



EFFICIENCY ENHANCEMENT IN PLASMONIC DYE-SENSITIZED SOLAR CELL EMPLOYING HIGH PERFORMANCE TiO₂ PHOTOANODE DOPED WITH SILVER NANOPARTICLES

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ABSTRACT

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High performance TiO₂ photoanodes undoped and doped with silver nanoparticles of size about 15 nm were fabricated. Employing these electrodes dye-sensitized solar cells (DSSCs) were fabricated using N719 dye as sensitizer and iodide-triiodide as redox couple. Current-voltage measurements were performed under the illumination of 100 mW cm⁻² (AM 1.5). The electrical parameters of the fabricated cells were extracted from the current-voltage data that include open-circuit voltage, short-circuit current, shunt resistance, series resistance, fill-factor, ideality factor and solar energy-to-electricity conversion efficiency. The comparison of parameters revealed improvement in both the photovoltaic and electrical parameters of the plasmonic cell. The conversion efficiency measured for the reference cell without Ag NPs in TiO₂ was 7.43 %, whereas the efficiency of plasmonic device with TiO₂:Ag NPs was 9.26 %, resulting an overall efficiency improvement of 23% with Ag NPs. The increased performance of the plasmonic DSSC can be assigned to the improvement of its photovoltaic and electrical parameters. The improved short-circuit photocurrent density appears to be boosted due the enhanced light harvesting capability of the photoanode caused by the localized surface plasmon resonance effect induced in Ag nanoparticles. While, the rise in Voc can be credited to the upward shift of Fermi level of TiO₂ due to the doping of Ag nanoparticles in TiO₂ network.

Contribution/Originality: This study is based on one of the few attempts on photoanode engineering employing plasmonic effect for developing higher efficiency DSSCs. The comparison with the existing data has revealed significant improvement in the photovoltaic and electrical properties of the plasmonic device. This study has reported that Ag nanoparticles hold a unique plasmonic effect employing which performance parameters of the DSSC are improved much greater as compared to other metallic nanoparticles.

1. INTRODUCTION

The dye-sensitized solar cells (DSSCs), initially reported by O'regan and Grfitzeli (1991) have attracted much interest of the scientists and researchers as next-generation alternative potential photovoltaic technology to the traditional silicon-based owing to their manufacturing ease, low price, reasonable efficiency, unique applications, design flexibility and clean source of renewable energy (Elbohy *et al.*, 2015; Toor *et al.*, 2016; Shah *et al.*, 2017; Shah *et al.*, 2018; Toor *et al.*, 2018; Wei *et al.*, 2018).

A DSSC comprises of a photoanode typically a mesoporous wide band semiconductor film deposited on a fluorine-doped tin oxide (FTO) glass which is sensitized with a dye, an electrolyte consisting of redox coupled solution and a counter electrode commonly consisting of a platinum coated conductive glass substrate (Nazeeruddin *et al.*, 2011). To make a device, the two electrodes are joined together and electrolyte is injected in between. Great efforts have been put until now for the manufacturing and optimization of various components of DSSC and have been the subject of a number of review articles (Gong *et al.*, 2012; Saranya *et al.*, 2015; Su'ait *et al.*, 2015; Wali *et al.*, 2015; Ye *et al.*, 2015; Fan *et al.*, 2017; Gong *et al.*, 2017; Yeoh and Chan, 2017; Yun *et al.*, 2018).

Since its birth, efficiency of DSSC has reached 14.5% under standard conditions (Lee *et al.*, 2017). Although, this has doubled since its birth, however, the theoretical limit for the efficiency of DSSC is 26.8% which is yet to be achieved (Tripathi *et al.*, 2015). The photoanode is an important component of the DSSC. This provides support for the adsorption of sensitizer and helps in the transportation of the photo-excited electrons from the sensitizer to the external circuit (Ye *et al.*, 2015). Light absorption by sensitizer and the capability of the photoanode material to collect and transfer the charges efficiently within the diffusion length is decisive for the high conversion efficiency of DSSC. Power conversion efficiency could be increased by manipulating the photoanode structure in different ways like increasing the surface area of the photoanode material, designing new dyes, inserting different nanostructured material like noble metals, etc (Nbelayim *et al.*, 2017).

