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## Plasmonics for Enhanced Power Conversion Efficiencies in Dye Sensitized Solar Cells

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**Abstract:** The results of the very simplified integration of AgNPs with different diameter sizes (40 nm, 80 nm and 120 nm) within the porous TiO<sub>2</sub> layer of DSSCs was demonstrated. The silver nanoparticle clusters (AgNPs) improve the values of Open circuit voltage (V<sub>oc</sub>), short circuit current (J<sub>sc</sub>), fill factor (FF), and efficiency of conversion ( $\eta$ ). The plasmonic effect as observed by introducing AgNPs with 40 nm in DSSC produces higher performance with J<sub>sc</sub> of 0.035 mAcm<sup>-2</sup>, V<sub>oc</sub> of 0.420 V, FF of 0.430, yielding  $\eta$  of 0.0064 %. These results are due to enhanced light absorption of the dye in strength and spectral range from the surface plasmon resonance (SPR) effect of the metallic silver nanoparticles. The improved charge transport also increases the value of J<sub>sc</sub> and reduces the resistance. The mechanism of getting the best utilization efficiency is also discussed.

**Keywords:** SPR; DSSCs; Silver Nanoparticles; Plasmonic; Natural dye.

### 1. Introduction

Dye-sensitized solar cells (DSSCs) have been given attractive attention as a promising technology for renewable energy production, in part due to their ease of fabrication and low cost [1]. However the major problem facing it, is the low conversion efficiency. To improve efficiencies of DSSCs, efforts have been directed at engineering the anode, cathode, dye, and redox shuttle [2]. Nevertheless, the photoanode has been regarded as paramount since the factors for improving efficiency such as presenting a high density of light harvesting molecules, fast electron injection from dyes to networks, fast electron transport within networks, slow back electron transfer to oxidized dyes and shuttles, and high open-circuit photovoltages (V<sub>oc</sub>) are determined, at least in part, by the properties of the anode.

Metal nanoparticles (NPs) can be effective in thin film solar cells because of their localized surface plasmon resonance (LSPR), which can increase the light absorption capability of an active layer within a range of wavelengths. Thus, the addition of metal NPs into a DSSC active layer can potentially enhance the absorption and increase the photo-generation of mobile carriers. Several groups have recently reported that, when combined, polymer and metal, semiconductor and metal nanoparticles NPs improve light absorption and cell efficiency [3-5]. To ensure that metal NPs have positive effects in organic photovoltaic devices (OPVs), we must diminish the possibility of transferring non-radiative energy, which quenches excitons in the DSSC active layer [3-5].

Our study demonstrates the effects that arise from the addition of Ag NPs with controlled diameter size in DSSC photovoltaic cells. Using successive ionic layer adsorption and reaction (SILAR) process, we can synthesize Ag particles with well controlled sizes. Specifically, we produced particles with diameters of 40 nm, 80 nm, and 120 nm. Betalain pigment from Flame Flower was then used as the sensitizer in a sandwich type DSSCs. The choice of betalains is due to its requisite carboxylic functional groups (-COOH) to bind better to the TiO<sub>2</sub> surface [6-8]. At a size of 40 nm, the power conversion efficiency increased from 0.0034 % to 0.0064 % which gave the best performing cell. Because aggregated small-sized nanomaterials can reflect and scatter incident light more efficiently than larger Ag NPs (of greater than 40 nm), light can be harvested more effectively [9].

## 2. Materials and Method

### 2.1. Materials

Acetonitrile, Platisol, propylene carbonate, acetaldehyde, and Triton-X 100 were purchased from BDH chemicals. Silver nitrate ( $\text{AgNO}_3$ ), and ethanol (99.8%), were purchased from Sigma-Aldrich and used as received. FTO was purchased from solaronix. The surface resistance of the FTO was  $15 \Omega/\text{m}^2$ , P25  $\text{TiO}_2$  powder and  $\text{SiO}_2$  were obtained from Alfa Aesar.

### 2.2. Synthesis of Nanocomposite Material for profiling

Dip coating method was used to synthesize the silver nanocomposite on the glass slide following the method previously demonstrated in [10, 11].

### 2.3. Preparation of the Natural Dye

The natural dye was extracted with deionized water employing the following procedure: fresh flowers of flame tree were washed and air dried. 80 g of the samples was crushed via the use of a porcelain mortar and a pestle with 50 ml deionized water as extracting solvent. The solution was filtered to separate the solid residue from the pure liquid and the filtrate was used as the light harvesting pigment without further purification.

