

Size Effects of Silver Nanoparticles on the Photovoltaic Performance of a Dye Sensitized Solar Cells.

M.Y. Onimisi¹, Danladi Eli¹, S. G. Sadiq², H.O. Aboh², Ezeoke Jonathan¹

¹ Department of Physics, Nigerian Defence Academy, Kaduna, Nigeria

² Department of Physics, Kaduna state university, kaduna, Nigeria

Authors' contributions

This work was carried out in collaboration between both authors. Author MY designed the study. Author DE undertook the experimental work, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors SA, HO and EJ managed the analyses of the study and literature searches. Both authors read and approved the final manuscript.

Abstract

The size effects of silver (Ag) nanoparticles (NPs) on the performance of a dye sensitized solar cells (DSSCs) through successive ion layer adsorption and reaction (SILAR) was investigated. A series of Ag NPs with different SILAR cycles were synthesized on fluorine tin oxide (FTO) glass slides. The size effects of Ag NPs on the photovoltaic performance (PV) of the formed DSSCs were investigated systematically. The performance, especially the photocurrent, and open circuit voltage of DSSCs containing Ag NPs was significantly affected by the particle size of Ag NPs. The PV performance decreased with increasing size of Ag-NPs from one silar cycle to three silar cycles, the best performance was achieved using the anodes prepared with one silar cycle. The best cell showed a conversion efficiency (η) of 0.00910%. The cell exhibited a 36% improvement over the performance (0.00669%) of bare FTO-based device. The related PV performance enhancement mechanism and surface-plasmon resonances in DSSCs with Ag nanostructures are discussed.

Key Words: Silver nanoparticles, DSSCs, silar cycles, surface plasmon, PV performance

Introduction

The dye-sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity, based on the sensitization of wide bandgap semiconductors. The performance of the cell mainly depends on a dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO₂ are important parameters determining the efficiency of the cell. However, dye sensitized solar cells DSSCs emerged as a new class of low cost energy conversion devices with simple manufacturing procedures, environmentally friendly, and the light-weight thin-film structures are compatible with automated manufacturing [1]. Dye-sensitized solar cells suffer from durability problems that result from their use of organic liquid electrolytes containing the iodide/tri-iodide redox couple, which causes serious problems such as electrode corrosion and electrolyte leakage. Consequently, it adversely affects long-term performance and durability. The efficiency of DSSC system can be increased by incorporating

metal nanoparticles NPs that can provide plasmonic enhancement. In surface plasmon resonance, the collective oscillation 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.

The first experiments on Plasmon enhanced photovoltaics were in fact performed on organic and dye solar cells. As early as 1991 Hayashi *et al.* [2] observed an improved efficiency of an organic solar cell when propagating surface plasmons were excited in a metal contact of the cell. The influence of a *localized* Plasmon excitation in metal clusters on performance of an organic solar cell was reported by Stenzel *et al.* [3]. In their experiments, Cu metal clusters outperformed Ag and Au particles. The enhancement was attributed to the intensified near-field around the particles. Recently, many efforts have been devoted to increasing the light harvesting efficiency by introducing plasmonic structures into various solar cells. Tzu-ming *et.,al* observed a 45% enhancement in the power conversion efficiency over a broad wavelength range with the inclusion of plasmonic gold nanoparticles (NPs) [4]. Won yeop rho *et.,al* fabricated a dye sensitized solar cells with Ag nanoparticle (NP)-embedded TiO₂ nanotube arrays by using UV irradiation. The energy conversion efficiency was increased from 4.64% to 6.14% by the Ag functionalization, a 32% enhancement, which is attributed to the surface Plasmon resonances present along the entire length of the TiO₂ nanotube arrays [5]. Furthermore, the Ag NPs more effectively enhanced the energy conversion efficiencies in front-illuminated DSSCs than in back-illuminated ones. Derkacs *et.,al* [6] reported that an engineered enhancement in short-circuit current density and energy conversion efficiency in amorphous silicon solar cells is achieved via improved transmission of electromagnetic radiation arising from forward scattering by surface plasmonpolariton modes in Au-nanoparticles deposited above the amorphous silicon film. The addition of Ag NPs into the active layer significantly enhances carrier mobility but decreases the total extracted carrier which lead to improved photovoltaic parameters [7]. Bartosz *et.,al* [8], reported an improved performance in photovoltaic polymer solar cells by increasing the amount of Ag in TiO₂ (by 3, 5, 7, and 10%). Higher PV performance was received by introducing TiO₂ with 5% of Ag. Also Iwan *et.,al* [9] investigated the influence of amount of silver in a hole transporting layer on the performance of a bulk heterojunction polymer solar cells. They obtained a power conversion efficiency (PCE) of 2.16% under 100mAc^{m-2} light intensity with 60 μL of Ag-NPs. But along with the increase amount of Ag-NPs from 60 to 150 μL, the PCE decrease was found.