A way to widen the surface area of photoanode material and to decrease the recombination of charges is to treat the TiO₂ films by TiCl₄ solution. By depositing a thin compact layer of TiO₂ particles prior to mesoporous TiO₂ film will reduce the recombination of charges at FTO/TiO₂ and FTO/electrolyte interfaces, while post treatment of photoanode with TiCl₄ increase the surface area of photoanode and the quantity of dye adsorption. Both of these result in the increment of incident light absorption and ultimately enhanced photocurrent (Lee *et al.*, 2012). The concept of insertion or doping of noble metals in photoanode has shown tremendous effect on the power conversion efficiency by boosting the photo-absorption cross-section of the dye (Saravanan *et al.*, 2017). In noble metals like silver, gold, etc, the localized surface plasmon resonance (LSPR) phenomenon is induced by the collective oscillation of electrons in the nanostructure which is further stimulated by the incident light, hence, the absorption of light and scattering effect is increased that rises the current generation of the cell and ultimately improves the efficiency of DSSC (Jun *et al.*, 2016; Villanueva-Cab *et al.*, 2016).

In spite of the accomplishment of record efficiency in DSSCs, scaling up of the technology new techniques and approaches are required with guaranteed price improvement and steadiness in efficiency (Sarker *et al.*, 2015). Knowledge of the substantial parameters affecting photovoltaic response of the solar cells are required for the designing, replication and their improvement (Ishibashi *et al.*, 2008; Kyaw *et al.*, 2012; Elbohy *et al.*, 2015). In this work, photovoltaic performance of the plasmonic DSSC employing high performance TiO₂ photoanode doped with silver nanoparticles is carried out. Current density – voltage (J–V) curve of the device is compared under light with the reference cell. The electrical parameters of the fabricated cells were extracted from the current-voltage data, that include open-circuit voltage, short-circuit current, shunt resistance, series resistance, fill factor, ideality factor and solar energy-to-electricity conversion efficiency. The comparison of these parameters of both types of devices are also made.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Silver Nanoparticles Suspension

Ag NPs of approximately 15 nm diameter were prepared by simple chemical reduction route. Silver nitrate AgNO₃ of analytical grade purity was used as starting materials without further purification. 1M AgNO₃ was added in 20 ml DI water. This solution was heated till boiling with slowly stirring. 1% sodium borax with 0.2% PVP in 5 ml DI water was separately prepared and was added to the heated solution of AgNO₃ drop wise until a bright yellow color was achieved.

2.2. Optical Absorption Measurements of Silver Nanoparticle Colloidal Solution

UV-Vis-NIR absorption spectra of Ag Nanoparticles solution was taken by a Varian Cary 5000 spectrometer. Transmission electron microscopy (TEM) images of NPs were acquired by a JEOL 2100F microscope.

2.3. Preparation of High Performance TiO₂ and TiO₂: Ag NPs Photoanodes

The high performance TiO₂ photoanodes were prepared and sensitized in N719 dye using a previously reported method (Elbohy *et al.*, 2016). For plasmonic cell, the photoanode was soaked in Ag nanoparticles suspension. The color of the photoanode changed from transparent to transparent yellowish after Ag nanoparticles were attached to TiO₂. The cells were assembled using method described in our previous work (Shah *et al.*, 2017). The current-voltage measurements of fabricated DSSCs were performed under solar simulator illumination light intensity of 100 mW.cm⁻² using the facility described in a previous work (Elbohy *et al.*, 2016).

3. RESULTS AND DISCUSSION

3.1. Absorbance Spectra of Colloidal Ag NPs

The silver nanoparticles were successfully synthesized by chemical reduction method. The creation of Ag NPs was detected with the appearance of yellowish stain solution (Mahmudin *et al.*, 2015). For the confirmation of formation and structural characteristics the UV-Vis spectroscopy of Ag NPs in colloidal solution was performed. The absorption spectra of the colloid shown in Fig. 1 makes it obvious that the absorbance peak is around 400 nm, that corresponds to surface plasmon resonance (SPR) of Ag NPs. The presence of this single peak signifies the presence of spherical or roughly spherical silver nanoparticles (Guzmán *et al.*, 2009) and is also confirmed by the TEM image (Figure 2).

