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## **Plasmonic Dye Sensitized Solar Cells Incorporated with TiO<sub>2</sub>-Ag Nanostructures**

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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 statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors MSA, ABB and OAB managed the analyses of the study and literature searches. All authors read and approved the final manuscript.*

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### **ABSTRACT**

We demonstrated an improvement in efficiency of Dye sensitized solar cells (DSSCs) decorated with silver (Ag) nanoparticles (NPs) through successive ion layer adsorption and reaction (SILAR). The DSSCs employing FTO/TiO<sub>2</sub>/AgNPs and FTO/AgNPs/TiO<sub>2</sub> as photoanodes show remarkably enhanced power conversion efficiencies up to about 36% and 25%, respectively, with an enhanced photocurrent densities of about 49% and 22% with respect to a reference cell containing FTO/TiO<sub>2</sub> photoanode. These enhancements can be mainly attributed to the enhanced dye absorption by the intensified near-field effect of AgNPs and plasmon-enhanced photocurrent generation. The related PV performance enhancement mechanism and surface-plasmon resonance (SPR) in DSSCs with Ag nanostructures are discussed.

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**Keywords:** DSSCs; silver nanoparticles; TiO<sub>2</sub>; cell performance; SPR.

## 1. INTRODUCTION

Solar energy is an area that is gaining more attention over recent years as the fossil and mineral energy sources are approaching inevitable exhaustion in the coming fifty years [1].

The escalated and savage consumption of conventional sources of energy are leading to forecasted energy and environmental crises. Renewable energy sources such as solar energy are considered as a feasible alternative because “More energy from sunlight strikes Earth in 1 hour than all of the energy consumed by humans in an entire year” [2]. Facilitating means to harvest a fraction of the solar energy reaching the Earth may solve many problems associated with both the energy and global environment [3]. The conversion of solar energy into electricity relies on photovoltaic devices, i.e., so-called solar cells, which have undergone three generations with an evolution from the initial single silicon solar cells [4] to the second generation solar cells based on semiconductor thin films [5,6] and, now, the third generation solar cells represented by dye-sensitized solar cells (DSSCs) and organic semiconductor solar cells [7-10]. Compared with the first and second generation solar cells based on conventional semiconductor materials with conversion efficiencies of ~20—30%, currently the third generation solar cells still demonstrate efficiencies relatively low [11,12]. However, the third generation solar cells have announced a lot of peculiarities superior to the first and second generation solar cells, for example, the large flexibility in shape, colour, transparency, performance also under diffuse light and low cost of materials and manufacturing procedure [7,13-16]. DSSCs could be integrated into large varieties of products, e.g. hand bags or clothing, indoor applications, and building-integrated photovoltaics such as rollable devices for walls of buildings or windows.

In DSSCs, dye molecules adsorbed on the oxide play a role of “antenna” for photon capturing. For this reason, accompanying with the development of DSSCs, organic dyes have been intensively studied with a focus on increasing the extinction coefficient and extending the optical absorption spectrum [17-23].

However, a major problem confronting these cells is the low efficiency of conversion.

Scattering from the noble metal nanoparticles is considered as potential candidates to enhance low energy photon absorption in solar cells and hence increase the cell efficiency. The use of plasmonic nanostructures has been proposed as a promising pathway to increase light absorption in active layers of solar cells, and has been demonstrated on several thin-film solar-cell materials [24-28]. In surface plasmon resonance, the collective oscillations of free electrons confined at the surface of the metals can be induced when the frequency of incident light matches the plasmon frequency of irradiated metals. These collective charge oscillations result in substantially enhanced electric fields near the surface of NPs, which can facilitate both light absorption and charge separation.

This study proposed simple design strategies for realizing how to improve photovoltaic properties of the cell using in-plane surface plasmon (SP) nanoparticles (NPs) of silvers coated on both the top and the bottom of a TiO<sub>2</sub> semiconductor. The conversion efficiency and short-circuit photocurrent density were increased by 36% and 49% when the surface plasmon (SP) structure was coated on TiO<sub>2</sub>, and were increased by 25% and 22% when the SP structure was placed on the bare fluorine doped tin oxide (FTO).

