PLASMON ENHANCED DYE SENSITIZED SOLAR CELL PERFORMANCE USING TIO₂/Ag NW NANOCOMPOSITE PHOTOANODE

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ABSTRACT

In this study, we have investigated the effect of incorporating silver nanowires (Ag NWs) into the TiO_2 photoanode on the performances of Dye Sensitized Solar Cells (DSSCs). Ag NWs with diameter 60-90 nm and length of 1-2 µm were synthesized via polyol reduction method using silver nitrate (AgNO₃), glycerol, polyvinyl pyrrolidone (PVP, MW = 44,000) and sodium chloride (NaCl). A series of DSSCs were fabricated by varying the Ag NW concentration in the photoanode from 0.0 - 2.6 wt%. The modified DSSC with 1.7 wt% of Ag NWs exhibited the optimum performance with the highest power conversion efficiency of 7.48% and open circuit voltage (V_{∞}), short circuit current density, (J_{sc}) and fill factor of 768.4 mV, 13.79 mA cm⁻² and 68.74% respectively. The efficiency enhancement of the DSSC with modified photoanode compared to the reference DSSC without Ag NWs was found to be 32%. This photovoltaic performance enhancement was ascribed mainly to the improvement in the short circuit current density evidently by improved light harvesting due to localized surface plasmon resonance (LSPR) effect from the Ag NWs.

Keywords: Dye sensitized solar cells, Silver nanowires, Plasmon.

1. INTRODUCTION

Developing photoanodes with smart light trapping techniques implementing to obtain 'optically thick' photo absorbers to allow near complete light absorption [1] can increase the efficiency of DSSCs. One such method is incorporation of metal nanostructures supporting plasmon oscillation to the DSSCs. Localized Surface Plasmon Resonance (LSPR) originating from metal nanostructures is an effective way to enhance the light absorption. In this work, silver nanowires (Ag NWs) are incorporated into TiO₂ photoanode of DSSCs in order to improve the efficiency.

LSSR effect is a result of collective oscillation of conduction electrons of metal nanostructures having sub wavelength dimensions where oscillation of electron cloud (plasma) is localized/confined around the nanostructure [2]. LSPR results strong extinction of light (absorption and scattering) and absorption of maximum energy. LSPR frequency depends strongly upon size, shape, surface, composition and surrounding dielectric [2]. There are mainly four types of light enhancement arising from LSPR. They are (1) near field coupling of electromagnetic fields, (2) far-field coupling of scattered light (3) plasmon resonance energy transfer and (4) hot electron transfer [3-7]. These light enhancement types contribute to generation of photoelectrons via LSPR. Nanowires are one-dimensional nanostructures. Depending upon their dimensionality and size confinement, unique optical, electronic, catalytic and thermal properties are arising in NWs [8]. Silver is a noble metal showing strong LSPR [9]. Therefore, incorporation of Ag NWs to TiO₂ photoanode should improve the performances of DSSC by increasing the photocurrent. In

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this work, a liquid phase bottom-up polyol reduction synthesis method was used as the Ag NW synthesis method. This method is rapid, scalable and provides high yield of Ag NWs.

2. EXPERIMENTAL

2.1 Silver Nanowires

2.1.1 Materials

Silver nitrate (AgNO₃, 99.8%) was obtained from Daejung, polyvinyl pyrrolidone (PVP, Mw = 44,000) was obtained from BOH Laboratories, Glycerol was obtained from Surechem Products LTD., sodium chloride (NaCl, 99.5%) was obtained from Sigma-Aldrich. All these materials were used as received without any further purification. The deionized (DI) water was used from the Millipore system.

2.1.2 Synthesis of silver nanowires

The Ag NWs were synthesized using polyol reduction process published elsewhere [8]. First, 47.5 ml of glycerol was added to a round bottom flask and 1.500 g of PVP was then added. Next, the solution was gently heated up to 80 °C until all PVP was dissolved. Then the solution was cooled down to room temperature. 0.395 g of AgNO₃ powder was then added to the solution. Subsequently, 0.125 ml of NaCl solution (5 mmol/L) was added to 2.5 ml of glycerol and the latter was added to the PVP dissolved solution containing AgNO₃ powder. Next, the reaction temperature of the solution was increased rapidly to 210°C, roughly 8 °C per min. with a magnetic stirrer at 50 r/min in aerobic condition. After the temperature increased to 210 °C, the reaction was stopped and the solution was allowed to cool down to room temperature. Finally, 50 ml of DI water was added to the flask and the mixture was centrifuged at 8000 r/min for 20 minutes. As obtained NWs were water washed 3 times to remove the residue PVP and any other impurities

2.1.3 Characterization

To study optical properties of synthesized Ag NWs, UV-visible absorption spectrum was obtained on a Shimadzu UV-1800 spectroscope. The dimensions and the morphology of the NWs were studied using a scanning electron microscope (SEM, EVO LS15).

