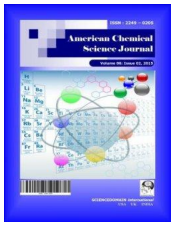

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Enhancement in Photovoltaic Parameters of a Dye Sensitized Solar Cell by Surface Plasmon Resonance of Metallic Silver Nanoparticles

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Authors' contributions

This work was carried out in collaboration between all authors. Author ED designed the study, undertook the experimental work, performed the analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors JAO and GOO managed the analyses of the study and literature searches. Author MYO edited the first draft of the manuscript and author AF managed literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The influence of silver nanoparticles in dye sensitized solar cell (DSSC) through successive ion layer adsorption and reaction was demonstrated. The results show that addition of silver nanoparticles (AgNPs) to titanium dioxide (TiO_2) photo anode significantly improved the performance of the DSSC. The modified silver photo anode presents an enhanced photovoltaic response compared to the reference electrode. The DSSC containing AgNPs, gave a short-circuit current density (J_{SC}) of 0.138 mAcm^{-2}, open-circuit voltage (V_{OC}) of 0.470 V and fill factor (*FF*) of 0.504, yielding an efficiency (η) of 0.065%. The cell exhibits (i) 63% improvement in efficiency over the efficiency (0.040%) (ii) 48.4% enhancement in short circuit current density over the *Jsc* (0.093 mAcm^{-2}) and (iii) 8.5% improvement in open circuit voltage over the V_{OC} (0.433 V) of bare fluorine doped tin oxide (FTO)-based device lacking AgNPs. The increase of *J*sc is attributed to the

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enhanced dye light absorption in strength and spectral range due to the surface plasmon resonance of AgNPs in photo anode, while the increase of V_{oc} may be related to the more negative level of the quasi-Fermi energy of Ag-TiO_2 composite system resulting from the added AgNPs. The related PV performance enhancement mechanism and surface-plasmon resonances in DSSCs with Ag nanostructures are discussed.

Keywords: Silver nanoparticles; DSSCs; TiO_2; SILAR; surface Plasmon; PV performance.

1. INTRODUCTION

A major problem confronting DSSCs is the low efficiency of conversion. Recent development on the dye sensitized solar cells is addressed to increase values of photovoltaic parameters by different plasmonic nanoparticles (NPs) introduction [1-6]. This kind of DSSCs is classified as third generation of photovoltaic devices. NPs could be applied as additives in (i) active layer, (ii) hole-transporting layer, (iii) electrodes, and (iv) inter layer in DSSCs [1–6].

Efforts for achieving higher efficiencies are focused in optimizing the morphology of the active photovoltaic layer and the charge transport properties of the absorber through thermal annealing treatment [7,8], use of various solvents [9], and the use of additives [10].

Metal nanoparticles (NPs), such as Cu, Ag and Au or their mixture, have been proposed to be used in DSSCs for light trapping [1-3]. It is well-known that several techniques such as inclusion of periodic nanostructures, diffraction gratings, metallic NPs, or combination of NPs and gratings are tested [1-3,11]. Metal NPs can be quite easily added to DSSCs to enhance the absorption of light. However, if metal NPs are added to the active layer, the value of power conversion efficiency depends on both the size and kind of metal NPs [3-5,12]. It was once reported that dye molecules in the vicinity of AgNPs can absorb more photons [3], presumably due to the intensified near-field effect of the surface plasmon resonance of metallic AgNPs [3].

The sensitization approach enables the generation of electricity with irradiation of energy lower than energy of the bandgap of the semiconductor. The progress of such devices occurred with the development of nanostructured semiconductor films onto which light absorbing dye molecules are adsorbed. Many efforts have focused on sensitizing dye, since dye plays a key role in harvesting sunlight and transforming solar energy into electric energy. Several organic dyes and organic metal complexes have been employed to sensitize DSSCs photo anodes [13].

Natural dyes have become a viable alternative to expensive and rare organic sensitizers because of its low cost, easy attainability and abundance in supply [14]. Various components of a plant such as the flower petals, leaves and bark have been tested as sensitizers [14-16]. The nature of these pigments together with other parameters has resulted in varying performance [14-16]. Here *carica papaya* extract was considered as the sensitizer due to its light harvesting capability in the visible region of the electromagnetic spectrum. Moreover, the chrorophyll pigment in *carica papaya* extract has a short distance between the dye skeleton and the point connected to TiO_2 surface which leads to high charge transfer effect due to good absorbance of the dye in the visible spectrum. *Carica Papaya*, belongs to the family of caricaceae. It is not a tree but a herbaceous succulent plants that posses' self-supporting stems of spongy and soft wood [17].

