC due to the present of Schottky barriers. Furthermore, promoted electron transport was observed by Kim et al. with silver and gold nanoparticle doped TiO₂ nanofibers used for the lithium-ion batteries [10].

In this Article, Ag-TiO₂ nanocomposite was fabricated and used for the photoanode. It was demonstrated that the addition of silver can enhance optical absorption of the dyes by localized surface plasmons and, at the same time, improve the electron transfer through the formation of a conductive percolation network, which has contributed to an increased photocurrent and an improved efficiency.

II. EXPERIMENTAL

A. Materials

Titanium(IV) isopropoxide and polyvinylpyrrolidone (PVP, Mw = 55000 g/mol) were from Sigma-Aldrich and used as received. Silver nitrate and glycerol (M.W. 92.09 g/mol) were purchased from S.D. Fine Chemicals Ltd. and used as received. Silver chloride, ethanol and nitric acid were from Sigma-Aldrich.

B. Synthesis of Silver Nanowires

Rapid synthesis of silver nanowires (Ag NWs) with high quality is challenging because of the low selectivity of the formation of multiply twinned particles at the nucleation stage for subsequent Ag NWs growth. Herein we have used the water-involved heterogeneous nucleation of Ag NWs with high rate (less than 20 min) in a simple and scalable preparation method. Using glycerol as a reducing agent and a solvent with a high boiling point, the reaction is rapidly heated to 210°C in air to synthesize Ag NWs with a very high yield in gram level. It is noted that the

addition of a small dose of water plays a key role for obtaining highly pure Ag NWs in high yield, and the optimal water/glycerol ratio is 0.25%.

In this procedure, 190 mL of glycerol solution containing 6 g of PVP was mixed and gently heated to 80 °C until all PVP is dissolved, and cooled to room temperature, then added into a round-bottom flask. AgNO₃ powder (1.58 g) was then added to the solution with vigorous stirring until the powder was fully dissolved. Subsequently, 58.5 mg of NaCl (5 mmol/L in total solution) was dissolved in 0.5 mL H₂O and added into 10 mL of glycerol.

The latter was added into the flask and the reaction temperature of the mixture was rapidly raised to 210 °C within 20 min, roughly 8 °C/min, keeping the magnetic stirrer at 50 r/min in the aerobic condition. When the reaction was stopped and the flask cooled down to room temperature, the deionized water was added into the flask by a 1:1 volume ratio, and then the mixture was centrifuged at 8000 r/min until all visible products were collected. The transparent supernatant was discarded and the as-obtained Ag NWs were washed by water three times to remove the PVP residue. During the reaction process, the color of the solution turns from pale white to light brown, red, dark gray, and eventually gray green (at about 200 °C). [11]

C. Synthesis of TiO₂ Nanoparticles using Sol-gel Method

The sol-gel synthesized TiO₂ NPs were obtained from Titanium isopropoxide dissolved in 50 mL absolute ethanol and distilled water was added to the solution in terms of a molar ratio of Ti : H₂O = 1 : 4. Nitric acid was used to adjust the pH and for restraining the hydrolysis process of the solution. The solution was vigorously stirred for 60 min in order to form sols. After aging for 24 hours, the sols were transformed into gels. In order to obtain nanoparticles, the gels were dried under 120 °C for 2 hours to evaporate water and organic material to the maximum extent. Then the dry gel was sintered at 550 °C for 2 hours to obtain desired TiO₂ NPs.

D. Synthesis of TiO₂-Ag Nanocomposite

The TiO₂-Ag composite was prepared using the sonication method. Firstly, 750 mg of TiO₂ powder was grinded in the mortar and then it was dissolved in 25 mL of ethanol. Then the TiO₂ NPs solution was subjected to ultrasonication for 15 min. Now, take 37.5 mg of silver (5% of TiO₂) and dissolve in 10 mL of ethanol to make a solution. Then the silver solution was added dropwise into the TiO₂ solution. After this, the mixture is subjected to ultrasonication for 15 min. Now make a paste of the nanocomposite in ethanol and grind it well in the mortar to convert it into powder form and store it in a sample container.