### 1.1 General Composition, Function and Parameters of DSSC

DSSC is composed of four elements, namely, the transparent conducting and counter conducting electrodes, the nanostructured wide bandgap semiconducting layer, the dye molecules (sensitizer), and the electrolyte. The transparent conducting electrode and counter-electrode are coated with a thin conductive and transparent film (such as fluorine-doped tin dioxide (SnO<sub>2</sub>)). The TiO<sub>2</sub> surface is stained with a dye. TiO<sub>2</sub> nanocrystals are used rather than a continuous layer to maximize surface area for light absorption. Between the electrodes is an electrolyte. Upon absorption of photons, dye molecules are excited from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbital (LUMO) states as shown schematically in Fig. 1. Once an electron is injected into the conduction band of the wide bandgap semiconductor nanostructured TiO<sub>2</sub> film, the dye molecule (photosensitizer) becomes oxidized. The injected electron is transported between the TiO<sub>2</sub> nanoparticles and then

extracted to a load where the work done is delivered as an electrical energy. The electrons flow through the  $\text{TiO}_2$  onto the electrode, through an electric circuit, and then to the counter electrode. The electrolyte carries electrons back to the dye from the counter electrode. Electrolytes containing redox ions are used as an electron mediator between the  $\text{TiO}_2$  photoelectrode and the coated counter electrode. Therefore, the oxidized dye molecules (photosensitizer) are regenerated by receiving electrons from the ion redox mediator that get oxidized.

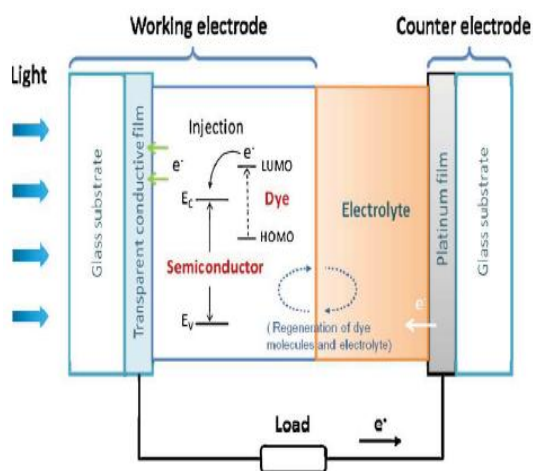


Fig. 1. Schematic diagram of the structure of a dye sensitized solar cell

## 2. EXPERIMENTATION

### 2.1 Dye Extraction

The flowers of *Hibiscus Sabdariffa* were air dried till they became invariant in weight. The dried flowers of *Hibiscus* were left uncrushed because previous attempts proved failure to extract the dye from crushed samples due to jellification [29]. The method of heating in water was used to extract the dye. Distilled water was the solvent for aqueous extraction. 5 g of the sample (Dried *Hibiscus Sabdariffa*) was measured using analytical scale and dipped in 50 ml of the solvent heated to  $100^\circ\text{C}$  for 30 min after which solid residues were filtered out to obtain clear dye solutions.

### 2.2 Preparation of $\text{TiO}_2$ Paste

The  $\text{TiO}_2$  films were prepared using a modified sol-gel method, in which 2 g of P25  $\text{TiO}_2$  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 for 24 hours.

### 2.3 DSSCs Assembling

Motivated by this analysis, we utilized SILAR and screen printing method to achieve two different design strategies of experiments including FTO/ $\text{TiO}_2$ /AgNPs and FTO/AgNPs/ $\text{TiO}_2$  cases. To create the particles, a thin ( $\sim 15$  nm) layer of the silver metal film was deposited onto FTO & P25  $\text{TiO}_2$  through successive ion layer adsorption and reaction and annealed at  $450^\circ\text{C}$  for 30 min and coated at 2500 rad/s for 30 sec and then sintered at  $450^\circ\text{C}$  for 30 min.

The sintered photoanode was sensitized by immersion in the sensitizer solution at room temperature overnight. The cells were assembled by pressing the photoanode against the platinum-coated counter electrodes slightly offset to each other to enable electrical connection to the conductive side of the electrodes. Between the electrodes, a  $40\ \mu\text{m}$  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  $100^\circ\text{C}$  for 1 min. the liquid electrolyte constituted by 50 mmols 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.

### 2.4 Characterization

The current-voltage ( $J$ - $V$ ) data was obtained using a Keithley 2400 source meter under AM1.5 ( $100\ \text{mW}/\text{cm}^2$ ) illumination from a Newport A solar simulator. The film morphology was obtained by scanning electron microscopy (Phenom Pro X model, Eindhoven de Netherlands). The absorption spectrum of the dye and various photoanode were recorded on Ava-spec-2048 spectrophotometer in the region of 350–1000 nm. The cell active area was  $0.5\ \text{cm}^2$ . Thickness measurement was obtained with a Dektac 150 surface profiler.

## 3. RESULTS AND DISCUSSION

Water extract of *Hibiscus Sabdariffa* shows absorption peak at about 550 nm which ascertains the presence of anthocyanin pigment (Fig. 2a).

Fig. 2b shows the absorbance of TiO<sub>2</sub> with water extract of hibiscus sabdariffa as sensitizer within the region of 500-590 nm (FTO/TiO<sub>2</sub>).