In this study, Ag-NPs with different SILAR cycles were synthesized on porous TiO₂ films fabricated on fluorine-doped SnO₂ (FTO) substrates. The size effects of Ag NPs on the PV performance of the formed DSSCs were investigated systematically. The performance characteristics of the plasmonic DSSCs were analysed. An overall conversion efficiency of 0.00910% was obtained when the size of Ag-NPs was around 16 nm, which had a 36% improvement over the performance (0.00669%) of bare FTO based device. The related PV performance enhancement mechanisms and surface-plasmon resonances in DSSCs with Ag nanostructures are analysed and discussed.

Experimental Section

2. 1 Synthesis of nanocomposite material for profiling

We used dip coating method to synthesize the Ag nanocomposite on the glass substrate. The microscope slide was cleaned with laury sulphate and then rinsed with water 3 times. Thereafter dipped into a beaker containing a mixture of 2mol concentrated tetraoxosulphate (iv) acid (H_2SO_4) and 2mol chromic acid to make the surface hydrophilic for 10mins, the sample was thereafter rinsed with water. After making it hydrophilic, it was immersed in 2mol SnCl_2 for 2mins then rinsed with distilled water for 2mins, then immersed at 0.35m silver nitrate (AgNO_3) for 2mins and rinsed with mixture of 5mol distilled water (H_2O) and 5mol hydrochloric acid (HCl) for 15secs. This procedure is called one cycle; the number of cycles were varied upto 3 cycles to obtain the thickness of the silver deposited.

2.2 Fabrication process

The FTO electrodes were washed with laury sulphate then later rinsed with water six times in an ultrasonication bath for 10mins then finally washed in propanol. The photoanode was prepared by first depositing a blocking layer on the FTO glass, followed by the nanocrystalline TiO_2 . The blocking layer was deposited from a 2.5wt% TiO_2 precursor and was applied to the FTO glass substrate by spin coating and subsequently sintered at 500°C for 45mins. The 9um thick nanocrystalline TiO_2 layer was deposited by screen printing. It was then sintered in air for 30mins at 500°C . The silver was deposited on the bare surface of the TiO_2 with different cycle through successive ion layer adsorption and reaction (SILAR). We used the SILAR because it allows us to control the thickness of the film by varying the number of cycles. We spin coat TiCl_4 (40mmoles) at 2000rpm and thereafter anneal at 300°C to 350°C for 30mins. To ensure the silver is protected, we treated it with 40mmoles solution of TiCl_4 prepared at 40°C , then raise the temperature to 70°C and finally annealed at 300°C to 350°C . SiO_2 was deposited on the Ag using SILAR method with sodium silicate ($\text{Na}_2\text{O}(\text{SiO}_3)$) as the precursor. The minimum number of cycles that gave the cells stability was five cycles. The first cell with one Ag cycle had five cycles of SiO_2 , the second cell with two Ag cycles had ten cycles of SiO_2 and the third cell with three Ag cycles had fifteen cycles of SiO_2 .