E. DSSC Fabrication

Dye Sensitized Solar cells were prepared using TiO₂-Ag nanocomposite deposited FTO coated glass as working electrode, natural and organic dyes as photosensitizers and Platinum coated glass as counter electrode.

1) Preparation of Dye Sensitizers :

Beetroot and Henna Extracts as dyes: Take a fresh beetroot, chop it into small pieces and put it into a beaker. Now chopped beetroot pieces were soaked in 200 mL of ethanol and heated at 75°C. Then the residual parts were filtered and filtrate is washed with hexane several times to remove any chlorophyll or oil present in the extract. Now this was directly used as a dye for sensitizing TiO₂-Ag composite electrodes.

For henna extract preparation, fresh henna leaves were put into 100 mL of ethanol and heated at 75°C for 30 min. After this, the solution is cooled to room temperature and filtered using filter paper. Now the filtrate was used as natural dye. [12]

Methylene Blue and Eosin Y were also used as synthetic dyes : Methylene Blue and Eosin Y were dissolved in 100 mL ethanol in separate beakers and then they were subjected to ultrasonication for 1 hour. Now the resulting solution was used as dye.

2) Preparation of Pt Counter Electrodes :

The counter electrodes were prepared by screen printing a thin layer of Platinum (Pt) with a size of 0.5 × 1.2 cm² using a platinum paste (Dyesol), on an FTO glass substrate (2 × 3 cm²), and then sintered at 450°C for 30 minutes.

3) Preparation of Ag-TiO₂ Electrode (Photoanode) :

The Ag-TiO₂ nanocomposite was used for preparing the working electrode of DSSC. The Ag-TiO₂ nanocomposite paste was prepared by grinding the nanocomposite powder (500 mg) in a mortar-pestle while adding solvent (about 5 ml acetic acid) dropwise. The paste preparation was done in ambient air at room temperature. The paste obtained was grinded and mixed with ethanol (10 ml). Then again the paste was grinded for about 10 min. and after this ultrasonication was performed for 15 minutes to homogenize TiO₂-Ag composite nanoparticles. Now we add some drops of PEG (PolyEthyleneGlycol) and Triton-X100 and grind the mixture to form a thick and shiny paste.

The DSSC working electrodes were prepared by immersing the FTO glass plates in ethanol and subjecting it to ultrasonication for 30 minutes and then rinsed with DI water and ethanol. A layer of Ag-TiO₂ paste was deposited on the above FTO glass by doctor-blade method using a scotch tape as the spacer. The paste was flattened with a glass rod. The developed DSSC working electrodes were placed in ethanol for a few minutes to reduce surface irregularities, and then dried for 5 minutes at 130 °C. The samples were sintered at 450 °C for 30 minutes in ambient air, and then cooled down to room temperature. Finally, the TiO₂/Ag electrodes were immersed in dye solution for 24 hours and prepared for dye-sensitized solar cells. [13]

Structural properties of the Ag -TiO₂ nanocomposite was observed using a scanning electron microscope and a transmission electron microscope (JEM1200-EX, JEOL) operating at an accelerating voltage of 200 kV. The phase and crystal structure of the Ag-TiO₂ nanocomposite was examined by X-ray diffractometer (XRD) (Siemens D5005) over a range of 2θ angles from 20° to 80°. UV-vis analysis was performed using a spectrometer (PerkinElmer

Lambda 950). The photovoltaic measurement of the DSSC samples was conducted by a solar simulator under AM1.5G condition. In this work, IR spectroscopy was carried out using FTIR Perkin- Elmer Spectrum 400 within the wave region of 4000 to 500 cm^{-1} . Dielectric measurements were carried out at room temperature using an impedance analyzer by applying an AC signal across the sample cell with a blocking electrode (silver) in a dielectric cell connected to a computer controlled HOIKI LCR Hi Tester 3532-50 setup. The real component of the complex dielectric function, the loss tangent, and the AC conductivity were calculated from the measured data.

