Silver Nanoparticles as Artificial Antennas for Enhanced Light-Harvesting and Charge Transfer in Dye-Sensitized Solar Cells

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Abstract: We present an investigation on introducing core-shell Ag@SiO₂ nanoparticles (NPs) into dye-sensitized solar cells. Ag@SiO₂ present the chemical stability to iodide/triiodide electrolyte, and help to localize most of dye molecules around plasmonic silver nanoparticles (AgNPs), hence increasing the optical absorption consequently the overall conversion efficiency of the device. Deployment of the silver-modified assembly as a photo anode in dye-sensitized solar cells leads to solar-to-electrical energy conversion with an overall efficiency of 0.0088% for Ag-TiO₂ photo anode and 0.0176% for Ag@SiO₂-TiO₂ photo anode. This represents a 100.7% improvement over the performance of otherwise identical solar cell lacking corrosion-protected silver nanoparticles. The improvement is manifested chiefly as an increase in photocurrent density due to enhanced light harvesting by the AgNPs. The results revealed that, the performance of DSSCs could be well improved through enhancing the light absorption by local surface plasmon (LSP) effect from Ag@SiO₂ NPs by electronically and chemically protecting the metal from recombination and corrosion. The mechanism of getting the best utilization efficiency of LSP enhanced optical field is also investigated.

Keywords: Silver Nanoparticles, DSSCs, TiO₂, SILAR, Surface Plasmon, Ag@SiO₂, Natural Pigment

1. Introduction

Solar Energy is seen as a remedy to the energy crises and environmental challenges facing the world today. This technology allows the direct conversion of photons into electrical power without resulting to both greenhouse gases and other polluting agents. The solar cell technology is categorized into three generations.

A new low cost solar cell was first reported in 1991, by Grätzel which was achieved by the successful combination of nanostructured electrode and efficient dye known as Dye-Sensitized Solar Cell (DSSC) which falls under the third generation photovoltaic cells [1].

Natural dyes as photosensitizers for DSSCs are very

attractive because they are of low cost, abundant in supply, and sustainable [2-6].

However, the efficiency of DSSC with natural pigments is still by a factor of 3–4 lower than with synthetic dyes [7]. But natural pigments are normally non-poisonous, can be disposed easily, and should be cheaper and more environmentally friendly than synthetic metal complexes which make them advantageous [7].

Several dye pigments from plant sources have been studied among the most exploited include: chlorophylls, anthocyanins and betalains [8].

As compared to the anthocyanins, which has the functional groups (-OH), betalains have the functional group (-COOH) which stand out to bind better to the nanoporous semiconductor surface [9-11]. The general structure of

betalain is shown in Figure 1. [8].

Figure 1. General structure of Betalain [8]

It is characterized by the presence of carboxylic functional group which allows short distance between the dye skeleton and the point connected to TiO₂ surface, and calls for good bond formation between the TiO₂ and the extract, thus enhancing the binding interaction between the pigment and the TiO₂ film, which brings about good electronic coupling and electron transfer reaction in the visible spectrum [2, 4, 8].

Introduction of metallic nanoparticles (NPs) in suitable places to trap or confine light inside the active layer and enhance the absorption in the organic semiconductor film could result to enhanced performances [12–30]. A major critical issue in plasmonic DSSCs is the stability of the NPs [31]. When introduced, metal NPs makes direct contact with the iodide/triiodide-based liquid electrolyte, some problems arise, such as recombination, back reaction of the excited electrons, and corrosion of NPs. Core shell have recently been applied to address these issues [31].

In enhancing the device performance and stability of DSSC, a lot of research efforts have been demonstrated on manipulating the corresponding architecture involving inorganic and organic systems as well as various interfaces so as to enhance the cell performance [32–35].

Metal NPs embedded in sensitive places strongly interact with light at their dipole surface plasmon resonance due to the excitation of a collective electron motion inside the metal particle [36]. The surface brings about good confinement of the conduction electrons inside the particle and creates an effective restoring force leading to Surface Plasmon Resonance (SPR) effect [37]. Among the metals that demonstrates SPR modes, noble metals (Au, Ag, Cu) exhibit resonances in the visible or near infrared region of the electromagnetic spectrum, which is the wavelength of interest for photovoltaic applications [37].

In this research work, we report the results of a study that demonstrates a positive effect that arise from the use of silver nanoparticles as sub-wavelength antenna in DSSCs.

AgNPs successive ionic layer adsorption and reaction

(SILAR) cycle was obtained, and the uniformly coated insulated SiO₂ layer effectively reduced the chemical attack of liquid iodide/triiodide electrolyte on AgNPs surface.

From our research work, it was shown that, by introducing Ag@SiO₂ NPs, the power conversion efficiency of DSSC is enhanced 433.3% from 0.0033% to 0.0176%. The related photovoltaic (PV) metrics enhancement mechanism and surface-plasmon resonances in DSSCs with Ag and Ag@SiO₂ nanostructures are presented systematically.

2. Materials and Methods

2.1. Materials

Acetonitrile, Platisol, propylene carbonate, acetaldehyde, and Triton-X 100 were purchased from BDH chemicals. Silver nitrate (AgNO₃), 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 Ω/m², P25 TiO₂ powder and SiO₂ were obtained from Alfa Aesar.

