

Research Article

Interface Dependent Plasmon Induced Enhancement in Dye-Sensitized Solar Cells Using Gold Nanoparticles

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We report a study on plasmon-induced photoelectrochemistry from gold nanoparticles incorporated in dye-sensitized solar cells, assembled in two different configurations: $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ and $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$. Although the presence of the plasmonic material resulted in enhanced photocurrent and energy conversion efficiency, a decrease of fill factor was observed. Electrical modeling of the solar cells was performed and revealed a simultaneous decrease of parallel resistance and increase of series resistance, related to the presence of gold nanoparticles. The enhancement in photocurrent was related to a combination of strong plasmon-induced electric fields and light scattering, which overcome the loss in electrical properties. In addition, the overall increase in efficiency was found dependent on the interface where the plasmonic material is placed. The highest efficiency obtained from $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ was attributed to a larger density of photoexcited electrons allowed to be transferred towards conduction band of TiO_2 .

1. Introduction

Great advances in nanofabrication have allowed the study of well-organized nanostructure arrays, such as nanoholes and surface relief gratings, providing better comprehension and description of the plasmon propagation modes [1–8]. Nevertheless, metallic nanoparticles presenting well-controlled shape and small size distribution have been attracting increasing attention, due to simple and efficient synthetic approaches, which requires minimum apparatus [9, 10]. Metallic nanoparticles with diameter smaller than the incident wavelength, present localized surface plasmons resonance, which result from the interaction between the electrons in the nanoparticles and the incident electromagnetic field. Charge separation within the nanoparticle

leads to extraordinary optical properties related to improved absorption and light scattering [11]. The plasmon mode is well described by Mie's theory for isolated metallic nanoparticles; however, concerning nanoparticles in a film, the electromagnetic theory developed by Maxwell is more appropriate, once plasmons coupling between adjacent particles should be considered [12, 13]. In addition to the nature of surface plasmons, their effect on the surrounding media has been intensively studied [14–19]. Metallic nanostructures have been widely applied in photoluminescence [20], Raman spectroscopy [21, 22], sensing [23, 24], and, more recently, the development of photovoltaic devices with high photoconversion efficiency [25–28]. These applications are based on the modification of the optical density of states that store and/or route the electromagnetic energy in a given medium.

Pristine TiO_2 presents a large band gap, which is a limiting factor for the development of efficient DSSCs. In order to overcome this disadvantage, the semiconductor is sensitized to increase the wavelength range for light absorption. Aiming to improve dye sensitization, charge transfer, and mobility, several TiO_2 nanostructures have been studied [29–31]. Concerning efficient sensitization of a $10\ \mu\text{m}$ thick mesoporous film composed of TiO_2 nanoparticles with ca. 20 nm in diameter, the effective dye sensitizer layer can be estimated as only ca. 100 nm thick; therefore, the layer is not thick enough to allow high absorbance of the solar spectrum. One alternative to overcome this issue is by adding a light-scattering layer of TiO_2 nanoparticles, which improves light harvesting. However, this scattering layer makes the devices thicker and opaque. Another alternative is the use of plasmonic substrates, such as metallic nanoparticles, nanohole arrays in metal films, and surface relief gratings. These substrates promote light trapping in the photoactive layer, which has resulted in improved absorption and enhanced energy conversion efficiency [23, 32–35]. The contribution of plasmonic materials to the efficiency of solar cells results from a variety of competing effects [36]; for example, as the plasmons are a surface phenomenon, the distance between nanoparticles and surrounding medium strongly affects the interaction between plasmon field and medium. In addition, the propagation of the surface plasmon electromagnetic field, and therefore the damping energy from the oscillator, depends on the surrounding properties [37].

In order to investigate the effect of an external field provided by gold nanoparticles on the efficiency of DSSC, in this work we have studied two different configurations of the DSSC: (i) gold nanoparticles placed between the semiconductor and the sensitizer ($\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$) and (ii) gold nanoparticles placed on top of the sensitized semiconductor ($\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$).