III.RESULTS AND DISCUSSION

Figure 3.1.1 shows the XRD patterns of pure TiO_2 nanoparticles. The diffraction peaks at 2θ values of 24.48° , 36.99° , 47.30° , 53.14° , 54.34° and 61.99° correspond to the crystal planes of (101), (004), (200), (105), (211) and (204), respectively, indicating formation of anatase phase of TiO_2 and for Ag- TiO_2 nanocomposite (as shown in fig 3.1.2), a similar pattern is observed except that some extra diffraction peaks at 2θ values of values of 37.34° , 43.56° , 63.94° and 76.89° , corresponding to the crystal planes of (111), (200), (220) and (311), respectively affirm presence of silver metal. [13]

The XRD patterns (Fig 3.1.4) suggest that metallic Ag with FCC structure is successfully produced through the reaction. The peaks at 36.5° , 42.3° , and 63.7° are assigned to the diffraction from the (111), (200) and (220) planes of Ag, respectively which is consistent with the literature (JCPDS card number 87-0717). [11]

It is also observed that the full width at half maximum (FWHM) of the diffraction peaks increases on doping pure TiO_2 with silver nanowires. The increase in FWHM along with decrease in peak intensity suggests that incorporation of Ag into the TiO_2 lattice results in decrease in grain size of nanoparticles.

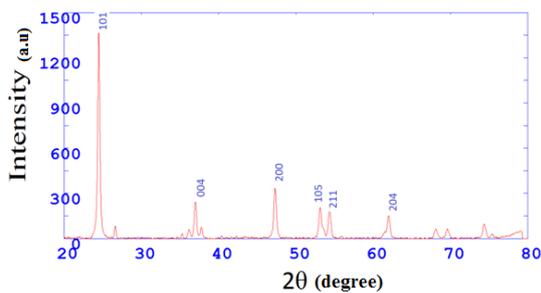


Fig. 3.1.1 XRD pattern of pure TiO_2

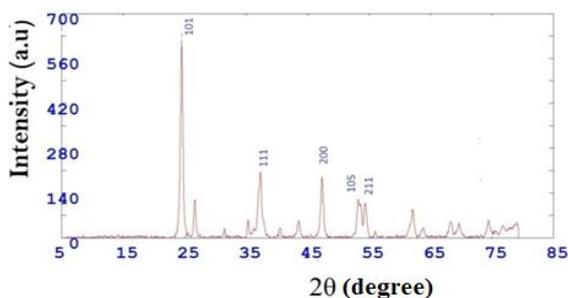


Fig. 3.1.2 XRD pattern of TiO_2 –Ag nanocomposite

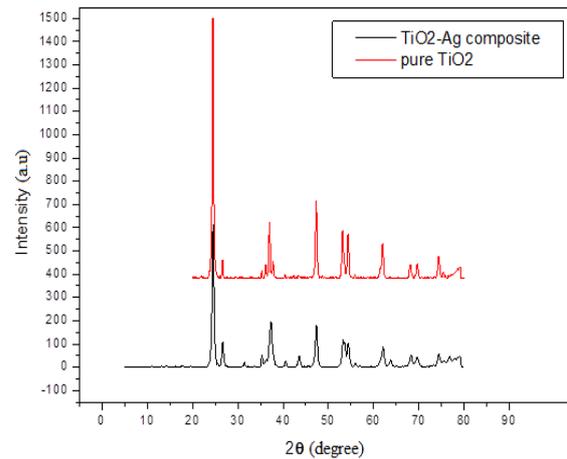


Fig. 3.1.3 Comparison of XRD patterns of TiO_2 and TiO_2 -Ag nanocomposite

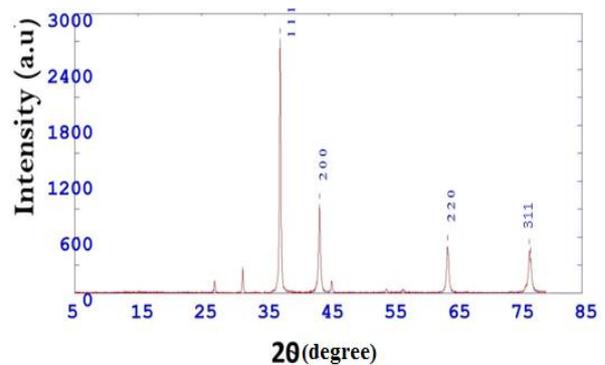


Fig. 3.1.4: XRD pattern of silver nanowires

Figure 3.2.1 gives the UV visible absorption spectra of pure TiO_2 , silver nanowires and TiO_2 .Ag nanocomposites. The absorption spectrum of pure TiO_2 shows absorption peak at 302 nm and for the TiO_2 –Ag nanocomposite; the absorption peak is at 323 nm. The absorption peak of pure TiO_2 is at lower wavelength than absorption peak of TiO_2 –Ag; thus showing red shift. The absorption spectrum of silver nanowires has peak at 438 nm. [13]