Fig. 2b also shows the absorbance of the various prepared AgNPs suspension with the dye within the wavelength range of 350-1000 nm with different design architecture (FTO/TiO<sub>2</sub>/AgNPs and FTO/AgNPs/TiO<sub>2</sub>).

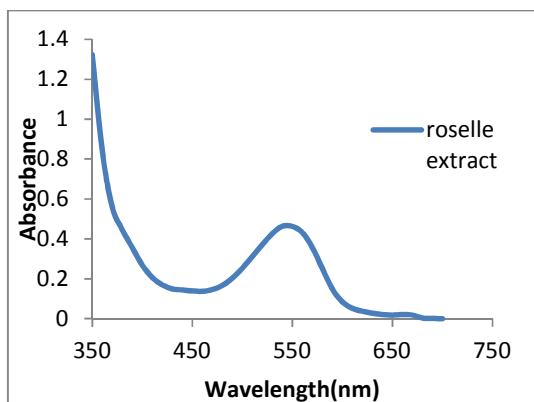


Fig. 2a. UV-Vis spectra of the dye

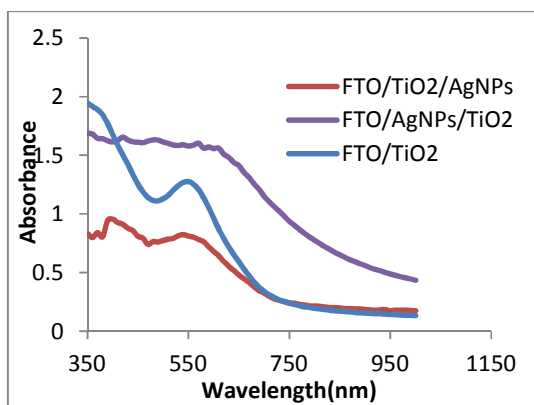


Fig. 2b. UV-vis spectra of various prepared Ag NPs suspensions with dye

The relatively broad and strong enhancement is observed in the range of 370–650 nm where two peaks were found: the first one around 390 nm while the second one at 550 nm as shown in Fig. 2b (FTO/TiO<sub>2</sub>/AgNPs) which coincides with the localized surface plasmon resonance (LSPR) band position of decorated AgNPs.

The morphology of the electrode reveals a random two dimensional array of AgNPs with a wide range of size, as shown in Figs. 3a and b. In the case of AgNPs on TiO<sub>2</sub>, isolated

nanoparticles were approximately spherical in shape. The two cases, which the size and distribution of nanoparticles were similar consist of about 20 nm diameter spherical clusters.

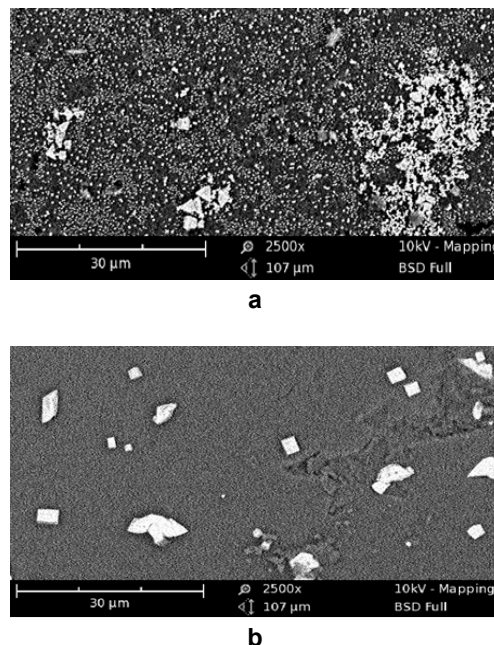


Fig. 3. SEM images of silver film coated upon (a) FTO/TiO<sub>2</sub> (b) FTO substrates

The strong absorption in the whole visible region was observed in comparison with pure TiO<sub>2</sub> standard electrode. The absorption of the entire visible region for the electrodes with AgNPs was stronger than that for the electrodes without AgNPs, which was attributed to the surface plasmon resonance (SPR) of metallic silver nanoparticles [30].