2. Materials and Methods

2.1. Materials. Titanium (IV) isopropoxide 97%, gold (III) chloride hydrate, and hexachloroplatinic acid were purchased from Aldrich. Ethanol and HCl 37% were purchased from Merck. *cis*-Diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II), Meltonix, and fluorine-doped tin oxide (FTO, $15\ \Omega/\text{sq}$) glass were purchased from Solaronix.

2.2. Synthesis of Gold Nanoparticles and Deposition of Gold Nanoparticle Film. Gold colloidal nanoparticles were prepared according to previous methods reported in the literature [38]. $1\ \text{mmol}\cdot\text{L}^{-1}$ $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ aqueous solution (100 mL) was refluxed at 120°C under vigorous stirring. Next, 2.5 mL of sodium citrate solution ($10\ \text{mmol}\cdot\text{L}^{-1}$) was quickly added to the reaction vessel. Ultrapure water was used throughout the experiments. The gold nanoparticles film was obtained by drop-casting $10\ \mu\text{L}$ of concentrated gold nanoparticles solution on the substrates followed by drying at 50°C .

2.3. Synthesis of TiO_2 and Paste Preparation. The approach used to obtain TiO_2 nanoparticles is based on Graetzel

work [39]: 5.7 mL of acetic acid was added quickly to 15 mL of titanium isopropoxide under stirring at room temperature for 15 min. After that the modified precursor was quickly added to 72.5 mL of deionized water under vigorous stirring and a white precipitate was formed. This mixture was kept under constant stirring for one hour at room temperature to complete the hydrolysis reaction. At this point, 1.0 mL of nitric acid 63% was added, with stirring for 8 hours at 80°C . Lastly, 95 mL of water was added to the mixture to be autoclaved and heat at 230°C for 12 hours. Finally, all samples were rinsed with anhydrous ethanol. The samples were calcinated at 450°C during 30 minutes, in order to obtain the anatase phase of TiO_2 .

2.4. Optical and Morphological Characterization. The absorption spectra from the mesoporous TiO_2 film, dye-sensitized TiO_2 (TiO_2/Dye), gold nanoparticles solution, gold nanoparticles film (AuNP film), gold nanoparticles adsorbed between TiO_2 and dye ($\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$), and gold nanoparticles placed on the dye-sensitized TiO_2 ($\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$) were obtained in a Shimadzu UV-2450PC spectrophotometer. The spectra of the scattering films were obtained by reflectance mode. The morphological characterizations of TiO_2 and gold nanoparticles were obtained by transmission electron microscopy (TEM) Libra Zeiss 120 and Scanning Electron Microscopy (SEM) Philips CM300.

2.5. Dye-Sensitized Solar Cells Assembly. The procedure to obtain the TiO_2 paste can be found elsewhere [40]. The paste was screen-printed on a transparent conductive substrate (FTO), previously immersed in $40\ \text{mmol}\cdot\text{L}^{-1}$ TiCl_4 aqueous solution at 80°C for 30 minutes. Next, the substrate was heated on a hot plate at 125°C for 20 minutes, followed by heating to 500°C for sintering. After cooling down to 40°C , the substrates were immersed in the sensitizer solution. The counter electrodes were prepared by coating the FTO surface with $1\ \text{mmol}\cdot\text{L}^{-1}$ of hexachloroplatinic acid solution ($30\ \mu\text{L}$) and heating at 500°C . The mediator, responsible for the regeneration of the dye, was placed between the dye-sensitized photoanode and the counterelectrode. The solar cell was sealed by using a polymeric film of low melting temperature (Meltonix). For the devices containing gold nanoparticles, two different solar cells configurations were assembled where $10\ \mu\text{L}$ of 20% of gold nanoparticles (w/w) dispersion was drop-casted (i) on top of the TiO_2 mesoporous film ($\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$) and (ii) on top of the dye-sensitized TiO_2 ($\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$) as shown in Figure 1.

2.6. Characterization of the Solar Cells. Current density versus voltage curves was performed using a Keithley 2400 source measure unit. A Xenon lamp (300 W) with an AM 1.5 filter was used and the light intensity corresponding to $100\ \text{mW}\cdot\text{cm}^{-2}$ (1 sun) was calibrated with an optical power meter (Newport). Incident photon-to-current efficiency (IPCE) measurements were performed using the same apparatus, in addition to a cornerstone monochromator.

