SIMULATION OF CHARGE CARRIER TRANSPORT MECHANISMS FOR QUANTUM DOT-SENSITIZED SOLAR CELL STRUCTURES

Ana Bărar [1], Doina Mănăilă-Maximean [2], Marian Vlădescu [3], and Paul Şchiopu[4]

This paper theoretically demonstrates the improvement of the incident-photon-to-current conversion efficiency (IPCE) with quantum dot doping for a ruthenium-based dye-sensitized solar cell. Due to the photon upconversion properties of quantum dots, the incident radiation in the 550-700 nm range is converted to the 350-460 nm range, which covers the 400 nm absorption peak of ruthenium, which is unexploited by the solar emission spectrum. This conversion provides an IPCE improvement of approximately 5%, which makes quantum-dot doping of dye-sensitized solar cells a viable technique for efficient solar energy harvesting.

Keywords: photovoltaic cell, dye-sensitized solar cell, ruthenium, quantum dots

1. Introduction

Dye-sensitized solar cells are an interesting alternative to inorganic photovoltaic devices, due to a series of advantages, such as simple, cost-effective fabrication technology and materials. The state-of-the-art dye-sensitized solar cell (DSSC) consists of a semiconducting titanium dioxide (TiO_2) layer, deposited on an ITO-coated glass substrate, and photosensitized through doping with dye molecules. The photosensitized TiO_2 layer, which represents the anode, is sandwiched against a second glass substrate, treated with a thin, metallic layer, which plays the role of the cathode. Finally, this structure is filled with a liquid electrolyte and sealed, in order to prevent leakage. The architecture previously described is illustrated in Figure 1. Alternative materials and structures, such as liquid crystal/polymer composites [1, 2] and liquid crystals dispersed in electrospun cellulose network [3–5], have also been extensively studied, and their superior responses to electric and magnetic fields makes them good candidates for photovoltaic applications. The main charge transport mechanisms that take place in dye-sensitized structures are hopping [6] and diffusion [7]. The internal parameters of the cell are determined through numerical methods, such as the Lambert W function [8, 9].

[1] Lecturer, Department of Electronic Technology and Reliability, University POLITEHNICA of Bucharest, Romania, e-mail: ana.d.barar@gmail.com

[2] Professor, Department of Physics, University POLITEHNICA of Bucharest, Romania

[3]Associate Professor, Department of Electronic Technology and Reliability, University POLITEHNICA of Bucharest, Romania

[4] Professor, Department of Electronic Technology and Reliability, University POLITEHNICA of Bucharest, Romania

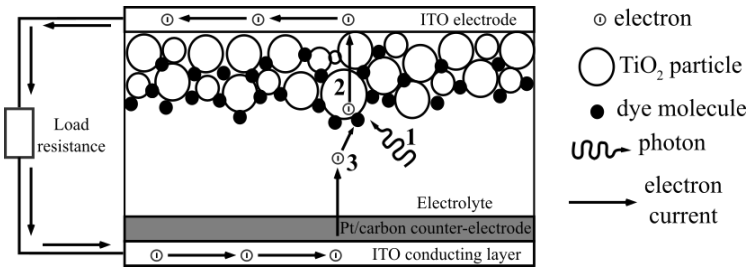

Fig. 1. Basic structure of a dye-sensitized solar cell [10]: 1 - An incoming photon is absorbed by the dye molecule, and it generates a free electron. 2 - The free electron diffuses through the TiO_2 layer and is collected at the electrode, which consists of both an ITO layer and TiO_2 molecules. 3 - The free electron is transported to the Pt/carbon counter electrode through the load resistance and is transported back to the dye molecule through the electrolyte layer by means of redox reactions.

The first dye-sensitized solar cell prototype was developed by Gratzel et al. [10], and it provided an efficiency of $7.1 - 7$ .9%. The highest efficiency recorded with a dye-sensitized prototype is over 14%, as reported in [11]. However, this value is still low, compared to the average efficiency obtained with commercial silicon solar cells ($\approx 20\%$) [12]. This poor efficiency of DSSCs is due to a number of reasons, such as sensitivity to high temperatures [13] and the limitation caused by light absorption spectrum of the dye, which is the interest of this paper.

The dyes that are most frequently used in TiO_2 photosensitization are ruthenium-based [7, 14–16]. As shown in Fig. 2, the light absorption spectrum of a commercial ruthenium-based dye (N719) has two absorption peaks, in 400 nm and 550 nm, respectively. It is also shown that the solar (AM1.5) emission spectrum only covers the 550 nm absorption peak, and the 400 nm peak is, therefore, not exploited, which leads to a reduction of the cell's potential efficiency. It should also be noted that the emitted radiation in the range of 600-800 nm is hardly absorbed by the N719 dye, and is, therefore, also unexploited.

