Optical Absorption Modeling of bilayer photoanode based on Cu@TiO2 Plasmonic Dye Sensitized Solar Cells towards Photovoltaic Applications

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Abstract

A periodic array of core–shell Cu@TiO₂ nanoparticle for plasmonic dye sensitized solar cells (DSSCs) in the wavelength range between 350–750 nm was studied. The size of copper nanospheres was 70 nm while the length and diameter of the copper nanorods were 100 and 10 nm, respectively. The UV-Visible absorption spectrum showed that the photo-anode based copper added TiO₂ has 29.3% absorption capability compared with copper-free TiO₂. TiO₂ with shell thickness of 5 nm coated copper exhibited the absorption efficiency of 71.9%, while short circuit current density of 17.52 mA cm⁻² for Cu@TiO₂ photo-anode. This was attributed to a strong localized electric field around ultra-thin TiO₂-coated copper nanospheres. The UV-Visible results of different geometries indicated that the spherical-shaped Cu@TiO₂ nanoparticles induced the high absorption capability of 3.4% compared to rod-shaped Cu@TiO₂ nanoparticles. The hybrid nanorods/nanospheres bilayer photo-anode showed the high optical UV-Visible absorption of 11.42% as compared with nanospheres/nanorods, ascribed to the large surface area for dye-loading excellent light scattering.

1. Introduction

In dye-sensitized solar cells (DSSC), the conversion of photons into electric current begins with the absorption of light through sensitized dye molecules [1–4]. The excited sensitizer is oxidized by the injection of ultra-fast electrons into the conduction band of the semiconductor material [5–6]. Various optimization methods are reported to improve the photovoltaic performance of DSSC, including molecular designs to expand the absorption spectrum of dye and suppress the recombination rate [7–8], improving the electrolytic redox system [9–10], applying resistance engineering to reduce the internal impedance of the cell and increasing the light harvesting efficiency through scattering or plasmonic effect [11–14]. The localized surface plasmon resonance (LSPR) spectrum of metal nanoparticles contains both absorption and scattering components, which depends on the size, material composition, morphology of the nanoparticles and the dielectric medium surrounding the nanoparticles, thus needs to be finely tailored [15–17]. Moreover, the LSPR of metal nanoparticles is sensitized by the presence of another nearby nanoparticles, which can be considered as extreme interaction with the dielectric environment. When one nanoparticle is placed within a few nanometer range to other nanoparticle, the light-dependent dipole moment of the particles are coupled to each other, causing a sudden change in the absorption and scattering cross-sections of the nearby particles. Plasmonic coupling also causes a confined and strong electric field between the gaps of coupled nanoparticles [18]. This high restricted and improved electric field significantly improves the incompatibility between photons and molecules. LSPR can effectively convert electromagnetic energy into heat [19], thus can increase local temperature and induce nanoscale phase transitions. This thermal effect of LSPR has been widely used in thermotherapy, solar vapor production and photon induced drug release [20].