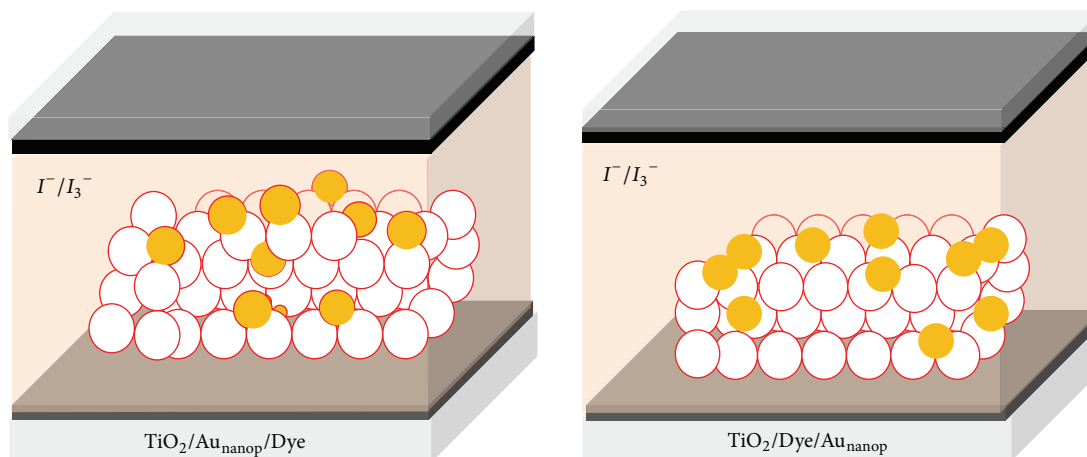


FIGURE 1: Schematic illustration showing the architecture of the devices: gold nanoparticles placed on top of the TiO_2 mesoporous film ($\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$) and gold nanoparticles placed on top of the dye-sensitized TiO_2 film ($\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$).

3. Results and Discussions

Figure 2 shows the TEM images of TiO_2 nanoparticles and gold nanoparticles presenting ca. 18 and 19 nm in diameter, respectively. Gold nanoparticles with this diameter present plasmon mode within the visible range, overlapping the absorption spectrum of the sensitizer (N3). In addition, according to McFarland and Tang [41], photoexcited electrons with energies of $\sim 1\text{eV}$ above the gold Fermi level have 20–150 nm free path in Au and other metals with low-lying or filled d bands. Therefore, in the assembling $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$, the photoexcited electrons in the dye should be able to pass through the gold nanoparticles towards TiO_2 conduction band.

Figure 3 shows the normalized absorption spectra of N3 in solution, mesoporous TiO_2 film, gold nanoparticles solution and gold nanoparticles deposited on a glass slide as a film. One can observe that TiO_2 presents absorption mode within the ultraviolet region, with band gap edge at ca. 400 nm. The gold nanoparticles in solution present extinction wavelength maximum at ca. 490 nm, corresponding to spherical shaped gold nanoparticles with average diameter of 20 nm as shown in the TEM images (Figure 2) [42]. Au nanoparticles in a film present plasmon mode shifted to lower energies when compared to Au nanoparticles in solution. This behavior is related to the coupling of the plasmon modes from nearby particles [43, 44]. In the film, photons with lower energy will match the electrons oscillation frequency within nanoparticle agglomerates. According to the literature, absorptions at lower energies (ca. 350 nm) are associated with interband transitions [45]. The sensitizer N3 presents broad absorption range with maximum at 400 and 530 nm, hence absorbing light from the UV region to nearly the entire visible spectrum. One can observe an overlap between the absorption spectra of the sensitizer and the extinction modes of the gold nanoparticles.

In addition to the particle nature, size and geometry, the dielectric function of the surrounding media also affects

the extinction spectra of plasmonic nanoparticles, once it affects the energy damping from the oscillator and the strength of the dipole created within the particle. In order to confirm whether the dye can be adsorbed on the gold nanoparticles, the plasmon energy was monitored before and after dipping a gold nanoparticles film in N3 solution (Figure 3(b)). One can observe a ca. 4 nm red shift indicating changes in local surface-refractive index of gold nanoparticles, due to a chemical adsorption, expected from molecules containing sulfur in the chemical structure [23, 46, 47].