The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at 100°C and fired at 450°C for 30mins. The method of heating in water ($Aq.$) was used to extract the dye. Distilled water was the solvent for aqueous extraction. 5 g of the sample was measured using the analytical scale (OHAUS Corporation-USA) and dipped in 50 ml of the solvent heated to 100°C for 30minutes after which solid residues were filtered out to obtain clear dye solutions. Roselle extract is rich in anthocyanins. It was reported that anthocyanin obtained from roselle are delphinidin and cyanidin complexes [10,11] The chemical structure of cyanidin and delphinidin in the hibiscus sabdariffa dye is shown in figure 4a

The sintered photo anode with different SILAR cycles were sensitized by immersion in the sensitizer solution at room temperature overnight. Sensitization was achieved by immersing the photoanode in the extracts. The cells were assembled by pressing the photoanode against the platinum-coated counter electrode slightly offset to each other to enable electrical connection to the conductive side of the electrodes (fig 1). Between the electrodes, a $50\mu\text{m}$ 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°C for 1min. the liquid electrolyte constituted by 50mmol of iodide/tri-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 with an epoxy based two part resin.

Characterization

The current-voltage (I-V) data was obtained using a Keithley 2400 source meter under AM1.5 (100 mW/cm²) illumination from a Newport A solar simulator. Scanning electron micrographs of the nanocrystalline TiO₂ films are taken with Carl Zeiss SEM. The absorption spectrum of the dye was recorded on Ava-spec-2048 spectrophotometer. The cell active area was 1.8 cm². Thickness measurement was obtained with a Dektac 150 surface profiler. Sheet resistance was obtained with a Signatone four point probe resistivity apparatus.

Results and Discussion

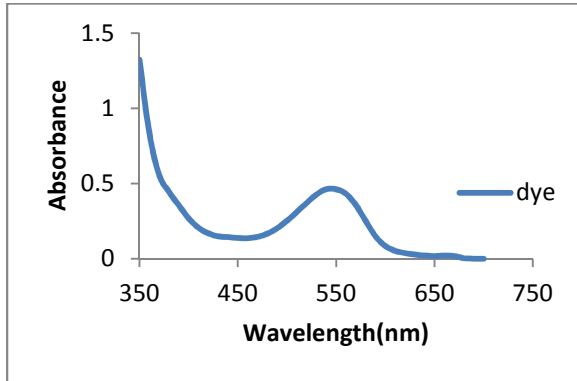


Figure 1a. UV-vis spectra of the dye

Figure 1 showed the absorbance of the dye and various prepared Ag-NPs suspensions with and without the dye within the wavelength range of 350–1000 nm along with the size growth of the Ag particle from 16 to 48 nm which correspond to the number of cycles. The absorption peak of hibiscus dye was observed around 550 nm (indicated in Fig. 1a), and the optical absorption enhancement was observed in the dye-loaded plasmonic nanocomposite films. The relative changes in optical absorption of the Ag-NPs suspension films are shown in Fig. 1b. The relatively broad and strong enhancement is observed in the range of 380–650 nm with a maximum enhancement around 550 nm, which coincides with the localized surface plasmon resonance (LSPR) band position of decorated Ag-NPs (Fig. 1c). This enhanced absorption and broadened spectrum absorption range of the photoanodes were mainly attributed to the SPR of Ag-NPs, which interacted with the dye, enhancing dye absorption that resulted in more charge carrier generation [12]. These features suggest that dye molecules in the vicinity of Ag-NPs can absorb more photons, presumably due to the intensified near-field effect of the surface plasmon and spectral overlap between the dye and surface plasmon, which may eventually lead to an increase in the number of charge carriers and J_{sc} values.

Figure 2 showed SEM images of differently sized Ag-NPs deposited on the FTO surface using SILAR method.

The particle size is around 16 nm, 32 nm and 48 nm as shown in figures 2(a), (b) and (c), respectively. Figure 3 showed the photocurrent density–voltage ($J-V$) curves of the DSSCs with varying silar cycles 0, 1, 2, 3 cycles. Based on the curves in Fig. 3, the fill factor (FF) and solar cell efficiency (η) were determined following the equations:

$$FF = \frac{P_{max}}{P_{in}} = \frac{J_{max} V_{max}}{J_{sc} V_{oc}}, \quad \eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{IRRADIANCE}} \cdot 100\%$$

Where V_{max} = maximum voltage (V); J_{max} = maximum current (mA/cm²); J_{sc} = short current (mA/cm²); V_{oc} = open circuit voltage (V) and $P_{IRRADIANCE}$ = light intensity (mW/cm²)

The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and overall conversion efficiency (η) are summarized in Table 1. The performance of DSSCs fabricated with anodes deposited on bare FTO substrates was provided for comparison in the table 1.