The optical band gap is calculated from Tauc plot by extrapolating the linear portion to the x-axis.

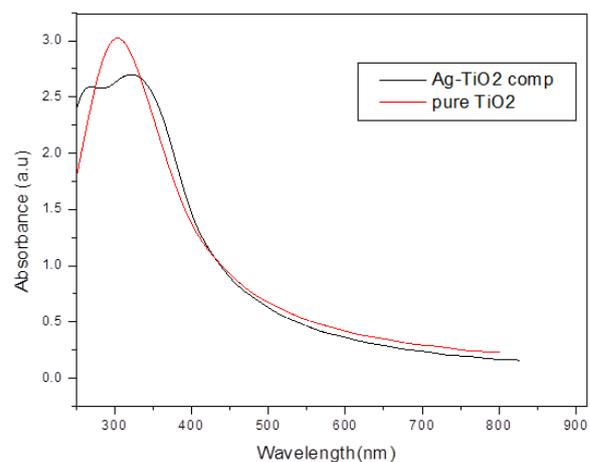


Fig. 3.2.1 (a) UV visible absorption spectra of pure TiO_2 and TiO_2 –Ag nanocomposite

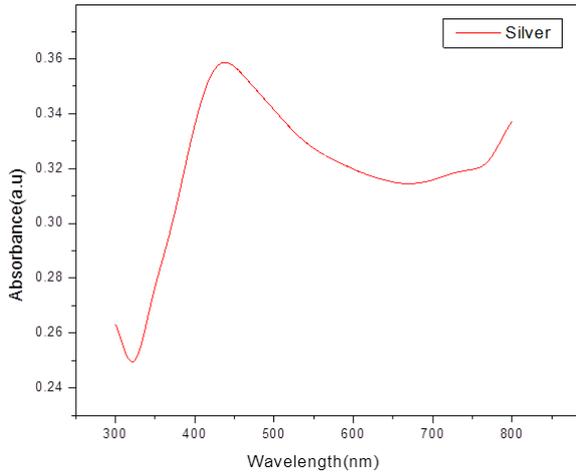


Fig. 3.2.1(b) UV visible absorption spectra of silver nanowires

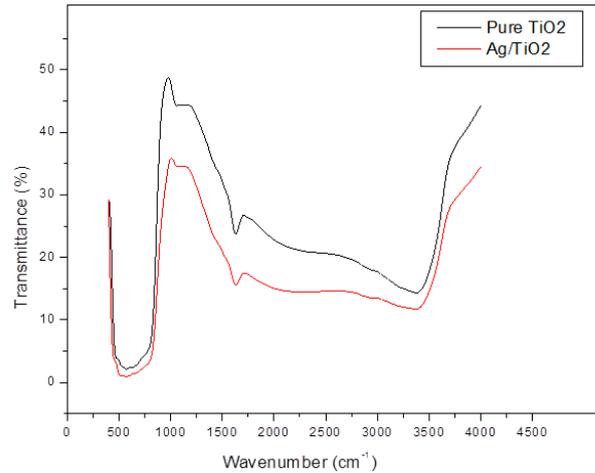


Fig 3.3.1 FTIR spectra of TiO₂ and silver doped TiO₂ nanoparticles

The band gap determined from the plot comes out to be 3.015 eV, 1.811 eV and 2.842 eV for pure TiO₂, silver and TiO₂ –Ag nanocomposite respectively. Thus we observe that the composite of Ag nanowires in TiO₂ leads to a variation of about 6% in optical gap. In fact, the decrease in optical band gap suggests a significant reduction of electron-hole recombination in dioxide (improving, so, the DSSCs efficiency) which is attributed to Surface Plasmon Resonance of the Ag nanoparticles. [14] Fig. 3.2.2 shows comparative UV visible absorption spectra of all dyes used. The characteristic absorption peaks are at 651 nm, 529 nm, 237 nm and 216 nm of Methylene blue, Eosin Y, Henna and beetroot respectively.