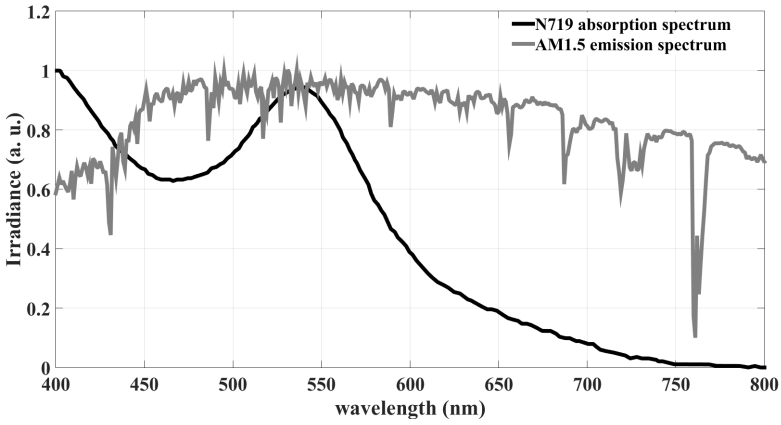

Fig. 2. Cross-reference between the AM 1.5 solar irradiance spectrum and the absorption spectrum of a ruthenium-based dye (N719) sample [17].

An alternative to converting the unused 600-800 nm radiation into 350-460 nm and, therefore, exploit the 400 nm absorption peak of the N719 dye, is to dope the photosensitized TiO_2 layer with graphene quantum dots. Quantum dots are widely known for their photon upconversion property [18–21] and, particularly, graphene quantum dots have been reported to upconvert radiation from 550-700 nm into 350-460 nm radiation [22].

This paper reports the theoretical study of a dye-sensitized solar cell doped with graphene quantum dots, focusing on the variation of its incident-photon-to-current-conversion efficiency (IPCE) and its short-circuit current (I_{sc}) as functions of quantum dot concentration in the cell. The performed simulations demonstrate an improvement in IPCE with the increase of quantum dot concentration, and also provide an optimum quantum dot concentration of $C_{QD} = 1.2\ mol/cm^2$.

2. **Proposed model**

For this theoretical study, a DSSC structure, whose TiO_2 is sensitized with an N719 ruthenium-based dye and graphene quantum dots, is considered. The study focuses on the variation of the incident-photon-to-current conversion efficiency (IPCE), which is defined as the ratio of extracted free charge carriers, measured as the photocurrent, to incident photons. The IPCE is given by the product between the light harvesting efficiency of the dye, the quantum yield of electron injection from the excited dye molecules into the TiO_2 layer, and the electron collection efficiency of the electrode from the TiO_2 layer:

$$IPCE(\lambda) = LHE(\lambda) \cdot \Phi_{inj} \cdot \eta_{coll} \tag{1}$$

where $LHE(\lambda)$ is the light harvesting efficiency of the dye, at a given wavelength λ. The $LHE(\lambda)$ is the ratio of incident photons absorbed by the dye to the total photons incident on the cell, and it is given by the following relation:

$$LHE(\lambda) = 1 - \exp(-\alpha_{abs} d) \tag{2}$$

where α_{abs} is the absorption length of the dye, and d is the thickness of the dye layer. Φ_{inj} is the electron injection efficiency, from the excited dye molecules into the TiO_2 layer. The electron injection efficiency is given by the amount of absorbed incident photons, which are converted into free electrons. η_{coll} is the charge collection yield, given by the ratio between the number of electrons collected by the electrode, and the total number of electrons injected in the TiO_2 layer. The purpose of this study is to verify if the insertion of quantum dots in a dye-sensitized structure improves its $IPCE$.

Furthermore, the study also focuses on the variation of the short-circuit current (I_{sc}) of the structure with quantum-dot concentration, in order to determine an optimum quantum dot concentration for $IPCE$ improvement.

3. **Results and discussions**

The simulation yielded an increase in $IPCE(\lambda)$ with quantum dot concentration. The results are illustrated in Fig. 3.