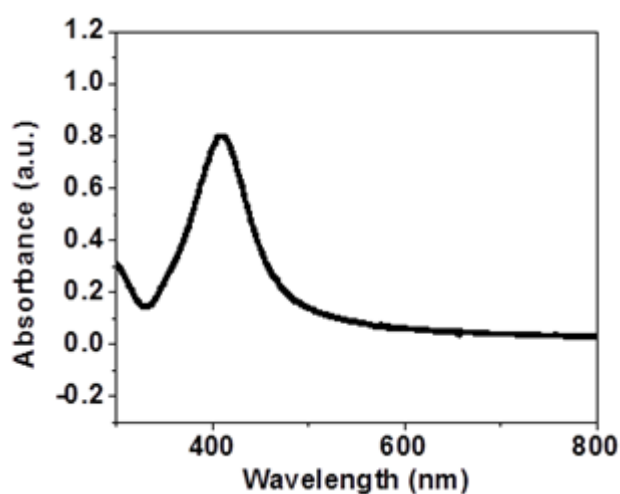


Fig-1. Absorbance spectra of colloidal Ag NPs.

3.2. Surface morphology of Colloidal Ag NPs

The TEM image of colloidal Ag nanoparticles is shown in Fig. 2. It is evident from the figure that the morphology of nanoparticles is almost spherical and average size is about 15 nm. The morphology is in agreement with the shape of the SPR band in the UV-Vis spectra.

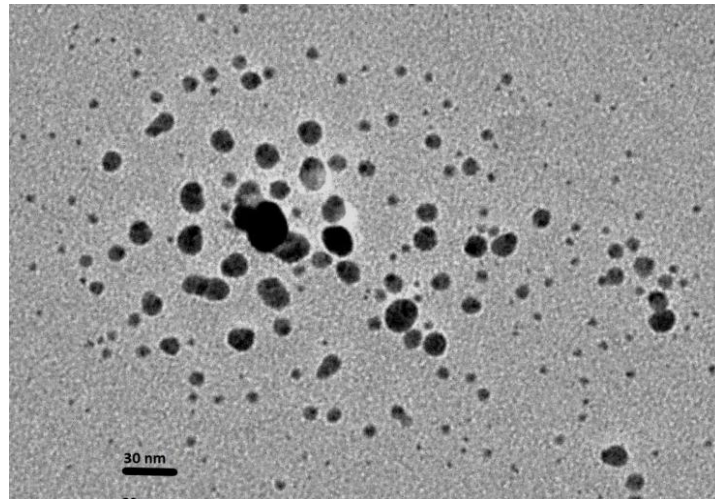


Fig-2. TEM images of Ag NPs.

3.3. Photovoltaic Performance

The short-circuit current density (J_s), open-circuit voltage (V_{oc}), fill factor (FF), ideality factor (n), series resistance (R_s), shunt resistance (R_{sh}) and photoelectric conversion efficiency (η) were determined to compare the performance of the DSSCs made employing undoped and silver nanoparticles doped photoanodes. These parameters can be expressed as follows:

The fill factor corresponds to the largest rectangular area that can fit in the J-V curve and can be calculated using the following relation:

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (1)$$

Where V_{max} and I_{max} represent the voltage and current at the point of maximum power output of the cell, respectively. The value of the ideality factor (n) under illumination was determined via the following relation (Würfel *et al.*, 2015):

$$n = \left(\frac{k_B T}{q} \frac{d}{dV} \ln \frac{J}{J_0} \right)^{-1} \quad (2)$$

Where J_0 is the saturation current, q is the electron charge, V is the applied voltage, and k_B is the Boltzmann constant.