We see that band gap of henna is the lowest and methylene blue has the highest band gap energy. The band gap energy from the Tauc plot comes out to be 3.197 eV, 3.930 eV, 4.295 eV and 4.72 eV of henna, beet-root, Eosin Y and Methylene Blue respectively.

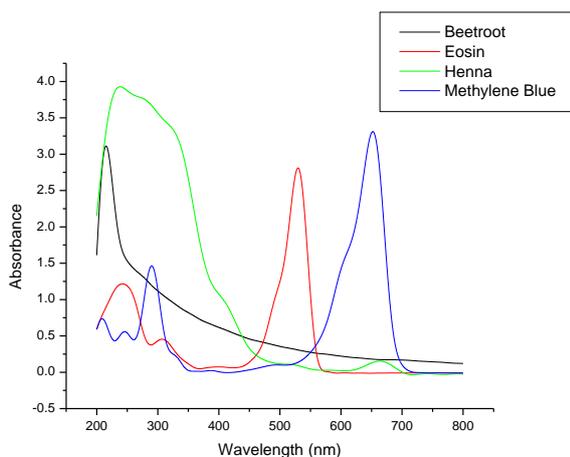


Fig. 3.2.2 Comparative UV visible absorption spectra of all dyes used

FT-IR spectrum has been recorded in solid phase using KBr pellets technique in the regions of 4000–400cm⁻¹. FTIR spectra of pure TiO₂ nanoparticles and silver TiO₂ nanocomposite treated at 400^oC is shown in Fig.3.3.1

Both the graphs show a TiO₂ characteristic broad in the region 400-900 cm⁻¹ attributed to Ti-O stretching vibration and O-Ti-O lattice. The O-H bending and O-H vibrations are respectively observed in the regions 1620-1640 cm⁻¹ and 3387-3395 cm⁻¹ due to adsorbed water molecules and hydroxyl ions. The latter peak also corresponds to the O-H stretch region. The vibration bands between 1300 cm⁻¹ and 4000 cm⁻¹ can be attributed to the chemisorption and/or physisorption of H₂O and CO₂ molecules on the surface of the compound. Both pure and Ag-TiO₂ exhibit similar vibration patterns. [15]

Fig. 3.3.2 shows the IR spectrum of silver nanowires. The peaks at 1618 and 3420 cm⁻¹ are assigned to C=C stretching and O-H broadening stretching peak. A peak at 1500 cm⁻¹ is due to C-H bending vibrations. [16]

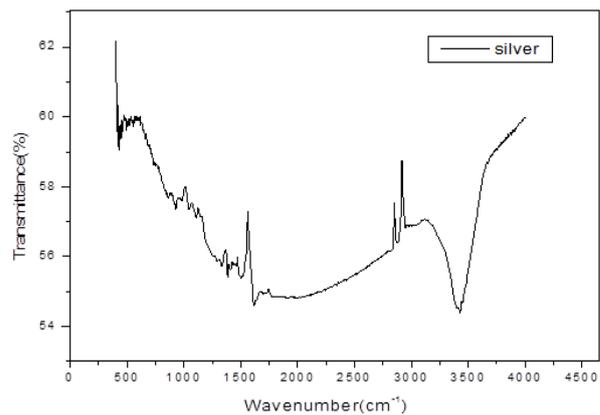


Fig. 3.3.2 FTIR spectra of silver nanowires

Both real(ε') and imaginary (ε'') part of the dielectric constant show a sudden decrease at lower frequency and become constant or slower decrease at higher frequency as shown in Fig. 3.4.1 and Fig. 3.4.2. The polarization in nanomaterials is contributed by space charge polarization, hopping exchange of charge carriers between localized states, and the resultant displacement of dipoles with respect to the applied field. Koops suggested that the effect of grain boundaries is predominant at lower frequencies. Loading of Ag onto TiO₂ thickens the grain

boundaries, causing a decrease in the polarization and hence of the dielectric constant. [17]