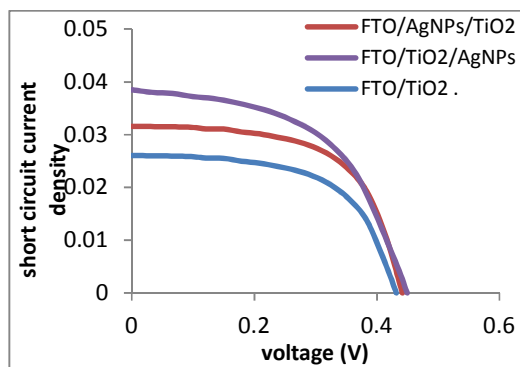


Fig. 4. Photocurrent density-voltage (*J-V*) curve under 100 mWcm<sup>-2</sup> light intensity

**Table 1. Performance characteristics of DSCs fabricated with different anodes under 100 mWcm<sup>-2</sup>**

Sample	$J_{sc}$ (mAcm <sup>-2</sup> )	$V_{oc}$ (V)	FF	$\eta$ (%)
FTO/TiO <sub>2</sub>	0.0259	0.432	0.594	0.00669
FTO/TiO <sub>2</sub> /AgNPs	0.0385	0.450	0.526	0.00910
FTO/AgNPs/TiO <sub>2</sub>	0.0316	0.442	0.606	0.00845

Fig. 4 shows the  $J$ - $V$  (current density–voltage) curves of electrodes in two differently designed cells under illumination.

Based on the  $J$ - $V$  curve, the *fill factor* ( $FF$ ) and *solar cell efficiency* ( $\eta$ ) were determined using equations (1) and (2) respectively [31].

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

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{IRRADIANCE}} \cdot 100\% \quad (2)$$

Where

$V_{max}$  = maximum voltage (V);  
 $J_{max}$  = maximum current density (mA/cm<sup>2</sup>);  
 $J_{sc}$  = short current density (mA/cm<sup>2</sup>);  
 $V_{oc}$  = *open circuit voltage* (V) and  
 $P_{IRRADIANCE}$  = light intensity (mW/cm<sup>2</sup>)

The total photon-to-current energy conversion efficiency ( $\eta$ ) for the standard, FTO/AgNPs/TiO<sub>2</sub> and FTO/TiO<sub>2</sub>/AgNPs electrodes are 0.0067, 0.0091, and 0.0084%, respectively. The short-circuit photocurrent density ( $J_{sc}$ ) of the electrode with AgNPs that was coated upon P25 titania was 0.0385 mA/cm<sup>2</sup>, an improvement from 0.0259 mA/cm<sup>2</sup> for the pure TiO<sub>2</sub> electrode, exhibiting a 49% enhancement in the photocurrent density and a 36% enhancement in the conversion efficiency. Also the short-circuit photocurrent density ( $J_{sc}$ ) of the electrode with AgNPs placed upon FTO was 0.0316 mA/cm<sup>2</sup>, an improvement from 0.0259 mA/cm<sup>2</sup> for the pure TiO<sub>2</sub> electrode, exhibiting a 22% enhancement in the photocurrent density and a 25% enhancement in the conversion efficiency. These results were close to those reported previously that revealed plasmon induced enhancement of molecular charge separation [30].

As shown in Table 1 above, for better performance, Metal plasmon must be located between TiO<sub>2</sub> semiconductor and dye molecule

to escape recombination and produce an enhanced photocurrent. The electric field of localized plasmon resonances only promotes few dye molecules close to silver surface, leading to limited enhancement. Therefore, light trapping of localized surface plasmon was mainly improved in DSSC fabricated with FTO/TiO<sub>2</sub>/AgNPs photoanode electrode in our system, leading to the enhanced photocurrent response in the whole visible region in comparison with the reference/standard titania electrode (Fig. 4). Plasmonic structure can trap light to the active layer to increase dye absorption and the degree of the enhanced photocurrent density by light trapping of plasmonic scattering [31]. Hence, the active TiO<sub>2</sub> film creates more photoelectron which can be able to enhance charge separation and dye absorption at the semiconductor/dye interface. When AgNPs was coated at the bottom of the TiO<sub>2</sub> semiconductor, light trapping of plasmonic structure for dye absorption and enhanced the charge separation of excited dye by near-field does not affect dramatically photocurrent density in cells as shown in Fig. 4.

#### 4. CONCLUSIONS

In the present work, we performed a comparative study on the performance of organic solar cells when silver nanoparticles (NPs) were placed in two distinct configurations within the organic photovoltaic structure; on top of the TiO<sub>2</sub> and on the FTO substrate. The plasmonic effects were quantified on the device. The results shows enhanced absorption in the visible spectral range for both configurations, but more pronounced in the case were the AgNPs was coated on TiO<sub>2</sub>. In this configuration, the SPR effect of AgNPs enhances their surrounding electromagnetic fields, which in turn boost the absorption of the active layer and increases the probability of exciton generation and dissociation, leading to an increase of the photocurrent generation. Nevertheless, this device suffered from poor fill factor value. On the other hand, placing the AgNPs on top of the FTO results to less overall performance of the device. The results obtained are encouraging and should prompt more

detailed studies to uncover the exact mechanism involved.

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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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