The current-voltage characteristics largely dependent on the series (R_s) and shunt (R_{sh}) resistance (Mali *et al.*, 2012; Shah *et al.*, 2017). The values of these resistances can be determined from the I-V curve using the relations (3) and (4) (Jiang *et al.*, 2008).

$$R_s = \left. \frac{dV}{dI} \right|_{I=0} \quad (3)$$

$$R_{sh} = \left. \frac{dV}{dI} \right|_{V=0} \quad (4)$$

The efficiency (η) of a solar cell is defined as the ratio of output power to total power incident on the cell and can be calculated by the following relation:

$$\eta = \frac{P_{max}}{P_{in}} \times 100 = \frac{J_{sh} \times V_{oc} \times FF}{P_{in}} \times 100 \quad (5)$$

Where J_{sh} is the short circuit current density, V_{oc} is the open circuit voltage, P_{in} is the intensity of incident light. The current density versus voltage (J-V) characteristics of the plasmonic and reference DSSC fabricated using N719 dye as sensitizer measured under 1 Sun illumination are compared in figure 3.

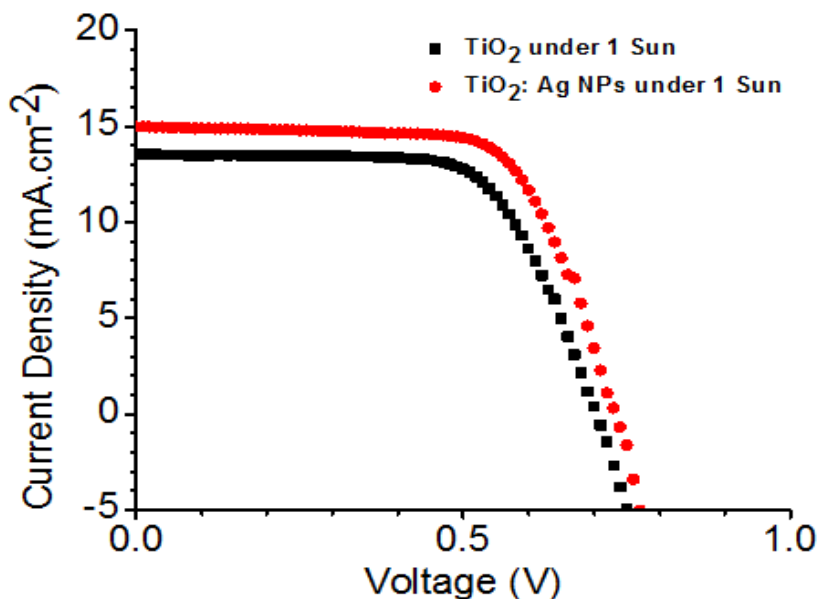


Fig-3. J-V curves recorded under AM 1.5G illumination on TiO_2 and TiO_2 :Ag NPs photoanodes based DSSCs.

The various parameters of the TiO_2 and TiO_2 :Ag NPs photoanodes based DSSCs are determined and shown in table 1. As can be observed from figure 3 and table 1, the plasmonic DSSC has exhibited better performance and provided a solar energy-to-electricity conversion efficiency (η) of 9.26 % with higher short-circuit photocurrent density (J_{sc}) of 15.82 mA/cm^2 , higher open-circuit photovoltage of (V_{oc}) 770 mV and higher FF of 76.0. The overall power conversion efficiency, short circuit current density, open circuit voltage and fill factor of the plasmonic device were observed higher than the reference cell by 25%, 12.4 %, 5.5 % and 5.6 %, respectively.

Table-1. Comparison of the parameters of TiO_2 and TiO_2 : Ag NPs photoanodes based DSSCs.

Photoanode	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (mV)	FF (%)	η (%)	n	R_{sh} (Ω)	R_s (Ω)
TiO_2	14.08	730	72.2	7.43	2.8	12.1 k	52
TiO_2 :Ag NPs	15.82	770	76.0	9.26	1.6	7.1 k	40

A relatively higher R_s is obtained owing to the potential blockade at the TiO_2 /dye interface, Mali *et al.* (2012). In the case of plasmonic DSSC the comparatively higher performance can be attributed to the lower value of R_s . The greater value of R_{sh} for the plasmonic DSSC specifies less leakage current through the cell. The enhanced performance of the plasmonic cell may be attributed to the decrease in the ideality factor of the cell.