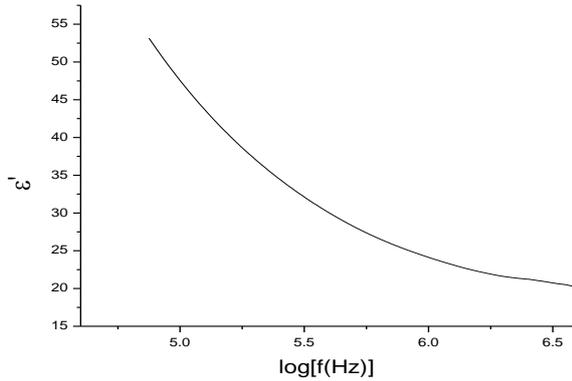


Fig. 3.4.1 Real part of the Dielectric constant of TiO₂-Ag composite

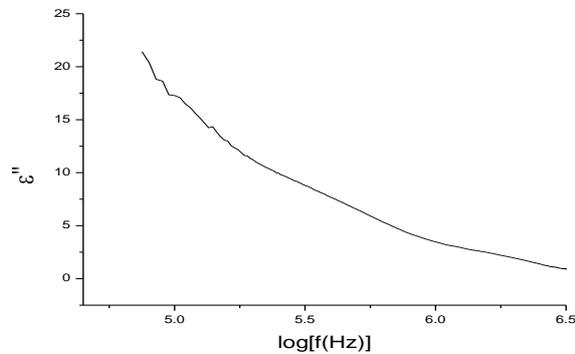


Fig. 3.4.2 Imaginary part of the Dielectric constant of TiO₂-Ag composite

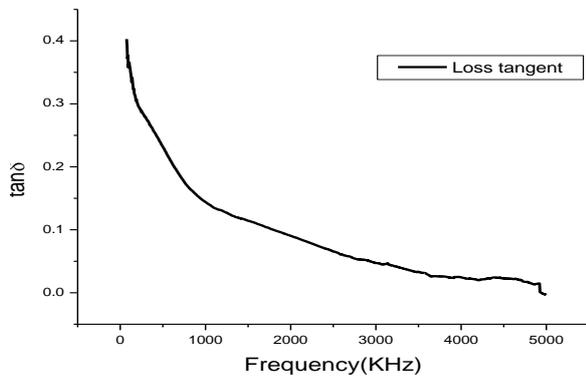


Fig. 3.4.3 Loss tangent of TiO₂-Ag composite

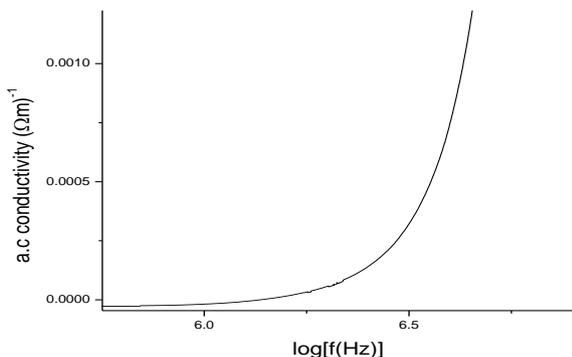


Fig. 3.4.4 Variation of ac conductivity with frequency of TiO₂-Ag composite

Fig. 3.4.3 shows the variation of dielectric loss with respect to frequency. The dielectric loss decreases with increase in frequency. The high value of dielectric loss at lower frequencies may be attributed to the high resistivity caused by grain boundary.