Researchers have designed and tested various plasmonic light-trapping geometries for enhancing conversion efficiency of DSSCs [18,19]. However, the interaction and working mechanism in DSSCs containing metal nanostructures are dramatically complicated. A detailed description of the kinetics of electrochemical and photoelectrochemical processes in plasmonic DSSCs has not been established yet [12].

In this work, we present the influence of AgNPs in TiO_2 layer on the photovoltaic parameters of DSSC based on *carica papaya* extract through successive ion layer adsorption and reaction. The effects of AgNPs on the PV performance of the formed DSSCs were investigated systematically. Comparative analysis on the performance of the DSSCs showed that the DSSC with AgNPs outperformed the DSSC lacking AgNPs with about 48.4% enhancement in *Jsc,* 8.5% in *Voc* and 63% in η. The related PV

performance enhancement mechanisms and surface-plasmon resonances in DSSCs with Ag nanostructures are analysed and discussed.

2. MATERIALS AND METHODS

2.1 General Comments

Silver nitrate ($AgNO_3$), and ethanol (99.8%), were purchased from Sigma-Aldrich and used as received. Hydrochloric acid (HCl) 36%, Tetraoxosulphate (iv) acid (H_2SO_4) 96%, Chromic Acid were purchased from BDH chemicals. FTO was purchased from solaronix. The surface resistance of the FTO was 8 ohms/m^2, P25 TiO_2 powder was obtained from Alfa Aesar.

2.2 Extraction of Dye

The pawpaw (*Carica papaya*) leaves were harvested and air dried. The leaves of pawpaw was crushed via the use of electronic blender with water as the solvent for extraction. The sample was filtered and stored in reagent bottle. The filtrate (extract) was used for sensitization in this research.

2.3 Synthesis of Nanocomposite Material

Dip coating method was used to synthesize the Ag nanocomposite on the glass substrate. The microscope slide was cleaned with sodium lauryl sulphate (SLES) solution and then rinsed with deionized water three times. Thereafter dipped into a beaker containing a mixture of 2 moles concentrated Tetraoxosulphate (iv) acid and 2 moles chromic acid to make the surface hydrophilic for 10 minutes, the sample was thereafter rinsed with distilled water. After making it hydrophilic, it was immersed in 2 moles Tin chloride ($SnCl_2$) for 2 minutes then rinsed with distilled water for 2 minutes, then immersed in 0.35 mole silver nitrate ($AgNO_3$) for 2 minutes and rinsed with mixture of 150 ml distilled water (H_2O) and 0.4 moles hydrochloric acid (HCl) for 15 seconds. This procedure is called one cycle.

2.4 Fabrication of the DSSCs

The sample of TiO_2 was prepared by the sol-gel technique in which 2 g of P25 TiO_2 powder was dissolved in 10 ml of deionized water mixed with 0.2 ml of Triton-X 100 and 0.4 ml of acetaldehyde, then vibrated ultrasonically using magnetic stirrer hotplate for 24 hours. The silver modified DSSC was fabricated on FTO glass with the structure of FTO/TiO_2/AgNPs. As reference sample, the device with architecture of FTO/TiO_2 was fabricated. The FTO glass substrate was first cleaned with deionized water and ultrasonicated in isopropanol for about 10 minutes. Motivated by this analysis, we utilized SILAR and screen printing method to achieve the design of FTO/TiO_2/AgNPs. To create the particles, a thin (~16 nm) layer of the silver metal film was deposited onto TiO_2 through successive ion layer adsorption and reaction and annealed at 450 ^{O}C for 30 minutes and coated at 2500 rounds/minute for 30 seconds and then sintered at 450ºC for 30 minutes. The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at 100ºC and heated at 400ºC for 30 minutes.

The sintered photo anode was sensitized by immersion in the sensitizer solution at room temperature overnight. The cells were assembled by pressing the photo anode against the carbon-coated counter electrodes slightly offset to each other to enable electrical connection to the conductive side of the electrodes. Between the electrodes, a 50 μm space was retained using two layers of a thermostat hot melt sealing foil. Sealing was done by keeping the structure in a hot-pressed at 100ºC for 1 minute. The liquid electrolyte constituted by 50 mM of tri-iodide/iodide in acetonitrile was introduced by injection into the cell gap through a channel previously fabricated at opposite sides of the hot melt adhesive, the channel was then sealed.