As can be seen from table 1, the performance, especially the photocurrent, and open circuit voltage of DSSCs containing Ag-NPs was significantly affected by the particle size of Ag-NPs. The PV performance decreased with increasing size of Ag-NPs from one silar cycle to three silar cycles, from table 1, the best performance was achieved using the anodes prepared with one silar cycle. The best cell showed a short-circuit current density (J_{sc}) of 0.0385mAcm⁻², open-circuit voltage (V_{oc}) of 0.45V and fill factor (FF) of 0.526%, yielding the highest efficiency (η) of 0.00910%. The cell exhibited a 36% improvement over the performance (0.00669%) of bare FTO-based device. 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.

From figure 3, the overall conversion efficiency of a DSSC is improved when Ag particles are added. Compared with pure TiO₂ films, the mixed films containing Ag particles exhibit an increase in the power conversion efficiency from 6.12% to 36%. It was once reported that DSSCs based on anodes containing Ag particles with 0.05-0.15wt% content exhibit an increase in the power conversion efficiency from 11.6% to 34.6% [12]. Better results were obtained using our proposed method. As shown in Fig. 3 and Table 1, the overall conversion efficiency was remarkably improved when plasmonic nano structures were included, which was caused by the increase in J_{sc} . Compared with the reference cell employing nc-TiO₂ as the photoanode.

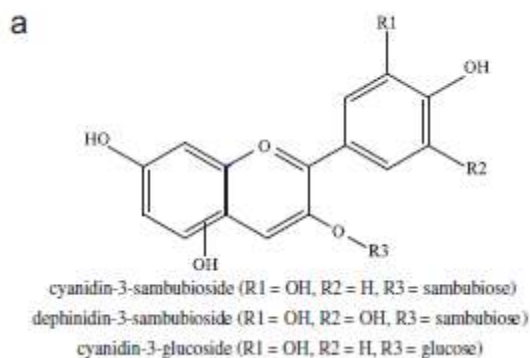


Figure 4a. Chemical structures of: (a) cyanidin and delphinidin in rosella dye

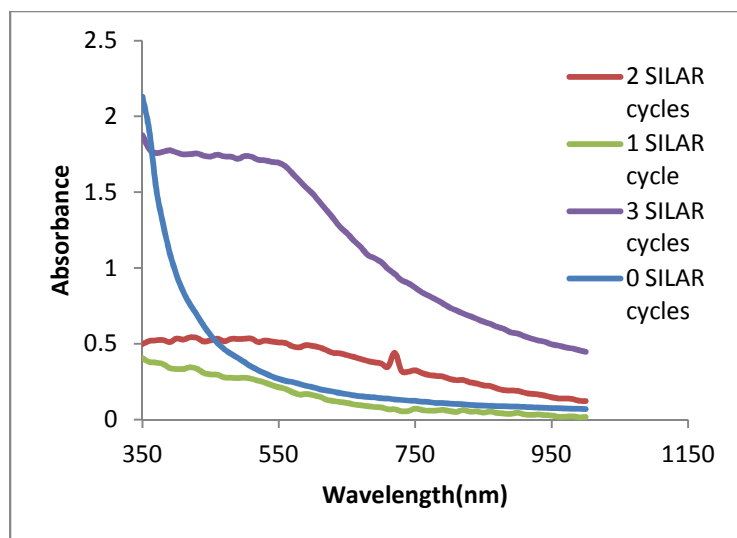


Figure 1b. U-V vis spectra of various prepared Ag NPs suspensions without dye.

