Barrier coating and plasmonic effect by using diamond-like carbon and silver nanoparticles on quantum dots sensitize solar cells

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Abstract
Effects of diamond-like carbon (DLC) and Ag nanoparticles (Ag NPs) on photoanode of quantum dot sensitized solar cell (QDSSCs) have studied for the first time. Photoanodes include thin films of the TiO₂ deposited on the FTO substrate, subsequently, graphene and CdS quantum dots (QDs) added on. Some photoanodes decorate by Ag nanoparticles and DLC thin film. Current density–voltage (J–V) characterization showed that the short-circuit current density (J_{sc}) and power conversion efficiency (PCE) of QDSSCs with localized surface plasmon resonance (LSPR) of Ag NPs and anti-corrosion, photon and electron barrier properties of DLC thin film increase photon harvesting and improve solar cells performance. J_{sc} of this configuration increased from about 8.87 to 14.6 mA cm⁻², nearly doubled. The Ag NPs scatter photon and increase the photon harvesting in QDs. Results were showing that the presence of a thin film of DLC on TiO₂/CdS/G photoanodes increased the efficiency by 97%, short circuit current by 64%, and open circuit voltage by 16%. Also, the efficiency change from 0.8 to 1.58 in the presence of both DLC and Ag NPs in cells in compare with cells without Ag NPs and DLC.

Keywords: QDSSC, photoanode, TiO₂, DLC thin film, Ag NPs, electron barrier, LSPR

(Some figures may appear in colour only in the online journal)

1. Introduction

The quantum dots sensitized solar cells (QDSSCs) have been considered more than other solar cells due to economically efficient and high efficiency because crossing the Shockley–Queisser limit. These solar cells were fabricated on semiconductor photoanodes such as TiO₂ and ZnO [1–5] doped with CdS quantum dots [6–8]. Photon harvesting enhancement is one of the most important challenges in QDSSCs. It has been shown that the use of metallic nanoparticles in QDSSCs [9–12] and the anti-reflection layer of DLC on Silcones cells [13–16] can be effective in light absorption enhancement which improves the efficiency. In several studies, the effects of trapping and light dispersion of nanoparticles have been investigated [17]. Due to its strong plasmonic resonance effect, Ag NPs has been used in photoanodes structure more than other metals [18].

One of the ways to increase efficiency is to use DLC on photoanodes. In reported studies, the effect of DLC on silicon solar cells investigated [14–16]. DLC properties such as high mechanical hardness, optical transparency in the visible light region, and NIR make it a special material to use in optical applications. DLC thin film has the wide bandgap that important for absorption in the visible area. In the number of studies the DLC effect in silicon solar cells such as anti-reflection [16], resistant to oxygen corrosion, radiation damage [19] and increase power conversion efficiency (PCE)
investigated, however, the results showed no significant increase in $V_{oc}$ and $J_{sc}$ [13].

In this study, the effects of Ag NPs and DLC on QDSSC were investigated. We used co-deposition of RF-PECVD and RF-sputtering methods to synthesis Ag NPs embedded into DLC. The characterization of synthesized samples had proved the new features of DLC film in contact by electrolyte, photon, and electron barrier, in photoanodes solar cells. The results confirm that short-circuit current, $J_{sc}$, and energy conversion efficiency were greatly increased.

2. Experimental

A thin film of titanium deposited on the FTO substrate by the RF-sputtering method. The chamber pressure maintains at 0.022 mbar, sputtering power was 80 W and argon gas flow of 30 cm$^3$ min$^{-1}$. For fabrication of TiO$_2$ nanoporous, samples were anodized with 0.6Wt% ammonium fluoride solution for one minute to obtain cauliflower structure of titanium oxide. Finally, samples annealed at 500 °C for 2 h to form the anatase phase and crystalline plane orientation. The details reported in our previous group work [20].

In the next step, the surface of TiO$_2$ with Ag NPs was decorated by co-deposition of RF-PECVD and RF-sputtering. The sputtering process performed with 99.9% purity silver and acetylene gas, RF power of 50 W, and deposition time was 3 min.

Subsequently, for the growth of CdS on the TiO$_2$ porous layer, we used the Successive Ionic Layer Absorption and Reaction (SILAR) method [7]. A solution of 0.05 M cadmium nitrate, Cd(NO$_3$)$_2$, in ethanol and 0.05 M sodium sulfide, Na$_2$S, in methanol were used as a cation and anion source respectively. Each SILAR cycle involves immersing photoanode in a cationic solution for 30 s, washing with ethanol, drying and then immersing in the anionic solution for 30 s, washing with methanol and drying. The cycle repeated three times for each sample.

The electrochemical method is one of the ways to fabricated few-layer graphene (G) with low impurities [21–23]. In this method, we used two graphite electrode and the electrolyte containing 0.1 M ammonium sulfate in ethanol. The voltage of 10 V applied to the electrochemical cell for 20 min. The dark yellow solution filtered and washed with DI water. The product dried in an oven at 80 °C. More details can be found in our previous work [24]. Then dissolved 0.3 g of graphene powder in 7 ml of ethanol and sonicated for 30 min. Solution centrifuged to separate the bulk particles. 100 μl of the solution was placed onto TiO$_2$/CdS cell by spin coating at 100 rpm.

