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 emerged as possible solution to confront the major environmental problems that result from uncontrolled use of fossil resource in energy generation. This technology permits a direct conversion of sunlight into electrical power without exhaust of both greenhouse gases and other polluting agents.

In 1991, Professor Grätzel reported a new low cost chemical solar cell by the successful combination of nanostructured electrode and efficient charge injecting dye, known as Grätzel cell or dye-sensitized solar cell 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].

Conversely to the anthocyanins, that present functional groups (-OH), betalains have the requisite functional groups (-COOH) to bind better to the TiO₂ surface [9-11], than the functional group (-OH) present in the anthocyanins. The
general structure of betalain is shown in Figure 1. [8].

![Figure 1. General structure of Betalain.](image)

It is characterized by the presence of carboxylic functional group which allows short distance between the dye skeleton and the point connected to TiO$_2$ surface, and calls for good bond formation between the TiO$_2$ and the extract, thus enhancing the binding interaction between the pigment and the TiO$_2$ 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 provide superior performances [12–30]. One of the important issues in plasmonic DSSCs is the stability of the NPs [31]. When introduced, metal NPs makes direct contact with the iodide/triiodide-based liquid electrolyte, several 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 optimizing the device performance and stability of DSSC, several research efforts have been expended 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 a dielectric matrix strongly interact with light at their dipole surface plasmon frequency due to the excitation of a collective electron motion inside the metal particle [36]. The surface confines the conduction electrons inside the particle and sets up an effective restoring force leading to resonant behavior at the dipole surface plasmon frequency, namely Surface Plasmon Resonance (SPR) [37]. Among the metals that support SPR modes, noble metals (Au, Ag, Cu) exhibit resonances in the visible or near infrared region of the electromagnetic spectrum, which is the range of interest for photovoltaic applications [37].

Herein we report the results of a study that demonstrates a positive effect that arise from the use of silver nanoparticles as antenna in dye sensitized solar cells.

Optimized AgNPs successive ionic layer adsorption and reaction (SILAR) cycle was obtained, and the uniformly coated SiO$_2$ layer effectively minimized the chemical attack of iodide/triiodide electrolyte on AgNPs layer. Therefore, the performance of dye sensitized solar cells was stabilized and long lasting.

Our research demonstrates that, by introducing Ag@SiO$_2$ NPs, the power conversion efficiency of dye-sensitized solar cell is enhanced 433.3% from 0.0033% to 0.0176%. The related PV performance enhancement mechanism and surface-plasmon resonances in DSSCs with Ag and Ag@SiO$_2$ nanostructures are discussed.

## 2. Materials and Methods

### 2.1. Materials

Acetonitrile, Platisol, propylene carbonate, acetaldehyde, and Triton-X 100 were purchased from BDH chemicals. Silver nitrate (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 $\Omega$ /m$^2$, P25 TiO$_2$ powder and SiO$_2$ 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, 30].

### 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 TiO$_2$ Paste

The TiO$_2$ films was prepared using a modified sol–gel method, in which 2 g of P25 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 [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].

TiO$_2$ were deposited on the FTO conductive glass by screen printing technique in order to obtain a TiO$_2$ with a thickness of 9 $\mu$m and an active area of 1.80 cm$^2$. The TiO$_2$ film was preheated at 200°C for 10 min and then sintered at 500°C for 30 min.
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 mL acetonitrile, 0.1 M propylene carbonate, 0.005 M LiI, 0.0005 M I₂. 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 comprising a xenon lamp, an AM 1.5 light filter, and a Electrochemical Analyzer (Keithley 2400 source meter) under an irradiance of 100 mW/cm². 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) TiO₂, (b) TiO₂-AgNPs and (c) TiO₂-AgNPs@SiO₂ fabricated using screen printing and SILAR procedure. Fig. 2a is the reference electrode that shows the presence of TiO₂ without AgNPs inclusion, Fig. 2b confirms the introduction of one SILAR cycle of AgNPs in the mesoporous TiO₂ layer and Fig. 2c demonstrates the presence of AgNPs with one SILAR cycle protected with five SILAR cycles of SiO₂ NPs. The surface morphology of the films appears not to be the same which can be attributed to the presence of AgNPs and AgNPs@SiO₂. From Fig. 2a, the image of the pure TiO₂ 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) TiO₂, (b) TiO₂-AgNPs and (c) TiO₂-AgNPs@SiO₂](image)

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 TiO₂ without dye within the wavelength range of 350-1000 nm. As depicted in the figure, TiO₂ 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 Jsc 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 TiO$_2$/AgNPs and TiO$_2$/AgNPs@SiO$_2$ without dye extract.
3.3. Photoelectrochemical Properties of DSSCs

Figure 8 shows the photocurrent density-voltage characteristics ($J-V$) curves of DSSCs with AgNPs, Ag@SiO$_2$ NPs and TiO$_2$-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]:

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

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

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

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

$J_{\text{max}}$ = maximum current density (mA/cm$^2$);