### 2.4. Preparation of $\text{TiO}_2$ Paste

The  $\text{TiO}_2$  films was 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 mol of Triton-X 100 and 0.4 g of acetaldehyde, then vibrated ultrasonically for 24 hours [12].

### 2.5. Preparation of Photo Anodes

FTO conductive glass sheets, were first cleaned in a detergent solution using an ultrasonic bath for 10 minutes, rinsed with water and ethanol, and then dried [11].

$\text{TiO}_2$  were deposited on the FTO conductive glass by doctor blading technique in order to obtain a  $\text{TiO}_2$  with a thickness of  $9 \mu\text{m}$  and an active area of  $0.72 \text{ cm}^2$ . The  $\text{TiO}_2$  film was preheated at  $200 \text{ }^\circ\text{C}$  for 10 min and then sintered at  $500 \text{ }^\circ\text{C}$  for 30 min.

The second, third and fourth photo anodes were prepared by depositing one, two and three SILAR cycles of AgNPs through successive ionic layer adsorption and reaction (SILAR) on the pre-grown  $\text{TiO}_2$  film then followed by depositing five, ten and fifteen SILAR cycles of  $\text{SiO}_2$  as protective shells against plasmons attack. The electrodes were immersed on the water extract of the delonix regia pigment for 10-12 hours [13].

### 2.6. Preparation of Counter Electrode

The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at  $100^\circ\text{C}$  and annealed at  $400^\circ\text{C}$  for 30 min [14].

### 2.7. DSSCs Assembly

The DSSCs photo anodes and the screen printed-Pt counter electrodes were assembled to form a solar cell by sandwiching a redox (tri-iodide/iodide) electrolyte solution. The electrolyte solution consist of 2 m L acetonitrile, 0.1 M propylene carbonate, 0.005 M LiI, 0.0005 M  $\text{I}_2$ . Therefore, the open side of the cell assembly was sealed properly with super glue.

### 2.8. Characterization and Measurement

The current density-voltage ( $J$ - $V$ ) characteristics of the cells were recorded using a setup comprising a xenon lamp, an AM 1.5 light filter, and a Electrochemical Analyzer (Keithley 2400 source meter) under an irradiance of  $100 \text{ mW}/\text{cm}^2$ . Scanning electron microscopy (SEM) images were obtained using Carl Zeiss at an acceleration voltage of 20 kV. Visible region extinction spectra of dye, electrodes without dye and electrodes with dye were recorded on Axiom Medicals UV752 UV-vis-NIR spectrophotometer.

## 3. Results and Discussion

### 3.1. Absorption Spectra

Fig. 3.1a shows the absorbance of the natural dye within the wavelength range of 350-1000 nm. The pigment is noticed to have its absorption peak around 410 nm which agrees with similar studies earlier reported [15, 16]. The absorption at this range is indicative that this pigment can be used as light harvesting pigment in this research. Fig. 3.1b shows ultraviolet (UV)-visible absorption spectra of synthesized Ag NPs with different diameters dispersed on  $\text{TiO}_2$  through SILAR. Thus, the one SILAR, two SILAR, and three SILAR cycles of Ag NPs have relatively broad and strong enhancement, observed in the range of 320–860 nm with a maximum enhancement around 430 nm, which coincides with the localized surface plasmon resonance (LSPR) band position of decorated AgNPs [14, 17].

### 3.2. Scanning Electron Microscopy (SEM)

Fig. 3.3a shows SEM images of differently sized AgNPs deposited on the FTO surface using SILAR method. The particle size is around 40 nm, 80 nm and 120 nm as shown in Figs. 3b, c and d, respectively. The SEM images revealed that the nanoparticles are almost uniformly dispersed in the TiO<sub>2</sub> film and are clearly coated on the substrate. As revealed by the results of energy dispersive X-ray (EDX) in Fig. 3.3b, the synthesized NPs are composed of elemental Ag. These Ag NPs are a good material for investigating the size effects of Ag in DSSCs.

### 3.3. Photoelectrochemical Properties of DSSCs

Fig. 3.2 shows the photocurrent density–voltage ( $J-V$ ) curves of the DSSCs with varying SILAR cycles 0, 1, 2, 3 cycles. Based on the  $J-V$  curves the fill factor (FF) and efficiency can be determined following equations (1) and (2) respectively [18]:

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

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

Where

$FF$  = Fill Factor which measures the ideality of the device, and describes how close to a square the shape of the  $J-V$  curve is

$\eta$  = solar cell efficiency

$V_{max}$  = maximum voltage (V);

$J_{max}$  = maximum current density (mA/cm<sup>2</sup>);

$J_{sc}$  = short circuit current density (mA/cm<sup>2</sup>);