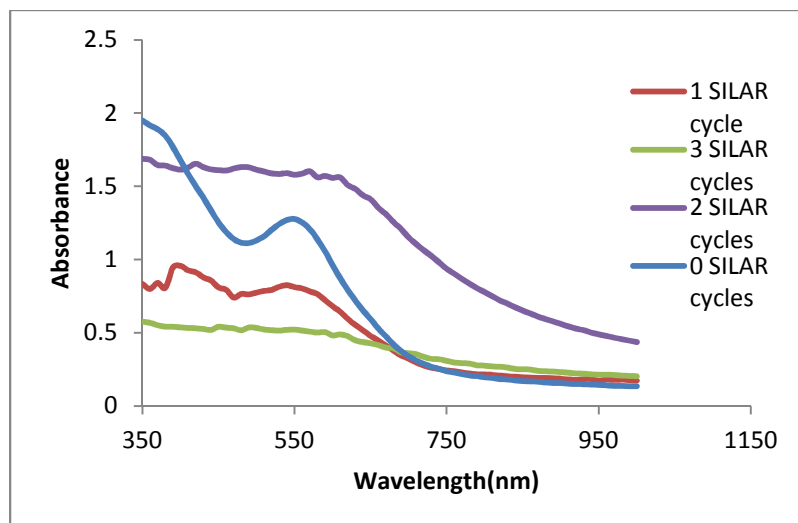


Figure 1c. U-V vis spectra of various prepared Ag NPs suspensions with dye

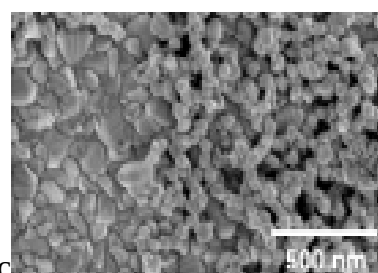
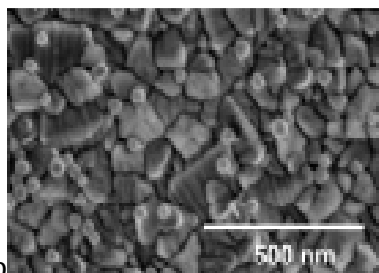
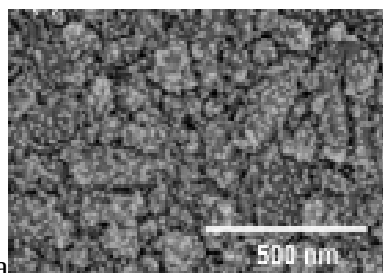


Figure 2. SEM images of (a) one SILAR cycle, (b) two SILAR cycles and (c) three cycles

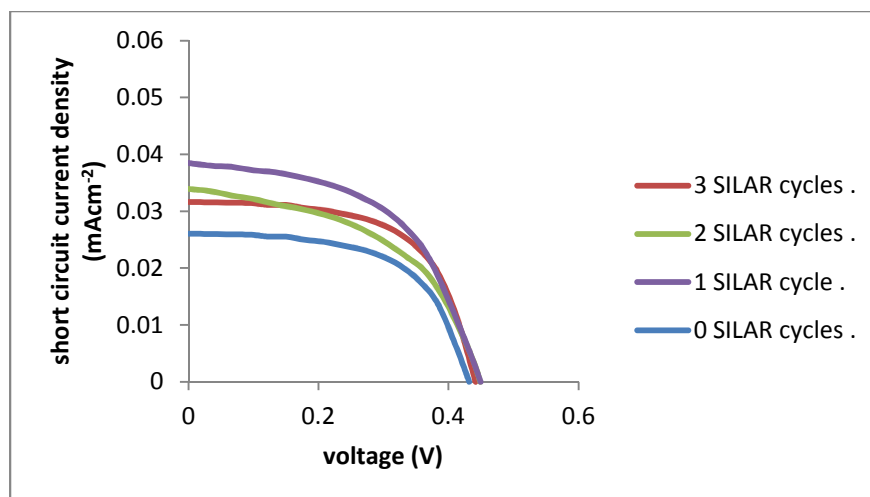


Figure 3. The photocurrent density–voltage ($J - V$) curves with varying silar cycles

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

Sample	$J_{sc}(\text{mAcm}^{-2})$	$V_{oc}(\text{V})$	FF	$\eta(\%)$
FTO/TiO ₂	0.0259	0.432	0.594	0.00669 ± 0.01
FTO/TiO ₂ /AgNPs(16nm)	0.0385	0.450	0.526	0.00910 ± 0.02
FTO/TiO ₂ /AgNPs(32nm)	0.0339	0.449	0.488	0.00743 ± 0.01
FTO/TiO ₂ /AgNPs(48nm)	0.0316	0.442	0.507	0.00708 ± 0.01

As well known, silver has long been regarded as being catalytically active. However, Ag-NPs dispersed on metal-oxide supports are active catalysts for a variety of chemical reactions. It has been demonstrated that the unique catalytic activity strongly depends on the type of metal-oxide support, the preparation method, and particularly the size of the Ag clusters.