One of the common deposition methods, suitable for the growth of DLC films, is Plasma Enhanced CVD (PECVD) [16, 25–28]. In this method acetylene gas (C$_2$H$_2$) or methane gas (CH$_4$) injected into the reactor. It is well known that the thin film deposited by this technique (RF-PECVD) is DLC. It has been reported in previous work from our lab [29–33].

To study the effect of DLC in a solar cell, thin films of DLC deposited on photoanodes using acetylene gas by RF-PECVD method at 0.04 mbar pressure and applied 50W power for 10 min.

Two types of photoanode fabricated: TiO$_2$/CdS/G with and without Ag NPs and some of the samples was covered with thin films of DLC. To assemble cells, we used platinum thin film as a counter electrode. The platinum electrode prepared with the RF-sputtering method using a platinum target on the FTO substrate with a chamber pressure of 0.015 mbar, 200W RF power applied and a deposition time of 25 min. The active surface of the cells was the square of 0.5 × 0.5 cm$^2$. Photoanodes and Pt-counter electrodes were sandwiched by Surlyn film. Polysulfide electrolyte used to complete the cell cycle. For solubilization of electrolyte, in 20 ml of DI water added 0.08 g of NaOH, 0.64 g of sulfur and 1.56 g of Na$_2$S, it was placed under argon gas on stirred.

The photocurrent–voltage ($I–V$) characteristics of solar cells measured under sun illumination (AM1.5 G, 100 mW cm$^{-2}$) with a solar simulator (Sharif solar simulator). Absorption properties of different photoanodes studied by UV–vis spectrometer (StellarNet, EPP-2000).

The morphology and EDX mapping of TiO$_2$/Ag/CdS/G were obtained by field emission scanning electron microscopy (FESEM- MIRA III- T-SCAN).
3. Result and discussion

3.1. Morphology

The morphology of TiO₂ on the FTO substrate shown in figure 1. According to figure 1(a), this structure consists of two levels; porous and dense layers, in the top and bottom, respectively. A high area of porosity surface can allocate more QDs. Also, the porosity increases the effective surface to trap and absorb the light as much as possible. Bottom dense layer prevented of recombination photoelectrons generated between FTO and electrolytes. Figures 1(b) and (c) show TiO₂ with Ag/CdS/G, and photoanode covered with a thin layer of DLC, respectively.

EDX mapping from Ti, O, Ag, Cd, and S are shown in figure 2. Mapping of Cd and S illustrate the uniform formation of CdS QDs. The weight percent of these elements listed in table 1.

3.2. UV–visible spectroscopy

Absorption spectra of photoanodes are given in figure 3(a). The figure shows the absorption edge of TiO₂/CdS/G photoanode about 410 nm. The direct bandgap of materials was calculated from Tauc formula which is about 3.02 eV. Increasing the absorbtance edge to 435 nm that is equivalent to 2.85 eV bandgap in TiO₂/Ag/CdS/G attributed to trapping light with Ag NPs. According to figure 3, TiO₂/Ag/CdS/G/DLC has higher absorbance in the visible region compared with TiO₂/CdS/G. The samples covered with DLC thin films also shifts absorbance edge up to 450 nm (2.75 eV) which is due to the new trapping states between the valence band and new electronic surface states. Increasing the absorption of photoanode with DLC film can have an optical source. The increase in absorption in DLC film is explained by the total reflection light at the boundary of dense DLC film with a 2.2 refractive index and air.

Result indicating visible light absorbance is intensified in TiO₂/Ag/CdS/G and TiO₂/Ag/CdS/G/DLC in comparison with TiO₂/CdS/G. In addition to the protective property of DLC film, the remission effect of absorbed light of DLC film in the visible spectral range is considered. This effect enhanced photon harvesting in CdS. Our result is consistent with other reports [15].

Moreover, we used a smooth, uniform surface of DLC for contact with air (in the UV–visible spectrum) and electrolyte contact (in solar cell photovoltaics). When light enters the sample from the FTO, this surface is the last layer received light that will reflect the light into the photoanod. As shown in figure 3(b), there is difference in light absorption when the DLC is the first receiving layer compared to the last. Our results show DLC act as a light collection layer.
3.3. Photocurrent–voltage

The photocurrent–voltage ($J-V$) characteristics of the QDSSCs photoanodes were measured at 100 mW cm$^{-2}$ light intensity for Ag NPs and DLC thin films. The $J-V$ curves are shown in figure 4 illustrates the strong increase in open-circuit voltage $V_{oc}$ and short-circuit current density $J_{sc}$ values of TiO$_2$/Ag/CdS/G/DLC. The corresponding photovoltaic parameters are listed in table 2.