$V_{oc}$  = open circuit voltage (V) and

$P_{IRRADIANCE}$  = light intensity (mW/cm<sup>2</sup>)

**Table-1.** Photovoltaic performance of DSSCs with 0, 1, 2, and 3 SILAR cycles of AgNPs photo anode under 100 mWcm<sup>-2</sup>

Sample	Photo anode	$J_{sc}$ (mAcm <sup>-2</sup> )	$V_{oc}$ (V)	$FF$	$\eta$ (%)
1	0 SILAR CYCLE	0.027	0.430	0.300	0.0034
2	1 SILAR CYCLE	0.035	0.420	0.430	0.0064
3	2 SILAR CYCLES	0.004	0.310	0.456	0.0005
4	3 SILAR CYCLES	0.002	0.330	0.380	0.0003

As displayed in Table 1 and Fig. 3.2, the fill factors of these DSSCs varies from 0.300 to 0.456. The  $V_{oc}$  varies from 0.310 to 0.430 V, and the  $J_{sc}$  changes from 0.002 to 0.035 mAcm<sup>-2</sup>. Specifically, a high  $J_{sc}$  (0.035 mAcm<sup>-2</sup>) and efficiency (0.0064 %) were obtained from the DSSC with 1 SILAR cycle. The cell with one SILAR cycle exhibits an enhancement of 29.63 % in  $J_{sc}$  over the reference cell and an increase of 88.24 % (from 0.0034 to 0.0064 %) in efficiency over the reference electrode. The efficiency enhancement in the presence of silver can be seen to arise chiefly from an increase in photocurrent density and  $V_{oc}$  values. The enhanced  $J_{sc}$  is related to the light harvesting capability of dye molecules by plasmon-enhanced excitation [14]. The Ag clusters increase the effective optical path length by means of scattering and the generation of electron-hole pairs from the surrounding excited fields of the Ag clusters. A TiO<sub>2</sub> film with Ag clusters has superior absorption because it can scatter the incident light through a whole range of wavelengths.

However, the use of larger Ag nanoparticles did not lead to positive effects. Individual Ag nanoparticles can act as hole conductors because their work function is well matched with the energy of the highest occupied molecular orbital (HOMO) of the natural dye. Therefore, large Ag nanoparticles did not transport holes more efficiently because there are more interfaces between Ag and the active layer.

Eli et.,al once reported that the decrease in efficiency due to increasing film thickness was found to be proportional to the light transmittance [14]. As a result, the recombination probability between electrons and holes may increase, so  $J_{sc}$  would decrease. In addition, higher concentrations of AgNPs may cluster to form larger AgNPs groups with lower electron storage capability, reducing the cell performance.

In our work, when AgNP was large, the catalytic effect of AgNPs sited on TiO<sub>2</sub> support could decrease the reaction rate between the TiO<sub>2</sub>/dye and the redox electrolyte in DSSCs, thereby increasing the corresponding electron transport resistance and subsequently forming islands. Conversely, as the silver size became smaller, AgNPs easily dispersed which could preferentially attach to specific sites on the TiO<sub>2</sub> surface, resulting in the increase of catalytic activity [14, 17].

Fig-3.1a. Absorption spectra of pure water extract dye

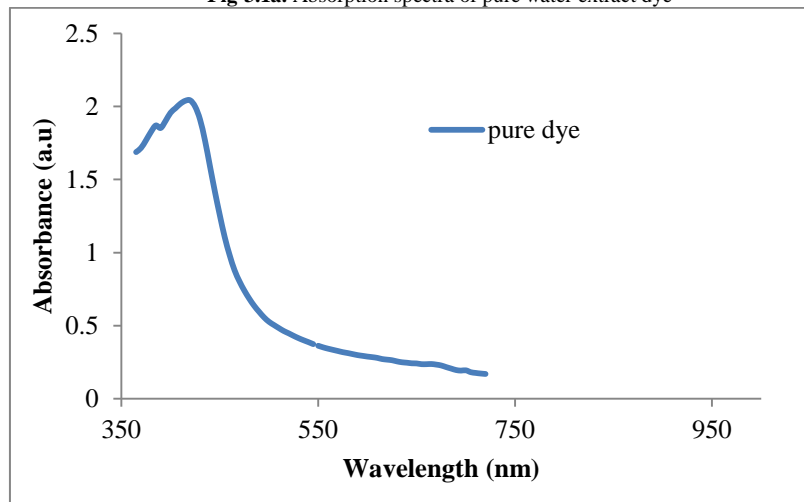


Fig-3.1b. UV-Vis spectra of (a) TiO<sub>2</sub> with 0 cycle (b) TiO<sub>2</sub> with 1 cycle, (c) TiO<sub>2</sub> with 2 cycles and (b) TiO<sub>2</sub> with 3 cycles