Small size gold nanoparticles present discrete energy levels and a larger shift in the Fermi levels is expected for a small electron accumulation [48, 49]. On the other hand, nanoparticle agglomerates behave like large particles and more electron accumulation is required to achieve the same upward shift of the Fermi level. According to the literature, electrons in nanoparticle agglomerates can recombine with the oxidized N3 molecules or with the Γ/I_3^- redox electrolyte before they can be transferred to the conduction band of TiO_2 , resulting in a poor photocurrent [50]. Hence, there is an ideal concentration of plasmonic material which will allow improved absorbance and photocurrent [51]. To avoid interference of concentration on the performance of the DSSC, the same amount of gold nanoparticles was used in both devices. In the $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$ configuration, the sensitizer N3 presents carboxylic acid groups that efficiently bind to Ti^{4+} and, as suggested in Figure 3(b), the dye molecules can bind to the gold nanoparticles. In the $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ configuration, gold nanoparticles can be anchored directly on TiO_2 by free carboxylate groups of citrates used to stabilize the particles. An efficient bind may occur with empty orbitals of Ti^{4+} , as result of a Lewis acid-base reaction.

Figure 4 shows the absorption spectra of TiO_2/Dye , $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$, and $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$. One can observe that higher absorbance is achieved when gold nanoparticles are present. This behavior is associated with the 5-order higher cross-section of gold nanoparticles compared to conventional absorbing dyes [42]. For nanoparticles of ca. 40 nm,