2.2. Synthesis of Nanocomposite Material for Profiling

Dip coating method was used to synthesize the silver nanoparticles on the glass slide following the method previously demonstrated by Eli et.al [29].

2.3. Preparation of the Natural Dye

The natural dye was extracted with deionized water employing the following procedure: fresh flowers of *Bougainvillea spectabilis* were washed and air dried. 50 g of the sample (*Bougainvillea spectabilis*) was grinded to small particles using a blender with 100 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 [6].

2.4. Preparation of TiO₂ Paste

The TiO₂ films was prepared using a modified sol–gel method, in which 2 g of P25 TiO₂ 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 [2].

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 [38].

TiO₂ were deposited on the FTO conductive glass by screen printing technique in order to obtain a TiO₂ with a thickness of 9 μm and an active area of 1.80 cm². The TiO₂ film was preheated at 200°C for 10 min and then sintered at 500°C for 30 min.

The second photo anode was prepared by depositing one SILAR cycle of AgNPs through successive ionic layer adsorption and reaction on the pre-deposited TiO₂ film.

The third photo anode was prepared by depositing five SILAR cycles of SiO_2 on the already AgNPs modified electrode. The electrodes were immersed on the water extract of the *Bougainvillea spectabilis* pigment for 10-12 hours [38].

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°C and annealed at 400°C for 30 min [6].

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 I_2 . Therefore, the open side of the assembled cell were sealed properly with epoxy resin gum.

2.8. Characterization and Measurement

The current density-voltage (J - V) characteristics of the cells were recorded using a setup made up of 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 Phenom Pro X model, Eindhoven de Netherlands operated at an acceleration voltage of 10 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. Scanning Electron Microscopy (SEM)

Fig. 2 shows the SEM images of (a) TiO_2 , (b) TiO_2 -AgNPs and (c) TiO_2 -AgNPs@ SiO_2 fabricated using screen printing and SILAR procedure. Fig. 2a is the reference electrode that shows the presence of TiO_2 without AgNPs inclusion, Fig. 2b confirms the introduction of one SILAR cycle of AgNPs in the mesoporous TiO_2 layer and Fig. 2c demonstrates the presence of AgNPs with one SILAR cycle protected with five SILAR cycles of SiO_2 NPs. The surface morphology of the films appears not to be the same which can be attributed to the presence of AgNPs and AgNPs@ SiO_2 . From Fig. 2a, the image of the pure TiO_2 film shows a dense surface, and there are no shining particles observed as compared to what is noticed in Fig. 2b and c. the shining surface is indicative that AgNPs has the ability to scatter incident light to increase light absorption surface area.

Figure 2. SEM images of (a) TiO_2 , (b) TiO_2 -AgNPs and (c) TiO_2 -AgNPs@ SiO_2 .

3.2. Absorption Spectra

Figure 3 shows the absorbance of the natural dye within the wavelength range of 400-700 nm. The pigment is observed to have three peaks at 410 nm, 460 nm and 660 nm which ascertain the presence of betalain pigment [39]. The absorption at the visible region is indicative that this natural extract meets the requirement for its use as light harvesting pigment in this research. Fig. 4 represents the absorption spectra of the TiO_2 without dye within the wavelength range of 350-1000 nm. As depicted in the figure, TiO_2 has poor absorbance in the absence of dye pigment. Fig. 5 and 6 represents various prepared AgNPs suspensions with and without corrosion protection with and without dye pigment within the wavelength range of 400-1000 nm which shows the AgNPs size around 16 nm

which corresponds to one SILAR cycle (Fig 7). The optical absorption enhancement was observed in the dye-loaded plasmonic nanocomposite films. The relative changes in optical absorption of the AgNPs suspension films are shown in Fig. 6. This enhanced absorption and broadened spectrum absorption range of the photo anodes were mainly attributed to the SPR of AgNPs, which interacted with the dye, enhancing dye absorption that resulted in more charge carrier generation [30]. These features suggest that dye molecules in the vicinity of AgNPs 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 [25].

Figure 3. Absorption spectra of pure water extract dye.

Figure 4. UV-Vis spectra of TiO_2 without dye.

Figure 5. UV-Vis spectra of $\text{TiO}_2/\text{AgNPs}$ and $\text{TiO}_2/\text{AgNPs}@ \text{SiO}_2$ without dye extract.

Figure 6. UV-Vis spectra of TiO_2 , $\text{TiO}_2/\text{AgNPs}$ and $\text{TiO}_2/\text{AgNPs}@/\text{SiO}_2$ with dye extract.