2.5 Characterization and Measurement

The current-voltage *(J-V)* data was obtained using a keithley 2400 source meter under AM1.5 (100 mW/cm^2) illumination from a Newport A solar simulator. Surface morphology was observed with scanning electron microscope (Phenom Pro X model, Eindhoven de Netherlands). The absorption spectrum of the dye, spectra of various prepared AgNPs suspensions was recorded on Ava-spec-2048 spectrophotometer. The cell active area was 0.52 cm^2. The thickness of the film was determined with a profilometer.

3. RESULTS AND DISCUSSION

Fig. 3.1 shows the ultraviolet (UV)-visible (vis) absorption spectra of pawpaw leaves extract. It

was deduced that the *carica papaya* dye absorbs photons best at a wavelength peak of 370 nm which is in agreement with Eli et al. [20]. The relatively broad and strong enhancement is observed in the range of 370–650 nm with peaks at about 390 nm and 550 nm as shown in Fig 3.2 (FTO/TiO_2/AgNPs) which coincides with the localized surface plasmon resonance (LSPR) band position of decorated AgNPs. This enhanced absorption and broadened spectrum absorption range of the photoanode was mainly attributed to the SPR of AgNPs, which interacted with the dye. The absorption of the entire visible region for the electrode with AgNPs was stronger than that for the electrode without AgNPs, which was the product of, an absorption attributed to the surface plasmon resonance of metallic silver nanoparticles in the TiO_2, and well-separated AgNPs with wide range of size and shape.

Fig. 3.3 shows the scanning electron microscope (SEM) image of TiO_2 and TiO_2 with Ag nanoparticles fabricated using screen printing and SILAR procedure. The image in Fig.3.3 shows the nanoparticle size is in the range of ~15–20 nm. The SEM image of Fig. 3.3 (b) also reveals that the Ag clusters from NPs are randomly dispersed on the top surface of active layer.

