RESEARCH PAPER

Effect of Various Shapes of Silver Nanoparticles on the Performance of Plasmonic Solar Cells Active Layer

Rupak Wasman Qadir\textsuperscript{1}, Karwan Wasman Qadir\textsuperscript{2,3*}, and Shujahadeen B. Aziz\textsuperscript{4,5}

\textsuperscript{1}Physics Laboratory, Erbil Environment Office, 44001 Erbil, Iraq
\textsuperscript{2}Department of Physics, College of Education, Salahaddin University-Erbil, 44001 Erbil, Kurdistan Region, Iraq
\textsuperscript{3}Department of Physics Education, Faculty of Education, Tishk University, 44001 Erbil, Iraq
\textsuperscript{4}Advanced Polymeric Materials Research Lab., Department of Physics, College of Science, University of Sulaimani, Qlayasan Street, Sulaimani, Kurdistan Regional Government-Iraq
\textsuperscript{5}Komar Research Center (KRC), Komar University of Science and Technology, Sulaimani, 46001, Kurdistan Regional Government, Iraq

ABSTRACT:
In this work, the enhancement of optical absorption in organic thin film active layer was investigated theoretically. The optical absorption results reveal that the introduction of periodic silver (Ag) nanoparticles (NPs) into the thin film active layer influences the absorption spectra. In this study, copper phthalocyanine (CuPc) as one of the organic solar cell materials has been used. Finite Different Time Domain technique has been used to demonstrate the role of the three different shapes of the silver nanoparticles (SNPs). It has been found that the NPs can result in broadband optical absorption enhancement in the wavelength range (350-550) nm due to the surface plasmonic resonance (SPR) phenomena. Moreover, the investigation has been performed the effect of the few shapes of (Cylinder with radius (R) = 20 nm and height (H) = 60 nm, radius (R) = 30 nm for Sphere NPs, and Ellipse NPs with radius R\textsubscript{1}, R\textsubscript{2} of 20 and 30 nm respectively) on the absorption in the organic thin films.

KEY WORDS: CuPc; plasmonic solar cell; Finite Different Time Domain; optical absorption enhancement; Silver Nano shapes.

INTRODUCTION:
Recently plasmonic effects have attracted much attention in solar cell research because they are deemed to be able to dramatically boost the efficiency of thin-film solar cells (Chen et al., 2012). In particular, the significant advances in nanoscale plasmonic open up new solutions for thin-film solar cells to improve light absorption and thus performance without varying their thickness (Gwamuri et al., 2013).

In addition, utilizing metal nanoparticles (NPs) with plasmonic enhancement effect is considered as one of the promising methods for increasing the optical absorption of solar cells (Wang et al., 2010, Qu et al., 2011, Yang et al., 2014). Light-trapping effects increase solar cell absorption and enhance the short-circuit photocurrent density (J\textsubscript{sc}) of not only new generation solar cells (organic solar cells and dye-sensitized solar cells) (Atwater and Polman, 2010), but textured screen-printed silicon solar cells (Zhang et al., 2012) which dominate the photovoltaic market (Catchpole and Polman, 2008). Using plasmonic light-trapping to increase the J\textsubscript{sc} of textured screen-printed solar cells by more than 2.5% is challenging (Zhang et al., 2012). Moreover, noble metal nanostructures that can concentrate and guide light have demonstrated...
the excellent capability for dramatically improving the energy conversion efficiency of both laboratory and industrial solar cells, providing an innovative pathway potentially transforming the solar industry (Gu et al., 2012). The metal NPs cannot only scatter and couple the incident light into the active layer but also confine the light surrounding their surfaces, which results in the light absorption enhancement of solar cells (Qu et al., 2011). Sub wavelength metal nanoparticles can support optically driven localized surface plasmons (Maier and Atwater, 2005). Indeed, the free electron of such NPs features a resonant oscillation upon illumination in the visible part of the spectrum. The spectral properties of this resonance depend on the constitutive material, the geometry of the NP and its environment. This resonant electronic oscillation is called localized surface plasmon (LSP), and the field of research that studies the fundamentals and applications of LSP is known as nanoplasmonics (Baffou and Quidant, 2014). Two types of plasmonic resonances, surface plasmon resonances (SPRs) and localized plasmonic resonances (LPRs), can be used for enhancing light absorption (Li et al., 2012). A surface plasmon is an optically generated wave, which propagates along a metal/dielectric interface. In tuning the light excitation, resonance can occur when the frequency of the incident photons equals the collective oscillation frequency of conduction electrons of metallic particles. Which is in photonics, this domain is known as appellation plasmonic (Duche et al., 2009). For different kinds of solar cell, the role of these two corresponding effects (i.e., surface plasmon enhanced scattering effect and localized surface plasmon (LSP) based field enhancement effect) in improving the light trapping should be different (Atwater and Polman, 2010). For silicon-based solar cells, the surface plasmon enhanced scattering effect dominates the optical enhancement, which had been demonstrated by our group and other researchers (Yang et al., 2011).