3.3. Photoelectrochemical Properties of DSSCs

Figure 8 shows the photocurrent density-voltage characteristics (J - V) curves of DSSCs with AgNPs, Ag@SiO₂ NPs and TiO₂-only. Since the three DSSCs function as junction solar cells therefore, their performance parameters can be obtained from the J - V curve following equations (1) and (2) respectively [2]:

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

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

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

η = solar cell efficiency

$V_{\max}$ = 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)

As demonstrated in Table 1, it is observed that the plasmon-enhanced DSSC without SiO₂ protection exhibits a power conversion efficiency (PCE) up to 0.0088%, which is increased by about 166.7% compared with 0.0033% of TiO₂-only DSSC, while the plasmon-enhanced DSSC with SiO₂ protection exhibits a PCE up to 0.0176%, which is increased by about 433.3% compared with 0.0033% of TiO₂-reference DSSC. In Fig. 8, the open-circuit voltage (V_{OC}) of plasmon-enhanced DSSCs and TiO₂-only DSSC are almost the same, while the short-circuit current density (J_{SC}) significantly increased by introducing Ag@SiO₂ NPs. The improvement of J_{SC} in the plasmon enhanced DSSCs was mainly caused by the increase of photocurrent due to the enhanced light absorption of dye with the help of localized surface plasmons

(LSPs) [23-25, 29-31].

Using Ag-TiO₂, Ag@SiO₂-TiO₂ and TiO₂ nanostructured photo anodes, photocurrent-voltage performance parameters were summarized in Table 1.

Table 1. Photovoltaic performance of DSSCs with TiO₂, TiO₂-AgNPs and TiO₂-Ag@SiO₂ photo anode under $100 \text{ mW}/\text{cm}^2$.

Photo anode	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
TiO ₂	0.015	0.571	0.400	0.0033
TiO ₂ -AgNPs	0.028	0.542	0.588	0.0088
TiO ₂ -AgNPs@SiO ₂	0.055	0.571	0.557	0.0176

The reference Solar cell exhibits a short-circuit photocurrent density (J_{SC}) of $0.015 \text{ mA}/\text{cm}^2$ and an open-circuit voltage (V_{OC}) of 0.571 V. On the other hand, the solar cell with AgNPs inclusion present photovoltaic performances with J_{SC} and V_{OC} values of $0.027 \text{ mA}/\text{cm}^2$ and 0.542 V. The DSSC with 5 SILAR cycles of SiO₂ on the Ag-TiO₂ photo anode gave J_{sc} and V_{oc} of $0.055 \text{ mA}/\text{cm}^2$ and 0.570 V. As it can be seen from Figure 3, the J_{SC} of all DSSCs with AgNPs increased with inclusion of the plasmonic nanoparticles but more pronounced in the case were the Ag@SiO₂ was coated on TiO₂. From the curves, it is clear that while the open-circuit voltage of the cell with TiO₂ only is similar to the cell containing TiO₂-Ag@SiO₂ photo anode, the short-circuit photocurrent density (J_{SC}) with TiO₂-Ag@SiO₂ electrode ($0.055 \text{ mA}/\text{cm}^2$) is 3.8 times higher than with TiO₂ only ($0.015 \text{ mA}/\text{cm}^2$).

The J_{SC} and η increase, demonstrates that SiO₂ nanoparticles layer may protect the Ag nanoparticles from the chemical attack by iodide/triiodide electrolytes, which will subsequently allow regeneration by the electrolyte and decrease the recombination reaction.

As shown in Figure 8, under the same Ag deposition cycles, the cell with SiO₂ capping layer presents both increased J_{SC} and V_{OC} , indicating that SiO₂ is indispensable to highly efficient dye sensitized solar cells. With the appearance of SiO₂ layer, J_{SC} of the cell with Ag SILAR cycle was improved from about $0.015 \text{ mA}/\text{cm}^2$ to $0.055 \text{ mA}/\text{cm}^2$. The cell efficiency reached a promising 0.0176%,

indicating a 2.67 times increase over the Ag-TiO₂ solar cell and a 5.33 times over the bare TiO₂ solar cell. In addition to the increase of the cell performance for the Ag@SiO₂ configurations, a significant increase of the photochemical stability of AgNPs takes place with the presence of the SiO₂ coating.

In our present work, the cell efficiency was still not high enough for practical application. The drawback limiting the energy conversion efficiency of this type of solar cells was

the rather poor fill factor. This low fill factor may be ascribed to the lower hole-recovery rate of the iodide/triiodide electrolyte, leading to a higher probability for charge recombination [31].

Better results could be obtained by introducing core-shell that will present not only the chemical stability to iodide/triiodide electrolyte, but also the adhesiveness to dye molecules.

Figure 7. Surface Roughness of deposited silver nanoparticles

Figure 8. Photocurrent density–voltage (J – V) curves of DSSCs with different photo anodes.

4. Conclusion

Surface plasmon resonance effects of silver nanoparticles protected with SiO₂ was demonstrated in dye sensitized solar cells. The power conversion efficiency and the current density, based on the betalain pigment were enhanced. We obtained a power conversion efficiency enhancement of 433.3% (i.e increases in η from ~0.0033% to 0.0176%) with incorporation of Ag@SiO₂ NPs, and a PCE improvement of 166.7% (i.e increases in η from ~0.0033% to 0.0088%) with incorporation of AgNPs lacking protection. Part of the enhancement can be attributed to increased dye loading by the photo anodes following silver incorporation, with the remaining improvement coming from LSPR enhancement of the effective absorption cross section of the dye pigment.

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