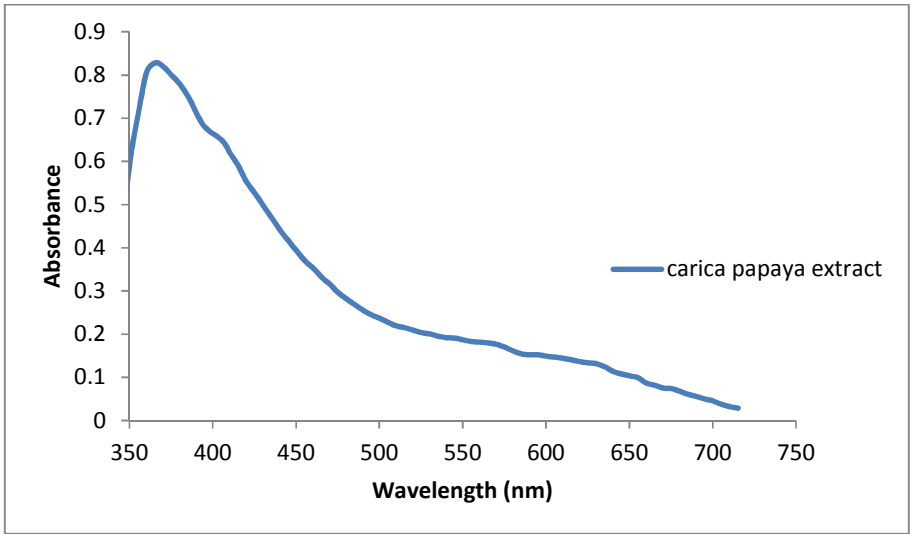

Fig. 3.1. UV-vis spectra of the dye

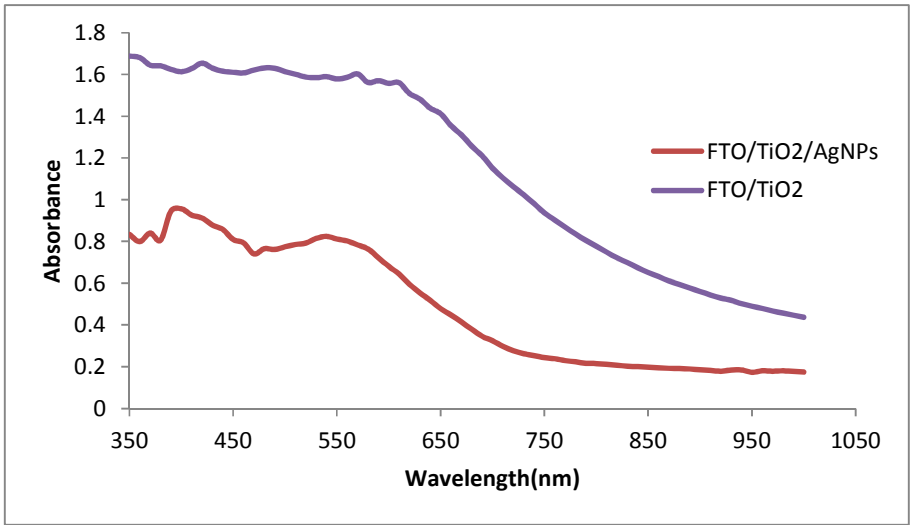

Fig. 3.2. UV-vis spectra of FTO/TiO_2, and FTO/TiO_2/AgNPs with dye

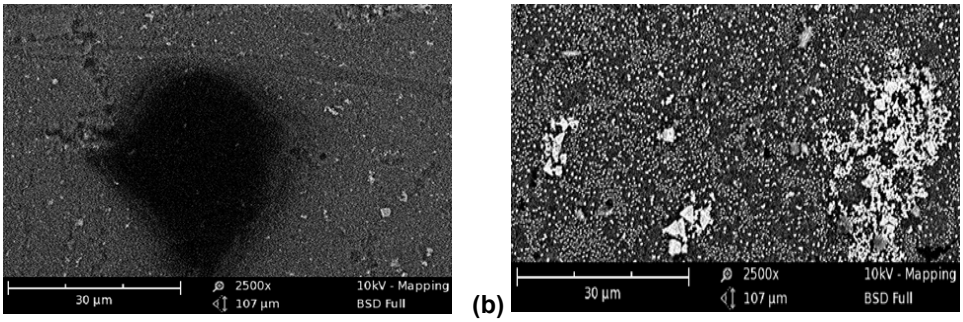

Fig. 3.3. SEM images of (a) FTO/TiO_2 and (b) FTO/TiO_2/AgNPs

The performance of the DSSCs based on only TiO_2 based and the TiO_2–Ag nanocomposite electrodes were examined under 1 sun AM 1.5 simulated sunlight with an active area of 0.52 cm^2. Fig. 3.4 and Table 1 compare the *J–V* characteristics for DSSCs prepared with the TiO_2–Ag nanocomposite and TiO_2 NPs electrodes. Based on the curves in Fig. 3.4, the fill factor (*FF*) which measures the ideality of the device, and the solar cell efficiency (η) were determined following the equations [20].

$$FF = \frac{P_{\max}}{P_{in}} = \frac{J_{\max} \times V_{\max}}{J_{SC} \times V_{OC}} \quad (1)$$

$$\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{IRRADIANCE}}.100\% \quad (2)$$

Where

V_{max} = maximum voltage (V);
J_{max} = maximum current density (mA/cm^2);
J_{sc} = short circuit current density (mA/cm^2);
V_{oc} = open circuit voltage (V) and
$P_{IRRADIANCE}$ = light intensity (mW/cm^2)
P_{max} = maximum power
P_{in} = power input

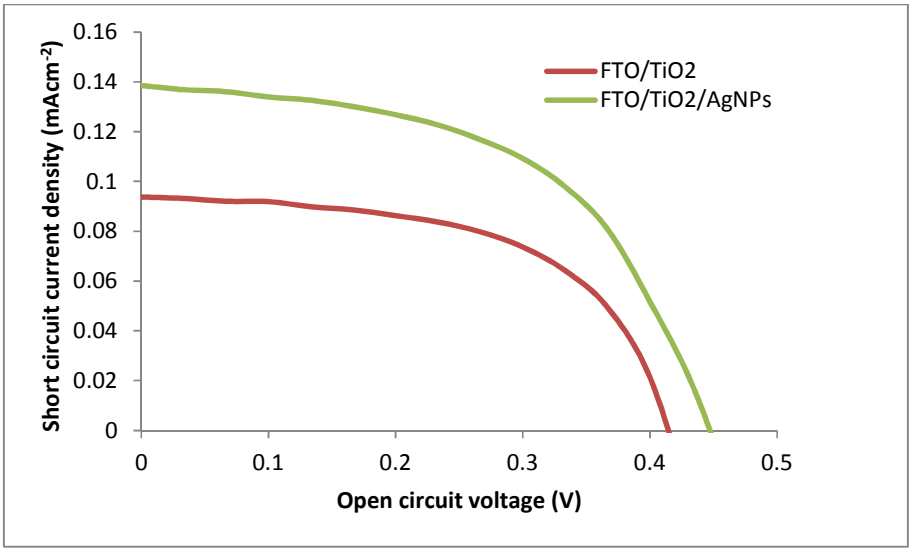

Fig. 3.4. The photocurrent density–voltage (*J –V*) curves with and without AgNPs

Table 1. Performance characteristics of DSSCs fabricated with different anodes under 100 mWcm^{-2}