Metal nanoparticles have been used in the last decade to capture light in plasmonic dye sensitized solar cells [21–22]. The importance of gold and silver nanoparticles is due to their fascinating optical
properties. Several successful reports of incorporating metal nanoparticle directly in the active layer of DSSC have been published. However, the concern about corrosion of metal nanoparticles when they come in contact with dye and electrolyte molecules is still at its infant [23]. Moreover, these metal nanoparticles are oxidized by surrounding environment. To overcome these issues some reports proposed the idea of shielding of metal core with dielectric or polymeric shells [24, 25]. Recently, Hao et al. [26] demonstrated the addition of Ag@SiO$_2$ nanoparticles in the active layer of organic solar cell, which resulted in enhancement of power conversion efficiency by 19.2%. They linked this improvement to two key phenomena. First, the rise in extraction and transportation of holes and second, optical absorption by near-field enhancement and far-field scattering. Zohreh et al. [27] improved the performance of DSSC by adding copper to TiO$_2$. Their results showed that power conversion efficiency of CuO/TiO$_2$ nanocomposite is 43% higher than that of pure TiO$_2$. Ünlü et al. [28] synthesized different amount of copper doped TiO$_2$ and used as photo-anode materials in dye sensitized solar cell. The PCE of undoped TiO$_2$, 0.5% and 1% copper doped TiO$_2$ were recorded as 4.77%, 4.98% and 5.09% respectively. They observed that this enhancement is attributed to doping which can interact with dyes and caused change in charge transportation and recombination. However, up to best of our knowledge, their research is still insufficient as it lacks systematic studies on the effect of plasmon enhancement for various shell thicknesses and geometries of core-shell Cu@TiO$_2$ NPs. Since the optical intensity of the near field decreases quickly from the metal-dielectric boundary, LSPR should be optimized by changing the thickness of the shell to increase absorption efficiency. In order for the metal core to trap the incident light, the shell must provide optimal gap, good electrical conductivity, adequate chemical stability, as well as excellent photo-voltaic properties. As reported, TiO$_2$ as shell material would have two key benefits (i) energy band gap compatibility to dye sensitize and (ii) provide lowered internal impedance for the solar cell [29]. However, at the nanometer scale, the optical properties of TiO$_2$ can be significantly changed with varying shell thickness, thereby affecting the plasmonic enhancement in DSSCs Therefore, the shell thickness and geometry of the nanoparticles need to be carefully designed to get optimal enhancement.

This study introduced core-shell Cu@TiO$_2$ as active photo-anode material to improve the optical absorption efficiency of DSSC devices. The incorporation of copper nanoparticle with two different spherical and rod shape morphology into photo-anode layer of DSSC and compare the effectiveness of nanoparticles morphology on the absorption capability of the device was introduced. Among the nanoparticle morphology studied, the highest optical absorption can be obtained by using the spherical-shaped copper nanoparticles coated with TiO$_2$. Considering the use of bilayer structures, the UV-VIS absorption of hybrid nanorods/nanosphere photo-anode is superior to nanospheres/nanorods, which are in accordance with obtained results [30]. The optical properties associated with these unique morphology and photo-anode structures will lead the copper nanoparticles for further development of solar cell technology.

2. Simulation Process
A typical core-shell Cu@TiO$_2$ based photo-anode structure of DSSC is schematically modeled. The computation was based on finite element method (FEM) that offers a standard 3-D discretization scheme, appropriate several high-frequency applications in frequency or time domain as reported in [31]. The basic idea of this numerical method is to apply the Maxwell's Equations in integral form which always mostly provide flexibility to the model. Here the absorption of photo anode is investigated from 35 to 750 nm wavelength range. Total absorption factor, $A_{\text{photon}}$, will estimate the optical absorption capability of model for different particle sizes arranged in different layers. $A_{\text{photon}}$ is the ratio of absorbed photons by the model to the total incident photons in unit area.

### 2.1 Materials, geometry and boundary conditions

A model of photoactive layer of DSSC is created in this study as shown in Fig. 1. In our model, tetrahedral meshing is employed for frequency domain solver. Materials selected are defined by optical properties such as refractive index ($n$) and extinction coefficient ($k$) for which the data is selected from [32]. Silica glass was used for its advantages in both antireflection properties and surface passivation. The thickness of this layer is chosen as 40 nm. Plasmonic Ag NP is placed in the center of TiO$_2$ in each model. The size of copper nanoparticle is fixed to 70 nm, while shell thickness of TiO$_2$ was varying in the range between 5–20 nm. The diameter and length of the copper nanorods were 10 and 100 nm, respectively. Air is assumed as surrounding medium for the Cu@TiO$_2$ nanoparticle. Tetrahedral meshing of 10 nm size was employed for precise calculation. Periodic (p) array of nanoparticles was assumed to place on the top of fluorine doped tin oxide (FTO) with boundary condition along $x$ and $y$ directions. The size of period was taken as 20nm. A perfectly matched layer boundary conditions were used in the model to prevent stray reflections toward the nanoparticles. Incoming light is a plane wave that travels along the $z$ direction and directions of magnetic and electric field are $x$ and $y$ respectively. The same DSSC model under same conditions without copper nanoparticles in the photoanode layer was also designed as reference to estimate the enhancement in absorption of Cu@TiO$_2$ based solar cell.