2.2 DSSC fabrication

2.2.1 Preparation of photoanode

To fabricate compact layer on FTO glass, a paste was prepared by grinding 0.250 g TiO₂ (Aeroxide P-90) with 1.0 ml of 0.1 M HNO₃ for 15 min. The mixture was spin coated on precleaned FTO glass substrate (Solaronix sheet glass 7 Ω /sq) at 3000 r/min for 60 s, followed by sintering at 450 °C for 45 min. On top of the compact layer, the mesoporous TiO₂ layer was fabricated as follows. First, 0.250 g of TiO₂ powder (Desgussa P-25) was ground for 30 min with 1.0 ml of 0.1M HNO₃, one drop of Triton X-100 and 0.050 g of PEG. Next, Ag NWs suspended solution was added to the TiO₂ paste and the mixture was ground for another 15 min to obtain homogeneous paste. The paste was then deposited on top of the compact layer by doctor blading method, followed by sintering at 450 °C for 45 min. After cooled down to room temperature, these glass substrates were dipped in an ethanolic dye (0.3 Mm) solution containing Ruthenium dye N719 [RuL2 (NCS)2:2TBA where, L = 2,2'-bipyridyl-4,4'-dicarboxylic acid TBA = tetrabutylammonium] for 24 h. In order to compare the effect of silver nanowires on the DSSCs, reference DSSCs were fabricated with pristine TiO₂ phonoanodes as above without adding Ag NWs.

2.2.2 Optimization of efficiency of DSSC by incorporating Ag NWs

To optimize DSSC efficiency by incorporating Ag NWs, DSSCs having different amount of Ag NWs in their photoanodes were fabricated. To achieve this, different volumes (0-0.30 ml in 0.1 ml or 0.05 ml incrimination) of Ag NWs suspended solution (2.17 g/ml) were added to the TiO_2 pastes.

3. RESULTS AND DISCUSSION

3.1 Characterization of Silver Nanowires

3.1.1. UV-Vis absorption

The UV-VIS absorption spectrum of the synthesized Ag NWs in an aqueous solution is shown in Fig.1. The absorption spectrum shows two peaks at ~350 nm and ~380 nm which are attributed to Ag NWs [8]. The shoulder peak around 350 nm corresponds to the longitudinal SPR which is equal to SPR of bulk Ag. The peak around 380 nm corresponds to the transverse SPR of Ag NWs which is LSPR [10].



Fig.1 Absorption spectra of the synthesized Ag NWs.

3.1.2 Scanning Electron Microscopy

The surface morphology of the synthesized Ag NWs was studied using SEM at 5 kV.



Fig.2 SEM images of the synthesized Ag NWs.

The average diameter and length of the synthesized Ag NWs analyzed from SEM images are 78 nm and 2.5μ m respectively and agree with the published UV-VIS absorption spectra taken for Ag NW synthesized using polyol process [8].

3.2 Characterization of Dye Sensitized Solar Cells

The photovoltaic performances of DSSCs containing different Ag NW concentrations were measured under the simulated sunlight illuminating at 100 m W cm⁻² (AM 1.5) and the corresponding J-V curves are shown in Fig.3.



Fig.3.Photocurrent density-voltage curves for DSSCs with Ag NWs in their photoanodes

The photovoltaic parameters derived from the photocurrent density-voltage measurements are given below.

Volume of Ag NWs suspended solution added (ml)	Correspondi ng conc.of Ag NWs in photoanode w.r.t TiO ₂ (wt. %)	J _{sc} (mAcm ⁻²)	V _{oc} (mV)	FF (%)	η (%)
0	0	10.96	765.5	67.34	5.65
0.05	0.4	12.13	770.0	68.54	6.39
0.15	1.3	12.87	777.7	71.61	7.17
0.20	1.7	13.79	768.4	68.74	7.48
0.25	2.2	13.49	774.7	69.13	7.22
0.30	2.6	11.56	780.7	68.10	6.15

Table 1: Photocurrent density-voltage curves for DSSCs with Ag NWs in their photoanodes.