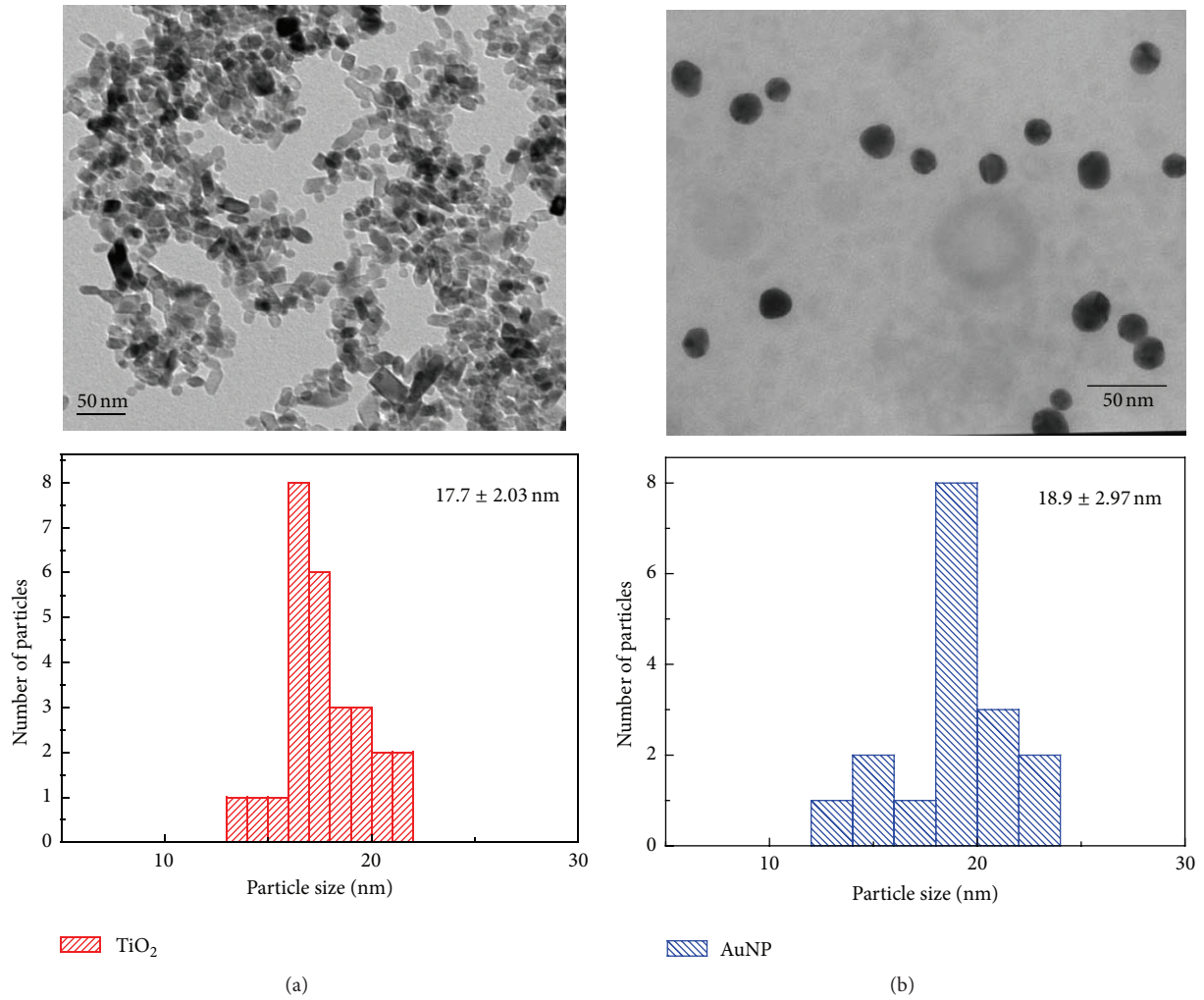


FIGURE 2: TEM images of (a) TiO₂ nanoparticles and (b) gold nanoparticles.

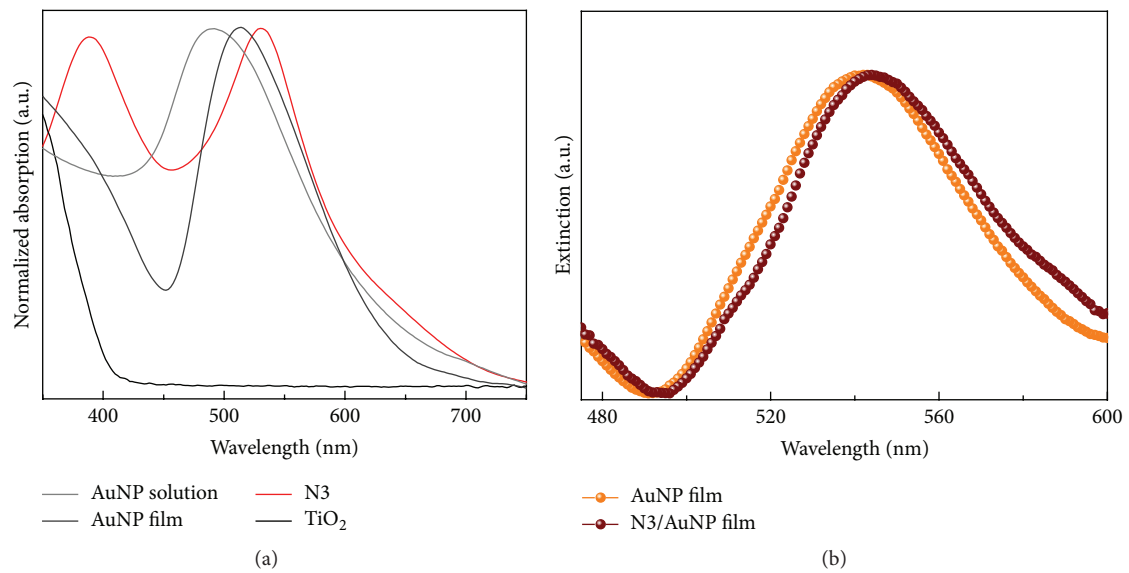


FIGURE 3: (a) Absorption spectra of N3, mesoporous film of TiO₂, gold nanoparticles in solution, and gold nanoparticles deposited on a substrate. (b) Normalized extinction spectra of gold nanoparticles and N3 adsorbed on gold nanoparticles.