### 3. Results And Discussion

#### 3.1 Localized surface plasmon resonance of core–shell Cu@TiO$_2$ nanospheres

In order to optimize the best suitable materials for photo-anode, we have studied the Tauc's curve of photo-anode based on TiO$_2$ coated copper nanospheres and copper-free TiO$_2$ nanospheres. It can be seen from Fig. 2 (a), the bandgap of bared TiO$_2$ (Cu-free TiO$_2$) and Cu@TiO$_2$ is 1.70 and 1.45 eV respectively. The reason of lower band gap is attributed to addition of copper nanospheres which increase the excitation rate of dye sensitizers by localized surface plasmon resonance [33]. A similar effect on the band gap was also reported by Babu et al [34]. Moreover, the metal cores can go through
charge equilibrium with the adjacent TiO$_2$ and alter its Fermi energy level, ensuing an enhanced cell potential.

The absorption enhancement of photo-anode based on Cu@TiO$_2$ is supported by the UV-VIS spectrum. UV-VIS spectrum of Cu-free TiO$_2$ and Cu@TiO$_2$ was compared in the range of 350–750 nm. As shown from Fig. 2 (b), the absorption capability of photo-anode based on Cu-free TiO$_2$ nanospheres and Cu@TiO$_2$ with 5 nm shell thickness is 55.6 and 71.9% respectively. The Cu@TiO$_2$ showed two significant absorption peaks at 510 and 695 nm while the Cu-free TiO$_2$ nanospheres showed the only peak at 540 nm. The absorption enhancement of photo-anode based on Cu@TiO$_2$ is 29.3% higher than that of copper-free TiO$_2$. This enhancement is attributed to the localized surface plasmon resonance excited by copper nanospheres which boosted up the optical performance of DSSC. Moreover, the addition of Cu metal core act as scattering centers for incident light and provides a longer path length for photons, resulting in improving their probability of being absorbed in the photo-anode layer, confirmed by the UV-VIS absorption curves (Fig. 2b).

### 3.2 Optimization of shell thickness

As the near-field effects are strongly distance dependent therefore the effect of shell thickness on the plasmon-based efficiency enhancement was investigated using Cu@TiO$_2$ nanoparticles with various shell thicknesses. The size of copper core is fixed at 70 nm, while the shell thickness ($t$) is varied from 5 to 20 nm. The comparative UV-VIS absorption spectrum of various shell thicknesses of Cu@TiO$_2$ and Cu-free TiO$_2$ is presented in Fig. 3 which clearly shows plasmonic resonance peaks around 510.5 and 695.5 nm with slight red shifts (3–10 nm). These red shifts of curves are attributed to dielectric behavior of copper nanospheres with changing shell thickness ($t$) from 5 to 20 nm. We have observed that optical absorption enhancement decrease with increasing the shell thickness ($t$). From Table 1, it can be seen that, enhancement of 20.1%, 23.5%, 25.8% and 29.3% is recorded for Cu@TiO$_2$ nanoparticles based photo-anode with shell thicknesses of 5, 10, 15 and 20 nm respectively compared to that of Cu-free TiO$_2$. This is because metal particles can act as optical antennas for incident light. When the copper nanospheres are placed near the TiO$_2$ Shell, LSPR produces strong near-field electromagnetic energy concentration which assists the direct injection of charge carriers from the plasmonic antenna into the conduction band of TiO$_2$ [35]
Table 1
Absorption enhancement and short circuit current density for different shell thickness of Cu@TiO$_2$ in comparison with Cu-free TiO$_2$.