Sample	J_{sc}(mAcm^{-2})	V_{oc}(V)	*FF*	η (%)
FTO/TiO_2/AgNPs	0.138	0.470	0.504	0.065
FTO/TiO_2	0.093	0.433	0.550	0.040

From Table 1, the enhancement in the photocurrent generation in the Ag plasmonic absorption regions is an indication of the fact that the attachment of metal nanoparticles is beneficial for enhanced absorption (local field enhancement) and charge separation. It can be seen that for the case of AgNPs nanocomposite, the J_{SC} is about 0.138 $mAcm^{-2}$ which is higher than that for TiO_2 nanoparticles case with *Jsc* of about 0.093 $mAcm^{-2}$. Higher J_{SC} value in the case of TiO_2-Ag composite can be assigned to plasmon induced charge transfer from silver nanoparticles to TiO_2. The V_{OC} of TiO_2–Ag nanocomposite based DSSC is 0.470 V and that for the TiO_2 nanoparticles based DSSC case is 0.433 V.

The efficiency obtained by our procedure for TiO_2 nanoparticles film is about 0.040% (without AgNPs). After AgNPs loading on TiO_2 nanoparticles through SILAR method, the conversion efficiency was improved from 0.040% to 0.065% (almost 63% enhancement). Addition of AgNPs is thus seen to reduce the electron–hole recombination centers generally attributed to the oxygen vacancies in TiO_2 in the surface layers [21]. Also, the silver plasmon mode energetically overlaps with dye absorption zone possibly rendering charge into the TiO_2 nanoparticles. Thus, the manipulation of plasmon absorption effects through AgNP functionalization can lead to superior optoelectronic performance of the system.

When AgNPs was added on top of the TiO_2 active film a further increase (48.4%) in the current density at the short circuit (*Jsc*) was observed. The V_{OC} was improved in comparison to the reference sample (8.5% improvement). These results were close to those reported previously by Eli et al. [1] that revealed plasmon induced enhancement of molecular charge separation.

The increment of *Jsc* was attributed to the enhanced light absorption and broadened light absorption range of the dye (shown in Fig. 3.2) resulting from the SPR of AgNPs, which stimulates the dye to generate more charge carriers [22]. Furthermore, the Schottky barrier at the Ag/TiO_2 interface [23,24] will form electron-hole separation centers which would be beneficial in improving the movement of photo-generated electrons shuttling through the porous TiO_2 network, reducing recombination of electrons and holes, thus increasing *Jsc* [25].

As well known, silver has long been regarded as being catalytically active. However, AgNPs dispersed on metal-oxide supports are active catalysts for a variety of chemical reactions [3]. In our work, when AgNP was added, the catalytic effect of AgNPs sited on TiO_2 support could increase the reaction rate between the TiO_2/dye and the redox electrolyte in DSSCs, thereby reducing the corresponding electron transport resistance. As a consequence, the recombination probability between electrons and holes may increase, so increasing the number of charge carrier, thus resulting in an increase in *Jsc* and *Voc*.

Unlike the non-apparently enhanced photocurrent for plasmonic near-field of Ag-assisted *carica papaya*-dye, the larger improvement of conversion efficiency in the whole visible region was observed, leading to a drastic increase of power efficiency. Silver particles can be used as scattering element and near-field concentration of light that can act as plasmonic scattering to trap light and near-field coupled to the dye molecules for different plasmonic structures, respectively. We suggested that the enhanced photocurrent response spectrum throughout the whole visible region is mainly attributed to plasmonic scattering. It caused an apparent increase of the optical absorption of dye, resulting in drastically enhanced photovoltaic properties (Fig. 3.4).

4. CONCLUSIONS

We demonstrated the impact of AgNPs on the performance of a dye sensitized solar cell (DSSC) through successive ion layer adsorption and reaction (SILAR). The photovoltaic performance was evaluated under 100 $mWcm^{-2}$ light intensity. The performance, especially the photocurrent, and open circuit voltage of the DSSC containing AgNPs was significantly affected by the AgNPs. The modified AgNPs photoanode shows a short circuit current density (J_{SC}) of 0.138 $mAcm^{-2}$, a photovoltage V_{OC} of 0.470 V yielding an overall conversion efficiency of 0.065%. This represents a 63% improvement in efficiency, 48.4% enhancement in short circuit current density and 8.5% improvement in open circuit voltage over the DSSC without AgNPs. The increase in the PV perfomance is attributed to the enhanced light absorption and broadened absorption spectral range of the composite photoanode due to the Surface Plasmon Resonance of the AgNPs. The results show the

merits of introducing AgNPs into TiO_2 photoanodes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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