In our work, when Ag-NP was small, the catalytic effect of Ag-NPs sited on TiO₂ support could increase the reaction rate between the TiO₂/dye and the redox electrolyte in DSSCs, thereby reducing the corresponding electron transport resistance. Conversely, as the silver size became larger, Ag-NPs easily aggregated and formed islands as shown in figure 2, which could not preferentially attach to specific sites on the TiO₂ surface, resulting in the decrease of catalytic activity.

In the conventional DSSCs, the dyes absorb incident light and generate electrons in excited states, which inject into the TiO₂ NPs. The oxidized dye molecules are regenerated by electrons transferred from iodide. The regenerative cycle is completed by reducing triiodide to iodide at the counter electrode. The electrons in TiO₂ diffuse to the current collector (FTO). In the plasmon-enhanced DSSCs using Ag-NPs, Ag-NPs were exposed to the electrolyte, resulting in slightly low V_{oc} which may imply that exposed AgNPs can act as recombination centres. In plasmonic solar cells, incorporated metal nanoparticles may have several roles: (i) to increase the light harvesting due to the strong near-field effects of LSPR; (ii) generation of hot electrons by surface plasmon excitation; (iii) to act as electron recombination sites, [13]. These factors can competitively have an impact on the device performance. The enhanced J_{sc} is related to the light harvesting capability of dye molecules by plasmon-enhanced excitation. Thus, the slight decrease in V_{oc} can be explained by the down-shifted Fermi level due to the plasmonic particles [14].

The J_{sc} and V_{oc} both decreased when the Ag-NPs content is above one silar cycle. The reason for this may be explained as follows: Not all of the Ag-NPs in photoanode were entirely coated by TiO₂ to form the mixed film. Therefore, some of the bare Ag-NPs in the Ag-TiO₂ network structure may be eroded by electrolyte and oxidized to Ag⁺ ions [15]. The latter act as a recombination center, reducing the number of charge carrier, thus resulting in a decrease in J_{sc} and V_{oc} . In addition, as the number of silar cycles increased the mixed films might result in blockage of sunlight which would prevent the incident light from reaching the TiO₂ NPs, resulting in the decrease in the photocurrent density. The combined effects of these factors resulted in the dependence of the performance of the plasmonic DSC on the Ag particle size. Hae-Jin Kim and Dae-Eun Kim once reported that the decrease in efficiency due to increasing surface roughness was found to be proportional to the light transmittance [16]. As a consequence, the recombination probability between electrons and holes may increase, so J_{sc} would decrease. In addition, higher concentrations of Ag-NPs may cluster to form larger Ag-NP groups with lower electron storage capability, reducing V_{oc} [17].

Conclusions

A series of TiO₂ photoanodes with differing amounts of AgNPs were investigated. Ag NPs with different sizes were grown on the TiO₂ deposited on the FTO through successive ion layer adsorption and reaction. The performance of the DSSC highly depended on the Ag particle size. The J_{sc} , V_{oc} and η decreased with increasing silar cycles. The results showed that adding Ag-NPs to TiO₂ photoanodes significantly improved the performance of the DSSCs by increasing short-circuit current and open-circuit voltage. The best performing DSSC contained one silar

cycle of Ag-NPs, The plasmonic DSSC based on hibiscus sabdariffa dye gave a short-circuit current density (J_{sc}) of $0.0385 \text{ mA cm}^{-2}$, open-circuit voltage (V_{oc}) of 0.45V and fill factor (FF) of 0.526%, yielding the highest efficiency (η) of 0.00910%. The cell exhibited a 36% improvement over the performance (0.00669%) of bare FTO-based device lacking Ag. The increase of J_{sc} is attributed to the enhanced light absorption and broadened absorption spectral range of the composite photoanode due to the SPR of the Ag-NPs, While the V_{oc} increase may be reasonably related to the more negative quasi-Fermi energy of the Ag-TiO₂ composite system due to the enhanced electron capture and storage capability resulting from Ag-NP doping [10](Kaimo et.,al 2012).

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