$J_{\text{sc}}$ = short circuit current density (mA/cm$^2$);

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

$P_{\text{BRAD}}$ = light intensity (mW/cm$^2$)

As demonstrated in Table 1, it is observed that the plasmon-enhanced DSSC without SiO$_2$ protection exhibits a power conversion efficiency (PCE) up to 0.0088%, which is increased by about 166.7% compared with 0.0033% of TiO$_2$-only DSSC, while the plasmon-enhanced DSSC with SiO$_2$ protection exhibits a PCE up to 0.0176%, which is increased by about 433.3% compared with 0.0033% of TiO$_2$-reference DSSC. In Fig. 8, the open-circuit voltage ($V_{\text{oc}}$) of plasmon-enhanced DSSCs and TiO$_2$-only DSSC are almost the same, while the short-circuit current density ($J_{\text{sc}}$) significantly increased by introducing Ag@SiO$_2$ NPs. The improvement of $J_{\text{sc}}$ 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-TiO$_2$, Ag@SiO$_2$-TiO$_2$ and TiO$_2$ nanostructured photo anodes, photocurrent-voltage performance parameters were summarized in Table 1.

**Table 1. Photovoltaic performance of DSSCs with TiO$_2$, TiO$_2$-AgNPs and TiO$_2$-Ag@SiO$_2$ photo anode under 100 mWcm$^{-2}$.**

<table>
<thead>
<tr>
<th>Photo anode</th>
<th>$J_{\text{sc}}$ (mAcm$^{-2}$)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.015</td>
<td>0.571</td>
<td>0.400</td>
<td>0.0033</td>
</tr>
<tr>
<td>TiO$_2$-AgNPs</td>
<td>0.028</td>
<td>0.542</td>
<td>0.588</td>
<td>0.0088</td>
</tr>
<tr>
<td>TiO$_2$-AgNPs@SiO$_2$</td>
<td>0.055</td>
<td>0.571</td>
<td>0.557</td>
<td>0.0176</td>
</tr>
</tbody>
</table>

The reference Solar cell exhibits a short-circuit photocurrent density ($J_{\text{sc}}$) of 0.015 mAcm$^{-2}$ and an open-circuit voltage ($V_{\text{oc}}$) of 0.571 V. On the other hand, the solar cell with AgNPs inclusion present photovoltaic performances with $J_{\text{sc}}$ and $V_{\text{oc}}$ values of 0.027 mAcm$^{-2}$ and 0.542 V. The DSSC with 5 SILAR cycles of SiO$_2$ on the Ag-TiO$_2$ photo anode gave $J_{\text{sc}}$ and $V_{\text{oc}}$ of 0.055 mAcm$^{-2}$ and 0.570 V. As it can be seen from Figure 3, the $J_{\text{sc}}$ of all DSSCs with AgNPs increased with inclusion of the plasmonic nanoparticles but more pronounced in the case where the Ag@SiO$_2$ was coated on TiO$_2$. From the curves, it is clear that while the open-circuit voltage of the cell with TiO$_2$ only is similar to the cell containing TiO$_2$-Ag@SiO$_2$ photo anode, the short-circuit photocurrent density ($J_{\text{sc}}$) with TiO$_2$-Ag@SiO$_2$ electrode (0.055 mAcm$^{-2}$) is 3.8 times higher than with TiO$_2$ only (0.015 mAcm$^{-2}$).

The $J_{\text{sc}}$ and $\eta$ increase, demonstrates that SiO$_2$ 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 SiO$_2$ capping layer presents both increased $J_{\text{sc}}$ and $V_{\text{oc}}$, indicating that SiO$_2$ is indispensable to highly efficient dye sensitized solar cells. With the appearance of SiO$_2$ layer, $J_{\text{sc}}$ of the cell with Ag SILAR cycle was improved from about 0.015 mAcm$^{-2}$ to 0.055 mAcm$^{-2}$. The cell efficiency reached a promising 0.0176%, indicating a 2.67 times increase over the Ag-TiO$_2$ solar cell.
and a 5.33 times over the bare TiO$_2$ solar cell. In addition to the increase of the cell performance for the Ag@SiO$_2$ configurations, a significant increase of the photochemical stability of AgNPs takes place with the presence of the SiO$_2$ 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.

4. Conclusion

Localized surface plasmon resonance effects associated with spatially dispersed and protectively coated silver nanoparticles was demonstrated. The light-harvesting efficiency, the photocurrent density, and the overall solar-to-electrical energy conversion efficiency based on betalain pigment were improved. We obtained a power conversion efficiency enhancement of 433.3% (i.e increases in $\eta$ from $\sim0.0033\%$ to $0.0176\%$) with incorporation of Ag@SiO$_2$ NPs. and a PCE improvement of 166.7% (i.e increases in $\eta$ from $\sim0.0033\%$ 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.
Based on natural pigments and wide-bandgap nanostructured performance of dye-sensitized organic photovoltaic cells