![Figure 3. The effect of Ag NPs and DLC in absorption spectra of photoanodes.](image)

![Figure 4. The photocurrent–voltage ($J-V$) characteristics of the QDSSCs with Ag NPs and DLC thin film.](image)

For TiO$_2$/CdS/G photoanode the $V_{oc}$, $J_{sc}$, and fill factor (FF) are 0.24 V, 8.87 mA cm$^{-2}$ and 0.374 respectively. Furthermore, the power conversion efficiency is 0.80%. Table 2 shows all parameters enhanced in TiO$_2$/CdS/G/DLC photoanode which compared to TiO$_2$/CdS/G photoanode. Most of the changes are seen in $J_{sc}$ (from 8.87 to 14.6 mA cm$^{-2}$) and power conversion efficiency is 97% improved (from 0.80 to 1.58). In silicon solar cells $J_{sc}$ in the presence of DLC thin film reduced [13], but in the present study, $J_{sc}$ shows a significant increase. The DLC thin film Deposition on photoanodes surface raise $V_{oc}$ to 0.28 V. In fact, DLC thin film, such as a barrier, decrease electron transfer and recombination of photoelectron generated in CdS QDs with electrolyte. This layer contacts with the electrolyte solution, and since the synthesized electrolyte water-based has a refractive index less than DLC about 1.33 and 2.2 [34] respectively, total internal reflection occurs. In this way, light remission to QDs increase photon harvesting and finally increase photoelectron generation. On the other hand, the anti-corrosion effect of DLC thin film makes cells more stability and not destruction by the electrolyte.

According to table 2, Ag NPs decorated TiO$_2$/Ag/CdS/G photoanode enhance cell characterization. So that power conversion efficiency recorded on 1.80, twice increase, and a significant increase in $J_{sc}$ to 18.8 mA cm$^{-2}$. Previous studies proved the strong field around the Ag NPs [35–37]. In this situation, electrons in the quantum dots exited in two ways: the direct absorption of light and the interaction between the QDs and the Ag NPs localized surface plasmon resonance (LSPR), this means that photon remission in the Ag NPs caused the increased photon harvesting in CdS QDs and photoelectron generation. The second factor is the reason for the increase $J_{sc}$ in comparison to the samples without Ag NPs.

As the band diagram of figure 5 shows, the CdS QDs and graphene are sites for the generation the electron-hole pairs that transferred to Ag NPs. According to the band diagram, the Ag Fermi level is below the TiO$_2$ conductive band [8, 15, 18, 38]. But the effect of Ag NPs LSPR on sites of electron-hole pair generation was so significant that increased the short circuit current and power conversion efficiency. As reported in previous studies, decorated photoanodes with Ag NPs causes these nanoparticles to join electrolyte [39]. The Ag$^+$ ions formed by electrolyte corrosion can act as recombining centers [39]. For the following reasons, consider DLC to be electron barrier: (i) chemically neutral properties of DLC [40–42] case no interaction with the electrolyte. (ii)
Wide optical bandgap of DLC thin film [13, 15, 42–44] prevent photoelectron generated in G and CdS QDs transfer to electrolyte. (iii) Total reflectance occurs due to the higher refractive index of the DLC (2.2) [34] than the aqueous electrolyte solution case remission light and enhanced photon harvesting in CdS QDs. The DLC coating on this structure prevents corroboration of nanoparticles by the electrolyte. The simultaneous presence of DLC thin film, and Ag NPs optimized properties for the cell.

4. Conclusions

In this study, we investigated cells performance and optical characteristics of QDSSCs that TiO2/ CdS/G photoanodes covered by DLC thin film and decorated by Ag NPs. The silver nanoparticles LSPR act as photon remission in the photoanode structure. This effect increased light harvesting in CdS QDs and increases the photoelectron generation. Consequently, photocurrent $J_{sc}$ increased. The increased in the short circuit current and the power conversion efficiency due to DLC thin film. DLC thin film, act as a dense transparent layer compared with electrolyte caused total reflective and remission photon to QDs, increases the absorption of light in the visible region and also prevents corrosion nanoparticles joined with electrolyte. Also, because increasing $V_{oc}$ attributed barrier DLC thin film that decreases recombination of photogenerated electrons in QDs with electrolyte. The effect of Ag NPs LSPR increased the short circuit current, and power conversion efficiency. In this case, the concurrent effect of DLC and Ag NPs on the efficiency of TiO2/CdS/G photoanode increased from 0.80% to 1.80%. Furthermore, using the Ag NPs and DLC thin film also resulted in an increase in open circuit voltage (20%) and short circuit current more than twice (18.8 mA cm$^{-2}$).

### Table 2. The photocurrent–voltage ($J$–$V$) characteristic of the QDSSCs with DLC and Ag NPs.

| Sample            | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF  | $\eta$ (%) |
|-------------------|-------------|--------------------------|-----|-------------|
| TiO2/CdS/G        | 0.24        | 8.87                     | 0.374| 0.80        |
| TiO2/CdS/G/DLC    | 0.28        | 14.6                     | 0.377| 1.58        |
| TiO2/Ag/CdS/G/DLC | 0.29        | 18.8                     | 0.330| 1.80        |

### Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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