Plasmonic metal nanostructures have been incorporated in an active layer made from polymer blend and a highly conductive buffer layer of poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) for enhancing light trapping properties of organic solar cells (OSC) (Zhang et al., 2013, Li et al., 2012). There are three different configurations of NPs that have been reported in the literature. First, Metallic NPs integrated with contact on the back of the solar cell, second, Metallic NPs placed on the front surface of the solar cell and third, Metallic NPs embedded inside of the active layer of solar cells (Qadir et al., 2014). In general, it is beneficial to place metal nanostructures on the rear side of the solar cell (Niesen et al., 2013). This is mainly because at the front of the cell they could give rise to destructive Fano interference and would parasitically reflect and absorb a significant amount of incident light before it reaches the active layer (Niesen et al., 2013).

In this work, the plasmonic effect of metallic (MNPs) on the absorption enhanced of Copper phthalocyanine (CuPc) organic thin film using the Finite Different Time Domain (FDTD) technique has been presented. In the case of study, silver NPs have been selected because they show superior scattering efficiency to any other metal NPs. The aim of our study was to investigate the effect of the shapes of Ag-nanoparticles (NPs) on the light absorption and carriers’ generation in organic thin films.

2. MATERIALS AND SIMULATION METHODS

Copper phthalocyanines is a Phthalocyanine that has a central copper atom bound by secondary valences of the isoindole nitrogen atoms, and which is blue in color. As a kind of critical photovoltaic materials, copper phthalocyanines (CuPc) have received increasing attention over the last decade (Siégert et al., 2016, Leznoff and Lever).

Among various methods, the FDTD method, also called the Yee algorithm, have been chosed of reported results. This modeling technique is used to solve Maxwell’s equations, in differential form over a grid-based domain. Since the FDTD method calculates the electric (E), and magnetic (H), fields everywhere in the computational domain as they evolve in time, it is straightforward to simulate the electromagnetic field movement through the model (Gu et al., 2012). In the simulation method, the optical constants of copper phthalocyanines (CuPc) and silver Ag were taken from ref. (Djuršić, 2019)

ZANCO Journal of Pure and Applied Sciences 2019
and (Palik, 1991), respectively. Using the Lumbrical FDTD technique, we chose three Ag-NP in order to embed inside CuPc thin films. The thickness of CuPc films was 80 nm. The ellipse NPs with radius ($R_1$) = 20 nm and $R_2 = 30$ nm, while radius ($R$) = 20 nm and height ($H$) = 60 nm for the cylinder NPs, and $R = 30$ nm for sphere NPs. The absorbance ($A$), reflectance ($R$) and transmittance ($T$) were calculated by placing the monitors at the proper places as shown in Figure 1. Perfectly matched layer (PML) absorbing boundary conditions are used on the upper and lower boundaries in the z-axis direction, and periodic boundary condition (PBC) for x-axis and y-axis are used on both sides. For each shape, we selected $(0.1 \times 0.1 \times 1)$ μm as simulation dimensions. The simulation was performed over the visible region of the solar spectrum. In the “Lumerical FDTD Solution” software in this study, the absorption rate is calculated as a function of wavelength for a flat spectrum. This is automatically done using Continuous Wave (CW) normalization in “FDTD Solutions” software. The sunlight is modelled with a plane-wave source. The power absorption is calculated by solving Maxwell’s equations. Absorbed power $L(\vec{r}, \lambda)$ per unit volume at each wavelength. In this study, we theoretically investigate the effect of introducing metallic Ag nanoparticle in thin-film CuPc on their optical absorption efficiency. We selected three different shapes of silver nanostructure as the research object. Firstly, we divided Ag nanostructure shapes into three types such as cylinders, spheres, and ellipses.