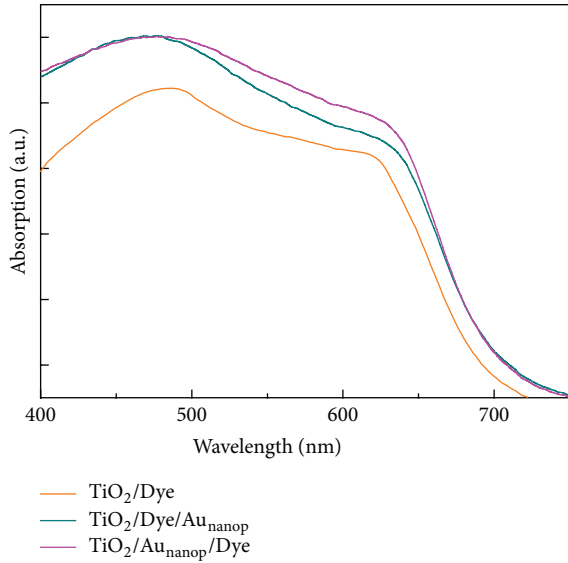


FIGURE 4: Absorption spectra of TiO_2/Dye , $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$, and $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$.

the absorption cross-section has been earlier calculated as $2.93 \times 10^{-15} \text{ m}^2$ and the molar absorption coefficient was ca. $7.66 \times 10^9 \text{ M}^{-1} \text{ cm}^{-1}$. Meanwhile, the N3 sensitizer extinction coefficient was $1.41 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $1.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 400 and 535 nm, respectively [52]. Concerning the two different configurations studied, $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ presented higher absorbance within the range between 500 and 650 nm.

In order to study the effect of the plasmonic materials on the performance of the solar cells, three different devices were assembled: (i) a standard device without plasmonic material (TiO_2/Dye); (ii) $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$; and (iii) $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$. Figure 5(a) shows the current versus potential curves obtained by illumination through the anode. The results clearly show an improvement in photocurrent allowed by the presence of gold nanoparticles [32–35]. The performance of the assembled devices was evaluated by the following parameters: short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and efficiency (η) (Table 1). In addition to enhanced photocurrent, a 30% improvement in efficiency was observed for the device assembled with gold nanoparticles deposited directly over TiO_2 layer ($\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$).

A slight shift of the open-circuit potential under polychromatic illumination was observed, induced by the plasmonic excitation of the nanoparticles [53]. V_{oc} is determined by the difference between the chemical potential of the electrolyte and the conductive band of TiO_2 , which is dependent on the external electrical field, such as the one from the plasmon fields [54]. The presence of the surface plasmon modes provides a strong external electric field, enhancing the open-circuit voltage of the solar cell (Table 1).

In order to further evaluate the contribution of the nanoparticles to the solar cells, a theoretical simulation

TABLE 1: Electrical parameters and the efficiency of the assembled devices.

	I_{sc} (mA)	V_{oc} (V)	FF (%)	η (%)
TiO_2/Dye	7.3	0.68	52	2.6
$\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$	11.9	0.71	50	4.3
$\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$	9.8	0.73	48	3.4

TABLE 2: R_s and R_{sh} obtained from data presented in Figure 5(b).

	R_s [Ω]	R_{sh} [Ω]
TiO_2/Dye	11.7	671
$\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$	21.2	649
$\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$	14.8	261

was carried out through an electrical modeling using (1), considering the temperature at 22°C and $n = 2$:

$$I = I_L - I_s \cdot e^{\frac{[(V+I \cdot R_s)]}{(n \cdot V_t)}} - \frac{(V + I \cdot R_s)}{R_{\text{sh}}}, \quad (1)$$

where I is the current output and I_L is the photocurrent, R_{sh} is the shunt resistance, and R_s is the series resistance. Using MATLAB to solve (1), from the experimental data and derivation of potential versus current at V_{oc} and I_{sc} , the R_s and R_{sh} values of all devices were determined (Table 2).

The simulated curves presented in Figure 5(b) show good fitting with the experimental data. Although $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ presents a much higher photocurrent, it also presents larger series resistance and much lower shunt resistance than TiO_2/Dye , while $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$ presents a much higher series resistance and a slightly lower shunt resistance.

IPCE measurements (Figure 6) show that the wavelength-dependent photocurrent response for all devices is consistent with the absorption spectrum of the sensitizer. In addition, both devices containing plasmonic material ($\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ and $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$) present higher conversion efficiency than the standard device (TiO_2/Dye). According to the literature, this enhancement in efficiency can be related to a sum of three effects: (i) increased dye excitation due to near-field effects around the nanoparticles; (ii) light scattering the plasmon-induced excited hot electrons on their transfer to the conduction band of TiO_2 [55, 56].