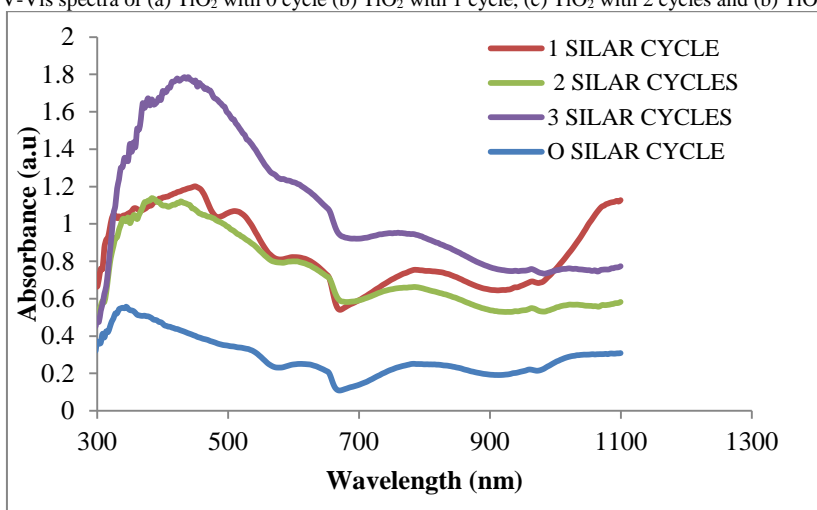
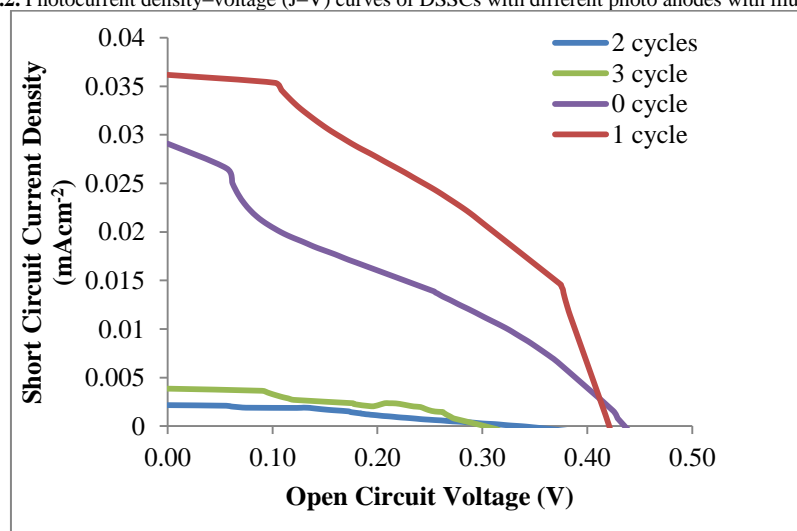
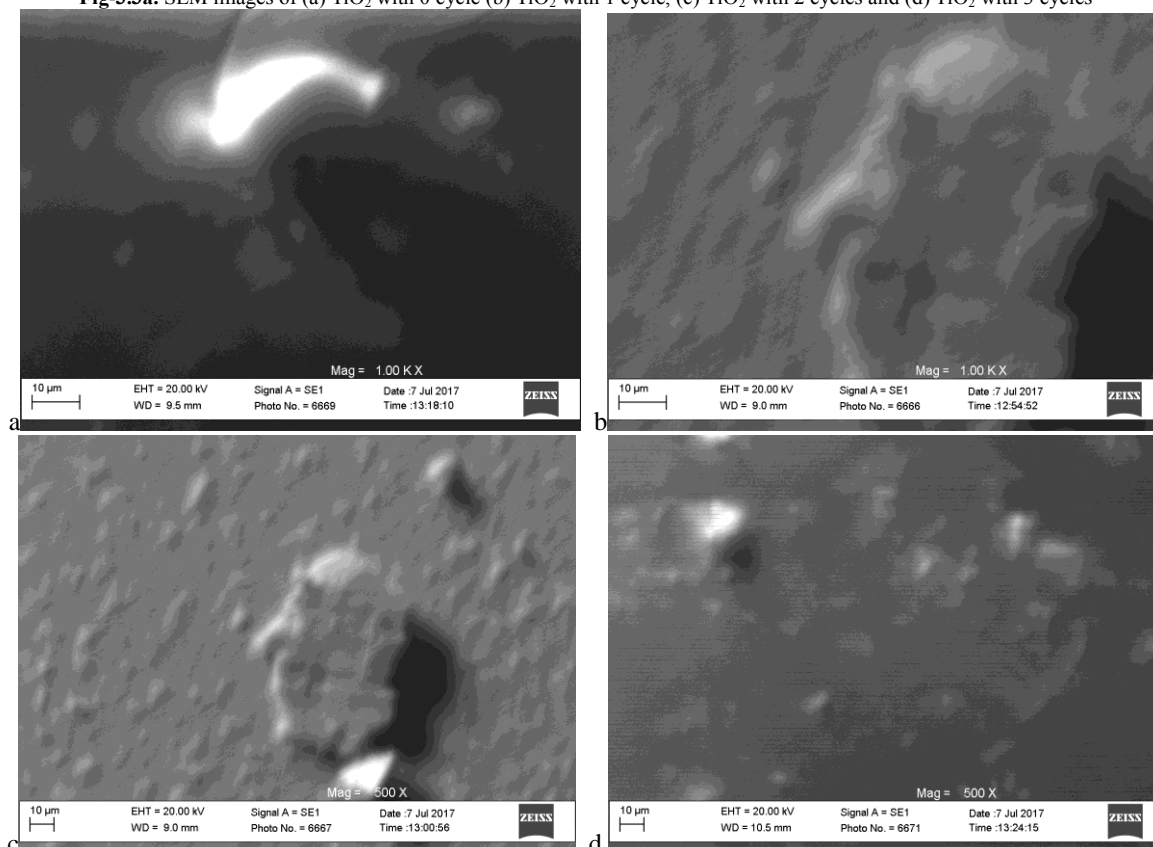
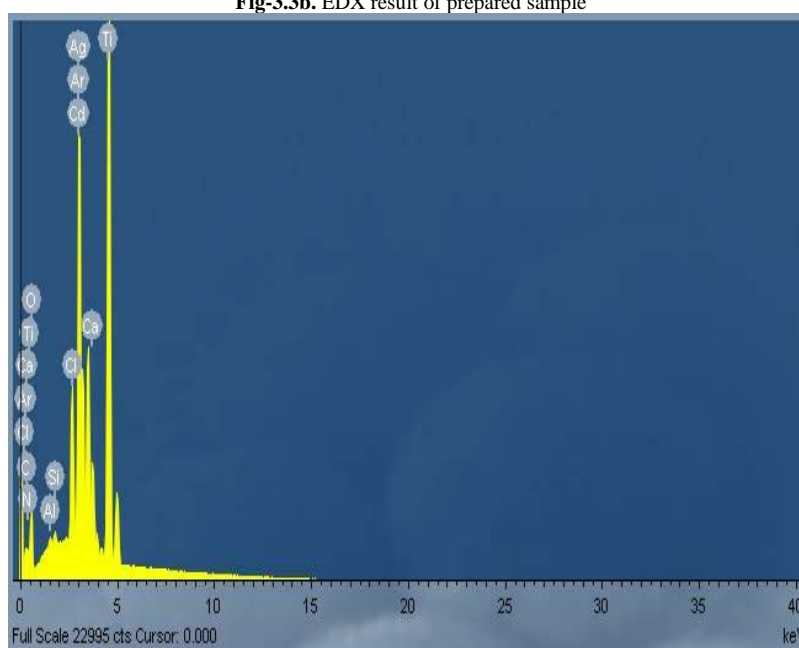


Fig-3.2. Photocurrent density–voltage (J–V) curves of DSSCs with different photo anodes with illumination



**Fig-3.3a.** SEM images of (a) TiO<sub>2</sub> with 0 cycle (b) TiO<sub>2</sub> with 1 cycle, (c) TiO<sub>2</sub> with 2 cycles and (d) TiO<sub>2</sub> with 3 cycles**Fig-3.3b.** EDX result of prepared sample

#### 4. Conclusion

The effect of silver (Ag) nanoparticles (NPs) with different diameter sizes on the performance of dye sensitized solar cells (DSSCs) through successive ionic layer adsorption and reaction (SILAR) was investigated. Studies indicate that, the short-circuit current density ( $J_{SC}$ ) and open-circuit voltage ( $V_{OC}$ ), of DSSCs containing 40 nm size of AgNPs was significantly improved. The photovoltaic (PV) performance decreased with increasing size of AgNPs from one SILAR cycle to two SILAR cycles, This selective enhancement in efficiency in the Ag plasmonic absorption regions is indicative of the fact that the incorporation of metal nanoparticles is beneficial for enhanced absorption and charge separation in DSSCs.

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