| Types of Photo-anode | Shell Thickness ‘t’ (nm) | Absorption (%) | Absorption Enhancement (%) | Short Circuit Current Density (mA cm$^{-2}$) |
|----------------------|--------------------------|----------------|---------------------------|-------------------------------------------|
| Cu-free TiO$_2$      | -                        | 55.6           | -                         | 12.89                                     |
| Cu@TiO$_2$          | 20                       | 66.8           | 20.1                      | 16.26                                     |
|                      | 15                       | 68.7           | 23.5                      | 16.79                                     |
|                      | 10                       | 70             | 25.8                      | 17.11                                     |
|                      | 5                        | 71.9           | 29.3                      | 17.52                                     |

Table 1 shows the enhancement in J$_{sc}$ due to plasmonic Cu nanoparticles based photoanode. The J$_{sc}$ increases from 12.89 mA/cm$^2$ to 17.52 mA/cm$^2$ after the incorporation of the plasmonic nanoparticles with shell thickness of 5nm. The J$_{sc}$ improves by about 36% for the shell thickness of 5 nm while it only improves by 26.14% for the shell thickness of 20 nm. This shows that photovoltaic performance of plasmonic metal nanoparticles based solar cell is more enhanced than that of without plasmonic nanoparticle. The improvement of short circuit current density of solar cell using plasmonic nanoparticle is also reported in [36–38]. The Tauc's curves of Fig. 3(b) also supports the highest absorption enhancement of Cu@TiO$_2$ with T$_{sh}$ = 5cm. Minute variation in the band gap energies is observed with varying shell thicknesses. These shifts are attributed to the dielectric properties of copper nanoparticles.

To gain insight on this phenomenon, we calculated the electric field intensity around metal nanospheres at the wavelength of $\lambda = 510$ nm. As it can be seen in Fig. 4 the electric field around the copper nanospheres is stronger for $t = 5$ nm. This reduced shell thickness encourages the near-field antenna effect associated with localized surface plasmon resonance and consequently enhances the absorption in the photo-anode layer.

### 3.3 Effect of Cu@TiO$_2$ nanoparticles geometry on absorption enhancement

In order to obtain the maximum improvement, it is necessary to understand the effect of particle morphology on the absorption performance of DSSC. In this study, we were able to provide good optical performance by comparing the spherical- and rod-shaped structures of nanoparticles which are confirmed by the broadband UV-VIS absorption analysis of Fig. 5. Based on results of Sect. 3.2, we have considered the results of spherical geometry of copper-free and copper incorporated TiO$_2$ nanoparticles with shell thickness of 5 nm for their best performance. By changing the morphology of copper
nanoparticles in the form of nanorods (NR), the UV-VIS absorption results showed 69.54% absorption capacity. The absorption capacity of the photo-anode based on rod-shaped Cu@TiO$_2$ nanoparticles is 25% higher than that of rod-shaped TiO$_2$ copper-free. It was observed that core-shell rod-shaped Cu@TiO$_2$ nanoparticles have a wider LSPR band with a peak at 420 nm. This absorption was owing to the high localized electric field strength of the Cu@TiO$_2$ nanoparticles. The nanorods structure of Cu@TiO$_2$ nanoparticles captured the incident light, which resulted in increased path length of the incident light. This higher path depth length greatly improves the interaction between the dye molecules and the photons, resulting in producing more charge carriers [39–40]. However, the absorption enhancement of spherical-shaped Cu@TiO$_2$ is little higher (3.45%) than that of rod-shaped nanoparticles. It may be due to the fact that the spherical-shaped Cu@TiO$_2$ provides large surface area for dye absorption. This increased light diffusion capacity resulted in more electrons injection into the Cu@TiO$_2$ conduction band [41]. Moreover, the improvement occurs in the longer wavelength, which is the most desirable wavelength range required for the light absorption efficiency in the DSSC. Nevertheless, the rod-shaped Cu@TiO$_2$ photo-anode has also very important effect on DSSC performance. Tauc's curve of Fig. 5(b), it can be seen that the bandgap energies for spherical- and rod-shaped geometries of Cu embedded TiO$_2$ were 1.3 and 1.45 eV respectively. The reason for the reduced bandgap energy for spherical-shaped Cu@TiO$_2$ is attributed to the large amount of dye molecules due to the large surface area provided by the spherical-shaped particles. According to the Beer–Lambert law, higher absorbance in the UV–vis spectrum means higher dye concentration.