The power conservation efficiency varies linearly with open-circuit voltage (V_{oc}), fill facor (FF) and photo current density (J_{sc}). According to the table 1, it is clearly evident that there is neither noticeable increase nor decrease in both V_{oc} and FF in the DSSCs with different amount of Ag NWs. Therefore, the variation in J_{sc} is responsible for efficiency variation in different DSSCs.

3.3 Optimization of DSSC efficiency by incorporating different amounts of Ag NWs to photoanode

The efficiency variation with amount of Ag NWs added to photoanode to is shown in Fig.4 below.



Fig.4.Variation of efficiency of DSSCs with the amount of Ag NWs solution added to TiO2 paste.

When the amount of Ag NW solution added to the TiO_2 paste is gradually increased (i.e the amount of Ag NWs in photoanode is increased) the efficiency of the solar cells increases and goes through a maximum and then decreases with further increase in added amount of Ag NWs.

The highest efficiency obtained for DSSC with Ag NWs is 7.48% and the corresponding DSSC contains 1.7 wt% Ag NWs in ptotoanode with respect to TiO_2 . The efficiency enhancement is 32% with respect to reference DSSC.

When the amount of Ag NWs in photoanode is increased, LSPR effect is also increases. Therefore, more light is absorbed thus more photocurrent is generated. The increase in photocurrent causes the efficiency enhancement. Concurrently, when the amount of Ag NWs too high, the cell efficiency reduces due to decrease in dye loading on mesoporous TiO_2 layer and blocking the porous of the TiO_2 layer causing decrease in diffusion of electrolyte into the TiO_2 film[8].

3.4 Effect of compact layer on efficiency of DSSCs incorporating Ag NWs

The photovoltaic performance of DSSC having only TiO_2 in photoanode (1) with compact layer and (2) without compact layer is shown in Fig.5.



Fig.5.Photocurrent density-voltage curves for DSSCs (1) with compact layer and (2) without compact layer.

It is clearly evident that, without the compact layer, the performance of DSSC incorporating Ag NWs is significantly low due to reduction in photocurrent. On FTO glass substrate, photoelectrons are accumulated after diffusing through TiO_2 layer. There will be plenty of back recombination near FTO glass substrate if the electrolyte reaches the FTO glass substrate.

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Compact layer acts as a barrier between electrolyte and FTO glass substrate reducing the back recombination hence enhancing the DSSC performance.

4. CONCLUSION

In this work, the effect of incorporating Ag NWs into photoanode of the DSSC has been investigated. The optimized DSSC efficiency is obtained for DSSC with 1.7 wt.% of Ag NWs in photoanode. The optimum efficiency enhancement is 32% with respect to reference DSSC. The efficiency enhancement is mainly because of increased short circuit current density (J_{sc}) due to increased light harvesting via LSPR. and reduction in back recombination in the vicinity of FTO glass substrate due to compact layer.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- How light trapping surfaces will boost solar cell efficiency [online] Available from: https://www.technologyreview.com/s/510016/how-light-trapping-surfaces-will-boost-solarcell efficiency/ [Accessed 22nd October, 2017]
- [2] Marchuk K., Willets K.A, Chemical Physics 445 (2014) 95–104
- [3] Schaadt D.M., Feng B., Yu E.T, Appl. Phys. Lett. 86 (2005), 063106, http:// dx.doi.org/10.1063/1.1855423.
- [4] Ihara M., Tanaka K., Sakaki K., Honma I., Yamada K., J. Phys. Chem. B 101(1997) 5153-5157.
- [5] Gangishetty M.K., Lee K.E., Scott R.W., Kelly T.L., ACS Appl. Mater. Interfaces 5(2013) 11044-11051.
- [6] Cushing S.K., Li J., Meng F., Senty T.R., Suri S., Zhi M., Li M., Bristow A.D., Wu N., J. Am. Chem. Soc. 134 (2012) 15033-15041.
- [7] Schuck P.J., Nat. Nanotechnol. 8 (2013) 799-800.
- [8] Yang C., Tang Y., Su Z., Zhang Z., Fang C., Journal of Materials Science & Technology 31(1) (2015) 16-22.
- [9] Ferry E.V , Munday J.N , Atwater H.A, Adv. Mater.22 (2010) 4794-4808
- [10] Meenakshi P., Karthick R., Selvaraj M., Ramu S., Solar Energy Materials Solar Cells. 128 (2014) 264-269.