Figure 3.4.4 shows the variation of the AC conductivity as a function of frequency for the sample at room temperature. The ac conductivity of TiO₂ –Ag nanocomposite slowly increases with the increase in frequency, but at higher frequencies, the ac conductivity increase rapidly which is attributed to the enhanced hopping phenomenon. [17]

Figure 3.5 shows an SEM image of silver-TiO₂ composite film electrode. The silver nanowires are well dispersed within the TiO₂ nanoparticles. Further observation also confirms the porous structure of the Ag/TiO₂ nanocomposite, which is favourable for the harvesting of light and transporting of electrolyte molecules. So the nanowires added TiO₂ film has an advantage to having higher adsorption of dye molecules and also supports the penetration of the I⁻/I₃⁻ redox couple into the TiO₂ film. [13]

Fig. 3.6 shows the TEM image of silver nanowires which were synthesized for doping into the TiO₂ nanoparticles. Moreover, the surface area of the TiO₂ films was larger, so the dye molecule adsorption space was also larger. Consequently, the increased surface absorption enhanced the solar energy conversion efficiency.

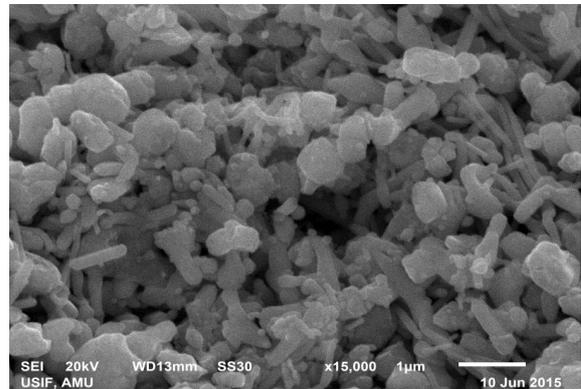


Fig. 3.5 SEM image of TiO₂-Ag nanocomposite



Fig. 3.6 TEM images of silver nanowires

I-V characteristics of the solar cell were calculated in lab using “AM 1.5G Solar simulator source. A solar simulator (also artificial sun) is a device that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for the testing of solar cells, sun screen, plastics, and other materials and devices. The cell was illuminated using a 1000 watt/cm² xenon arc lamp bulb.

Fig. 3.7 shows J-V curves of DSSC using pure TiO₂ and Ag-TiO₂ nanocomposite. We can see from the Fig. 5.7(c) that the Open circuit voltage of the DSSC using pure TiO₂ is greater than DSSC using Ag- TiO₂ nanocomposite. The conversion efficiency of solar cell increases in DSSC using Ag- TiO₂ nanocomposite from 4.159% to 4.576% . The current density has increased by from 7.815 mA/cm² to 9.724 mA/cm² by using Silver Nanowires in DSSC. However, there is a slight decrease in fill factor from 0.723 to 0.690.

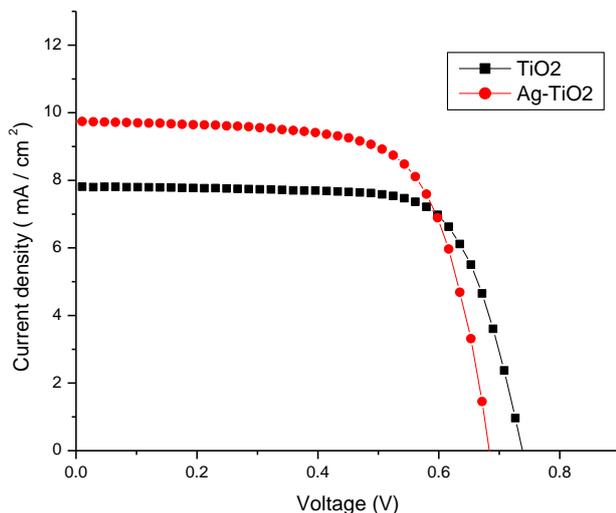


Fig. 3.7(c) J-V curves of DSSC using pure TiO₂ and Ag-TiO₂ nanocomposite

IV. CONCLUSION

In conclusion, a dye sensitized solar cell with a photoanode of Ag -TiO₂ nanocomposite was fabricated and characterized. Compared with the pure TiO₂ based DSSC sample, the short circuit current density of the Ag-TiO₂ nanocomposite based DSSC sample was improved by 24.42% resulting in a conversion efficiency improvement of 10.02%. Two effects were found to have contributed to the improved performance, an enhanced optical absorption due to the Ag plasmon effect and a faster electron transport in the Ag -TiO₂ nanocomposite photoanode.

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