### 3.4 Bilayer hybrid structure of Cu@TiO$_2$ nanorods and nanospheres

Nanostructured bilayer photo-anode has been modeled for high optical absorption photoanode by modifying with nanospheres (NS) and nanorods (NR). As discussed in Sect. 3.3, the modification of Cu@TiO$_2$ morphology in the form of nanorods causes the coming light to trap and increases the path depth length of light. This can substantially increase the photon interaction with the dye molecules and resulted in boosting the performance of photoanode. The spherical-shaped morphology of Cu@TiO$_2$, on the other hand, will provide adequate surface area which produces many excited electrons that are injected into the conduction band of Cu@TiO$_2$ and led to effective charge transportation. Comparing with the different photo-anode structures [42, 43], the novel hybrid photoanode in this study is capable to offer good optical performance as confirmed by broad band UV-VIS absorption spectrum (Fig. 7). The model for Cu@TiO$_2$ nanorods over Cu@TiO$_2$ nanospheres (NR/NS) bilayer and Cu@TiO$_2$ nanospheres over Cu@TiO$_2$ nanorods (NS/NR) structures are shown in Fig. 6. The UV-VIS absorption spectrum showed that the overall improvement in absorption of photo-anode based on NR/NS and NS/NR is 78.33 and 70.30% respectively. So, the NR/NS Cu@TiO$_2$ layer has 11.42% higher absorption compared to NS/NR because of following reasons (1) the upper NR layer exhibits higher light-scattering ability; and (2) the bottom Cu@TiO$_2$ nanospheres layer offers large surface area for dye absorption and thus provide more electrons in the conduction band of electrode. The enhancement takes place in the higher wavelength side, which is
more suitable wavelength range for light absorption efficiency in DSSCs [44]. However, the role of NS/NR Cu@TiO$_2$ photo-anode has also very important influence on the performance of DSSCs.

The Tauc’s curve of Fig. 7(b) shows that the bandgap energies of photoanode’s based on nanorods/nanospheres and nanospheres/nanorods are 1.4 and 1.51 eV, respectively. The reason for the reduced bandgap energy of the nanorods/nanospheres photoanode is attributed to the scattering effect of large-sized particles in the top layer of the rod-shaped nanoparticles. The light scattered by the top layer triggered an enhancement in the optical absorption. Thus, the combination of localized surface-plasmon resonance and the narrow bandgap of the bilayer structure led to the photoanode’s enhanced light harvesting efficiency.

3.5 Normalized absorption and short circuit current density values of different photo-anode structures

- From Table 2, it is evident that all structures of photo-anode based on copper incorporated TiO$_2$ have higher absorption than that pure TiO$_2$. The enhancement in absorption attributed to addition of copper which exhibits localized surface plasmon resonance effect. Moreover, the bilayer photoanode structures have higher absorption capability than single layer structures (nanospheres and nanorods) which is endorsed to higher optical depth length of bilayer structure. The light confined for more time which gave rise further dye interaction with photons and resulted in higher absorption efficiency and short circuit current density.

The photoanode layers do not produce free carriers directly on photo excitation, instead producing a bound electron-hole pair (exciton). This exciton is separated to form free carriers at the electron-donor and electron-acceptor interface of the photovoltaic device. The effective generation of free carriers upon photoexcitation is therefore dependent on the retention of the exciton as it successfully creates free carriers. This is determined by the lifetime and diffusion length of the exciton. Free charges are easily created from the excitons generated close to the p-n interface. Increasing the interface area for dye absorption boosts the charge generation. It is the reason that the short circuit current density of photoanode based on nanospheres is 4.03% higher than that of nanorods. The generation of more charges due to more surface area resulted in efficient charge transport. Similar is the case of photoanode based bilayer nanosphere and nanorod. The nanorod/nanosphere (NR/NS) provides more area for dye absorption compared to that of nanosphere/nanorod therefore an increment of 11.4 % is observed in higher short circuit current density of NR/NS than NS/NR.
Table 2
Absorption enhancement and short circuit current density for different photo-anode structures based on Cu@TiO\(_2\) in comparison with Cu-free TiO\(_2\).