The increment in the J_{sc} value for the Ag NPs doped photoanode based device can be attributed to plasmon induced charge transfer from Ag nanoparticles to TiO_2 (Ahmad *et al.*, 2017). The V_{oc} of a DSSC is equal to the difference between the quasi-Fermi level in the TiO_2 layer and Fermi level of the redox couple, therefore, the improvement in V_{oc} can be assigned to upward shift of Fermi level of TiO_2 with the doping of Ag NPs (Ahmad *et al.*, 2017; Shah *et al.*, 2017).

4. CONCLUSIONS

In this study, Ag nanoparticles doped high performance TiO_2 photoanode has been investigated for enhancing the performance of DSSCs. Photovoltaic study showed improvement in the device parameters and performance. The enhanced performance of the plasmonic cell is attributed to the lower value of R_s , larger value of R_{sh} , less shorts or leaks, lower value of ideality factor, enhanced light harvesting caused by the localized surface plasmon resonance effect, the plasmon induced charge transfer from Ag nanoparticles and upward shift of Fermi level of TiO_2 with the addition of Ag nanoparticles.

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Competing Interests: The authors declare that they have no competing interests.

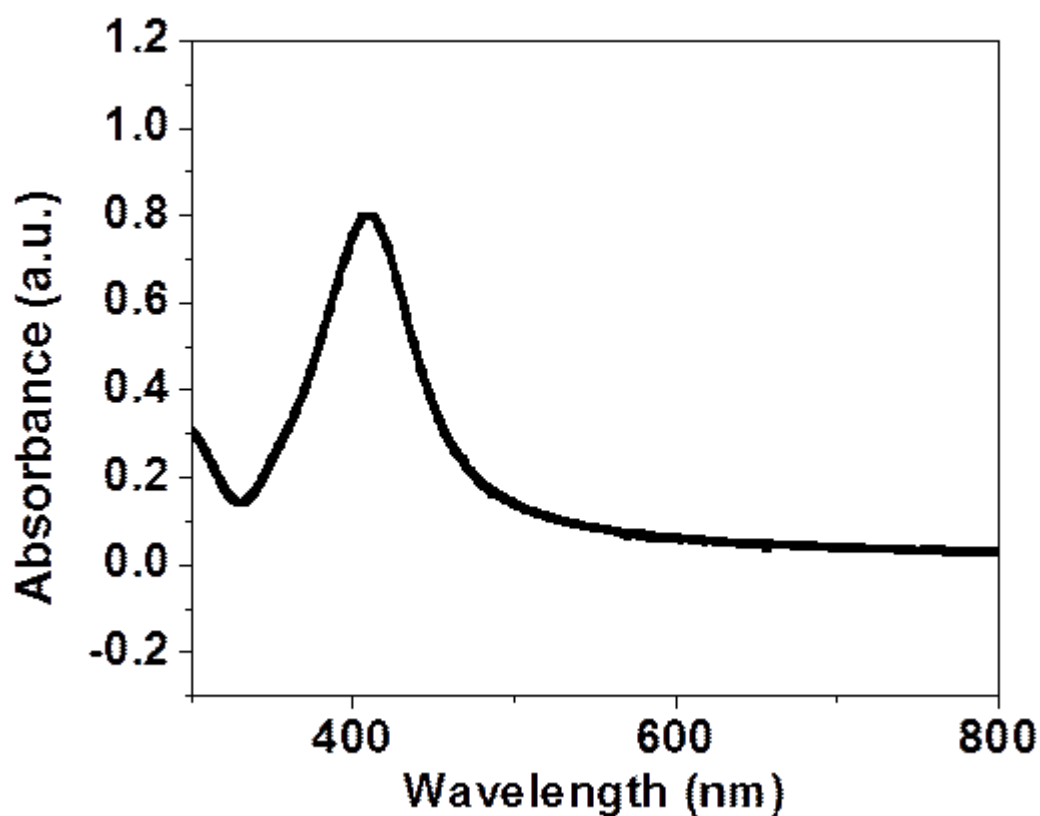
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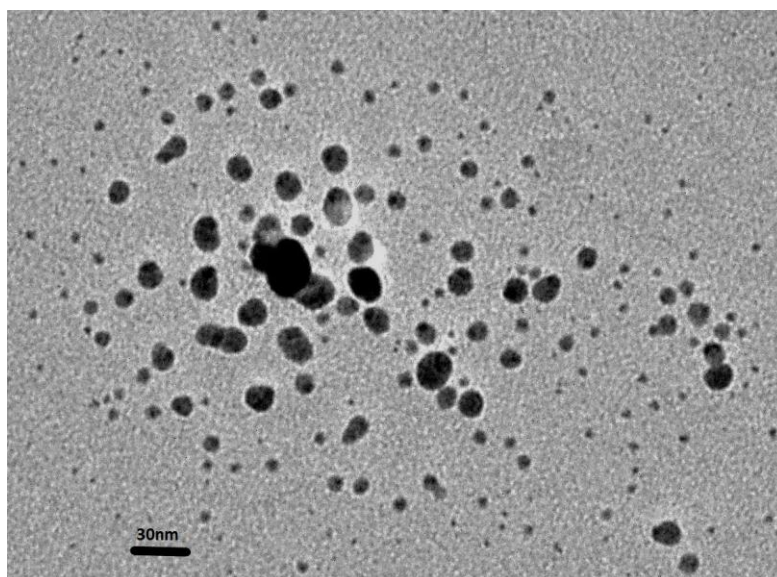
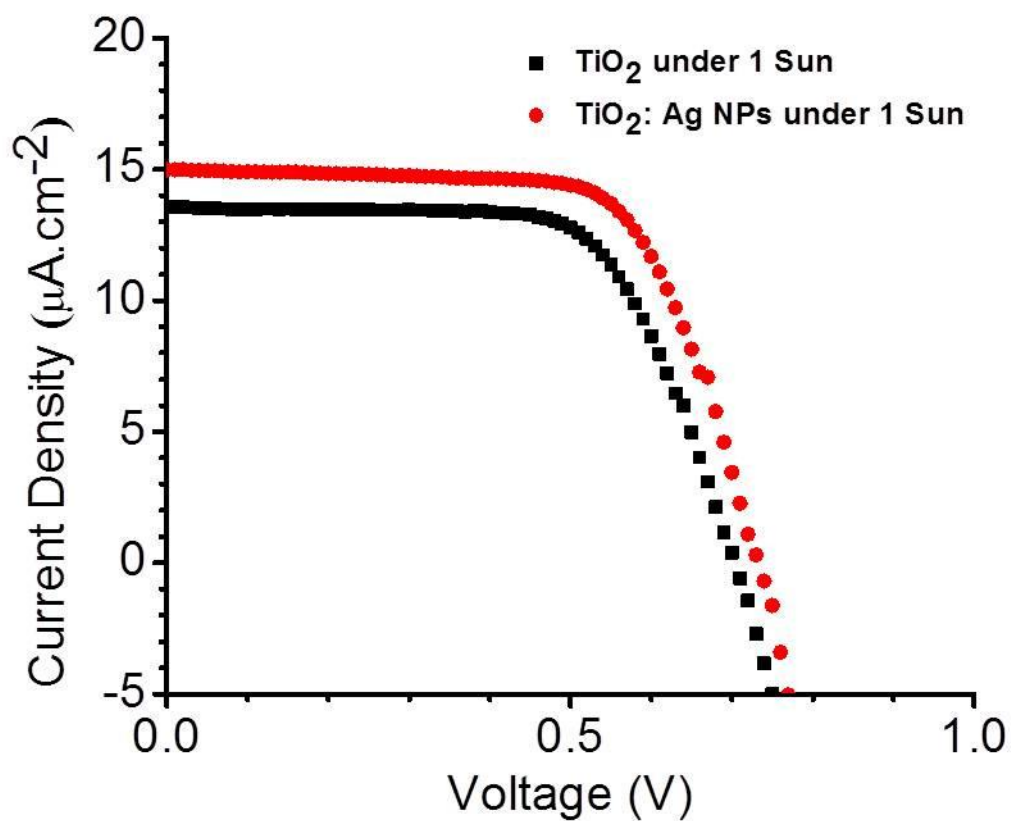
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