For both $\text{TiO}_2/\text{Au}_{\text{nanop}}/\text{Dye}$ and $\text{TiO}_2/\text{Dye}/\text{Au}_{\text{nanop}}$, light scattering will result in a longer path length, increasing the probability for light absorption. In addition, previous studies have shown that gold nanoparticles absorb light and the energy is then available for dye molecules in an evanescent near field. In the presence of strongly absorbing dyes, such as the N3 studied in this work, the energy from the localized plasmons is transferred to the sensitizer molecules [57].

As the plasmon mode corresponds to discrete states of possible coupling between the incident light and the oscillation of the electronic density within the nanoparticles, the energy of the photon is shared by many electrons; therefore, one should not expect the electrons to have

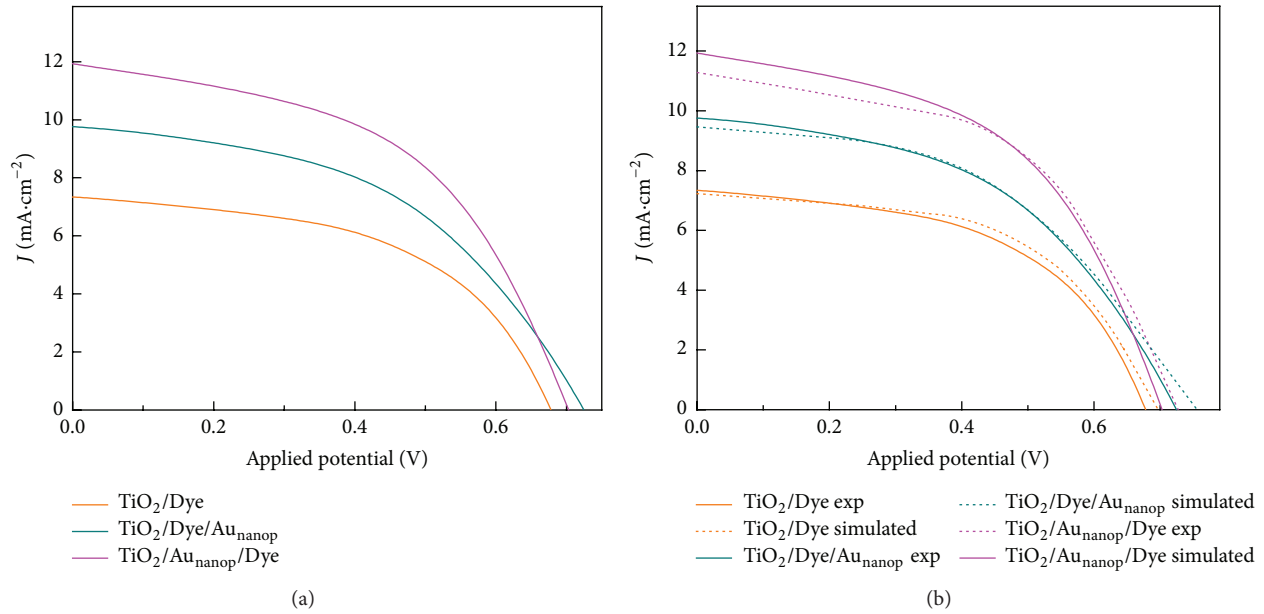


FIGURE 5: Current versus potential for (a) gold nanoparticles deposited after sensitizing the TiO₂ (TiO₂/Dye/Au_{nanop}), before sensitization (TiO₂/Au_{nanop}/Dye), and for the standard DSSC (TiO₂/Dye). (b) Comparison between the experimental and simulated data from electrical modeling.