| Types of Cu@TiO\(_2\) photo-anode structures | Absorption (%) | Absorption enhancement w.r.t Cu-free based photoanode (%) | Short circuit current density (mA cm\(^{-2}\)) |
|--------------------------------------------|----------------|----------------------------------------------------------|----------------------------------------------|
| Nanospheres                                | 71.9           | 29.3                                                     | 17.52                                        |
| Nanorods                                   | 69.54          | 25.12                                                    | 16.84                                        |
| Bilayer nanosphere/nanorod                 | 70.30          | 26.43                                                    | 16.91                                        |
| Bilayer nanorod/nanosphere                 | 78.33          | 40.88                                                    | 18.84                                        |

Conclusions

In this study, we have systematically studied the different morphology of copper as plasmon nanoparticles in photo-anode to enhance the absorption efficiency of DSSCs. The UV-Visible absorption spectrum showed that the photo-anode based on copper added TiO\(_2\) nanospheres has 29.3% higher absorption capability than that of copper-free TiO\(_2\). This enhancement is attributed to the strong electric field localization originated around plasmonic core–shell copper nanospheres. The optical response and short circuit current density of Cu@TiO\(_2\) nanospheres were also studied with varying shell thickness. It was found that Cu@TiO\(_2\) nanospheres with 5 nm shell thickness exhibited the highest absorption efficiency and enhanced short current density of 71.90% and 17.52 mA cm\(^{-2}\) respectively. This enhancement is credited to strong surface plasmon resonance effect which is higher for small shell thickness [44]. Addition of Copper nanoparticles with both the spherical- and rod-shaped geometries resulted in improvement in the performances of DSSC. The photo-anode based on spherical-shaped Cu@TiO\(_2\) nanoparticles has 29.3% higher absorption than that of the Cu-free TiO\(_2\). Similarly, the absorption enhancement of the rod-shaped Cu@TiO\(_2\) nanoparticles was 25% higher as compared to Cu-free TiO\(_2\). The enhancement of spherical- and rod-shaped Cu@TiO\(_2\) photo-anode was attributed to large surface area for dye-loading as well as excellent light scattering enhancement capacity. Bi-layered Cu@TiO\(_2\) photo-anode consisting of nanospheres/nanorods and nanorods/nanospheres was also investigated for DSSCs. The bilayer nanorods/nanospheres Cu@TiO\(_2\) exhibited 11.42% improved optical absorption as compared to the photo-anode based on nanospheres/nanorods Cu@TiO\(_2\).

Declarations

Conflicts of interest
There are no conflicts to declare.

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Figures
Figure 1

Model of photo-anode layer of DSSC with core-shell Cu@TiO2 nanoparticle

Figure 2

Results of Photo-anode based on Cu-free TiO2 and Cu@TiO2 nanospheres with 5 nm shell thickness (a) Tauc's curve (b) UV-VIS absorption
Figure 3

Results for photo-anode based on Cu-free TiO2 and Cu@TiO2 nanospheres with different thickness of the shell (a) UV-VIS absorption spectrum (b) Tauc’s curves

Figure 4

Electric field intensity distribution of Cu@TiO2 at 510 nm for shell thickness of (a) 5 (b) 10 (c) 15 and (d) 20 nm
Figure 5

Results for photo-anode based on spherical- and rod-shaped geometries of Cu-free TiO2 and Cu@TiO2
(a) UV-Vis absorption curves (b) Tauc's curves

Figure 6

Schematic presentation of the Cu@TiO2 photo-anode based on (a) nanorods/ nanospheres (NR/NS) and (b) nanospheres/nanorods (NS/NR)
Figure 7

Bilayer Cu@TiO2 photo-anode based on nanorods/ nanospheres (NR/NS) and nanospheres/nanorods (NS/NR) (a) UV-VIS absorption (b) Tauc's curve