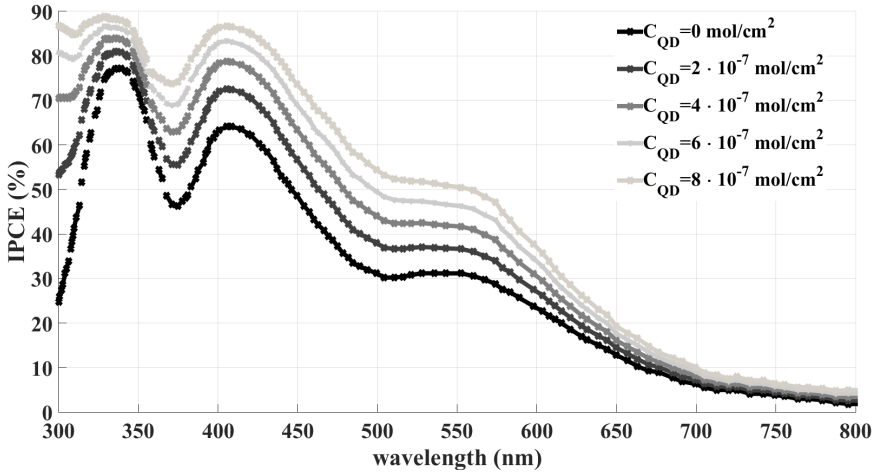

Fig. 3. IPCE of the considered DSSC sample, for different graphene quantum dots concentrations

The *IPCE* of the structure is improved, particularly in the range of 300-400 nm. This is due to the graphene quantum dot upconversion, which provides a surplus of photons with wavelengths comprised in that range, as discussed earlier in this paper.

The results presented in Figure 3 demonstrate the positive impact that quantum dot concentration increase has on the cell's photon-conversion efficiency. However, this result is still vague, since an optimum quantum dot concentration is needed. In order to obtain this concentration, the short-circuit current I_{sc} of the cell was calculated as a function of the quantum dot concentration in the cell. The resulting variation is presented in Fig. 4.

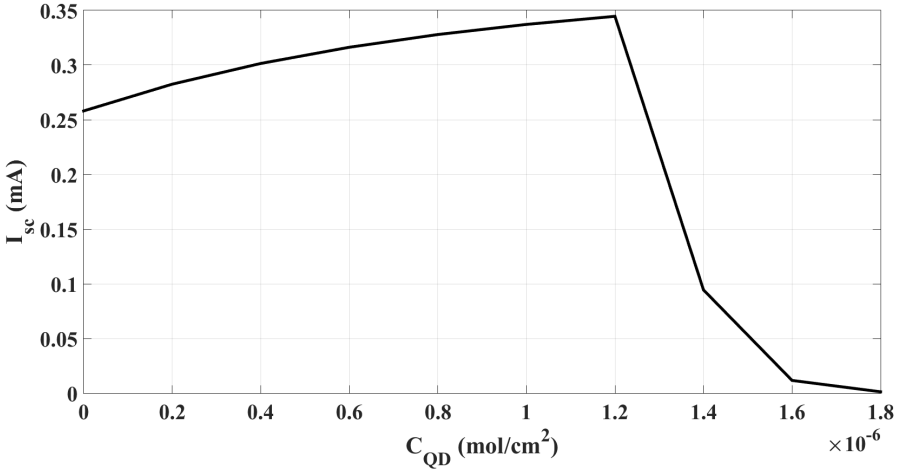

Fig. 4. Variation of the short-circuit current I_{sc} with graphene quantum dots concentration, for the considered DSSC sample

Short-circuit current I_{sc} increases with quantum dot concentration, it reaches a maximum at $C_{QD} = 1.2 \cdot 10^{-6}\ mol/cm^2$, thus yielding the optimal quantum dot concentration

for the considered dye-sensitized structure. However, short-circuit current decreases for quantum dot concentrations over $1.2 \cdot 10^{-6}\ mol/cm^2$. A high number of quantum dots absorb the greatest part of incident photons, leaving very little radiation for the dye molecules to absorb, therefore interfering with the incident-photon-to-current conversion process and reducing the cell's short-circuit current.

4. Conclusions

It has been theoretically demonstrated that the incident-photon-to-current conversion efficiency *IPCE* of a ruthenium-based DSSC sample is improved with graphene quantum dot doping. Graphene quantum dots upconvert radiation from 550-700 nm into 350-460 nm radiation, which exploits the UV absorbtion maximum of ruthenium-based dyes.

The $IPCE\,(\lambda)$ of a ruthenium-based DSSC structure, doped with graphene quantum dots, was theoretically calculated for different graphene quantum dot concentrations. The results demonstrated that the presence of quantum dots in the DSSC structure improve the sample's *IPCE*, especially in the 300-400 nm absorbtion range.

An optimum graphene quantum dot concentration was also theoretically obtained $\left(C_{QD} = 1.2 \cdot 10^{-6} \quad mol/cm^2\right)$, by studying the variation of the short-circuit current I_{sc} as a function of quantum dot concentration, for the considered sample.

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