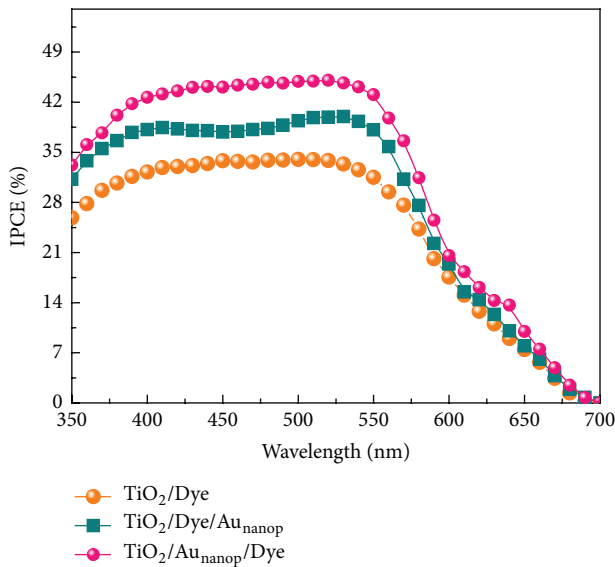


FIGURE 6: IPCE of TiO₂/Dye, TiO₂/Au_{nanop}/Dye, and TiO₂/Dye/Au_{nanop}.

sufficient energy to get over a 1.0 eV Schottky barrier at the interface between gold and TiO₂ [41]. However, experimental and theoretical studies describe an ultrafast (<240 fs) [58] mechanism involving the plasmon-induced electron transfer from metallic nanostructure to TiO₂ nanoparticles [55, 59, 60]. Figure 7 shows a schematic illustration of the Schottky junction between gold and TiO₂ nanoparticles for the assembled devices. A band bending creates an energy barrier, which allows an electron photoexcited in the gold nanoparticle to

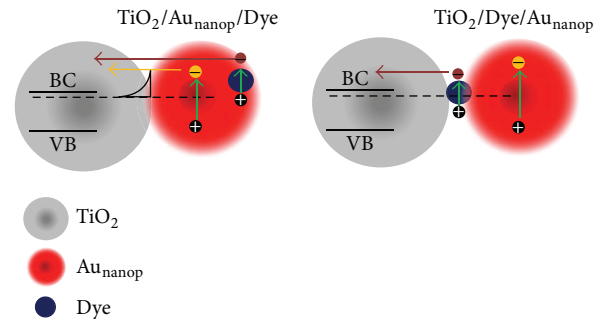


FIGURE 7: Schematic illustration of the plasmonic excitation mechanisms taking place within the assembled devices.

be transferred to the conduction band of the TiO₂ [41]. In addition, earlier reports on transient spectroscopy analysis evidences a simultaneous process where photoexcited electrons are injected into TiO₂ bulk; meanwhile electrons from a donor in the electrolyte are injected into the oxidized gold nanoparticles [43, 58]. Concerning the free path of the photoexcited electrons in Au nanoparticles with diameter used in this work, a significant amount of the electrons generated in the dye and injected through the gold nanoparticle will reach the Schottky barrier [56]. Therefore, concerning the two configurations for plasmon enhanced DSSCs, one can assume that, in the TiO₂/Au_{nanop}/Dye, the photoexcited electrons in the dye can be injected directly into the conduction band of TiO₂. In addition, hot electrons can be transferred from the gold nanoparticles to TiO₂ conduction band, improving photocurrent. On the other hand, for the TiO₂/Dye/Au_{nanop}, we suggest two effects to explain the lower photocurrent

improvement: (i) a smaller amount of dye molecules is affected by the near-field plasmon modes and (ii) a smaller fraction of photoexcited electrons in the gold nanoparticle can be transferred to TiO_2 , due to the additional potential layer created by the dye molecules.

4. Conclusion

The interface where the gold nanoparticles are placed in the assembled device affects the plasmon contribution to the overall energy conversion efficiency. The plasmonic material improves the efficiency of DSSC by increasing light scattering (increasing the light trapping by near-field effects) and transference of hot electrons (increasing the electrons density that reaches the Schottky barrier). These contributions are strongly dependent on the DSSC configuration, once the interface $\text{Au}_{\text{nanop}}/\text{TiO}_2$ is more appropriate for injecting photoexcited and hot electrons into TiO_2 conduction band. Further studies on these systems are warranted to provide important information about the plasmon energy either to excite electrons in the photoactive layer or to generate hot electrons within the nanoparticles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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