**Figure 1.** FDTD optical model For CuPc thin film.

### 3. RESULTS AND DISCUSSION

In order to investigate the effect of NSs on the absorption efficiency of CuPc, the combinations of the absorber layer vs NP shapes have been studied. The Lumerical FDTD optical simulation has been employed to exploit the ultimate efficiency potential for different NPs as a function of shapes of the NPs. The optical properties of CuPc thin films before and after embedding MNPs have been studied in the spectral range (300 – 800) nm.

In Figure 2/A we compare the reflection spectra of CuPc thin film without Ag NPs and CuPc thin film with Ag NPs, i.e. CuPc with the cylinder, ellipse and sphere NPs. It is clear that different Ag NPs shape has a different effect on reflection of light. Generally, reflection spectra of CuPc thin film were increased after embedding Ag NPs especially in the wavelength range of (380) nm onwards. Figure 2/B shows light transition spectra of CuPc thin film without metallic NPs and CuPc thin film with the cylinder, ellipse and sphere NPs. As it can be seen from this figure, the light transition of CuPc organic thin film with metallic NPs is significantly decreased as compared of CuPc organic thin film without metallic NPs especially in the wavelength range of (350 - 600) nm and (700-800) nm. Clearly, different Ag NPs shape have a different effect on light transmission. Figure 2/C shows the absorption spectra in CuPc thin film without metallic NPs and CuPc thin film with the cylinder, ellipse and sphere NPs. As can be seen from this figure, the absorption spectra of CuPc organic thin film with metallic NPs are significantly enhanced as compared to the spectrum of CuPc organic thin film without metallic NPs. This improvement is evident in the wavelength range of 350–550 nm. It is noticeable in Figure 2/C that different Ag-NSs have different effects on the absorption enhancement. The data obtained from the simulations, compared with the experimental results from reference (Shamjijd et al., 2017). The experimental results might be in close agreement with the theoretical simulations in present work. In the case of CuPc with Ag-NSs, change in the particle shape (from cylinder to ellipse and sphere)
led to a reduction of the absorption in CuPc organic thin film. This may be due to the reduced near-field intensity for the shape of an ellipse and sphere NPs.

The influence of the silver nanoparticles on the performances of solar cells was investigated through the relationship between short circuit current density ($J_{sc}$), a parameter directly related to the light trapping effect of the solar cells. The ideal ($J_{sc}$) values were calculated within FDTD Simulation methods. It is evident that within the integrated particle the Photovoltaic parameter ($J_{sc}$) increased for the different NP shapes as shown in Figure 2/D. As shown from the result, after incorporating cylinder Ag-NPs into the CuPc layer, the short-circuit current ($J_{sc}$) increased significantly from (67.1 to 134) mA/cm$^2$, where the enhancement ratio was as much as two times which might be due to the induction of a strong near-field to enhance the absorption of the active layer because of the insertion of Ag-NPs (Qadir et al., 2014).

**Figure 2.** (A) Reflection, (B) Transition, (C) Absorption spectra of CuPc with different Ag NPs and (D) shows the photovoltaic parameter $J_{sc}$ for the various NPs shapes
4. CONCLUSIONS

In conclusion, this study demonstrated an increased optical absorption of an organic semiconductor material CuPc by embedding plasmonic Ag-NPs. The numerical simulation was performed to interpret the photocurrent enhancement via an FDTD model. By depositing the Ag-NPs inside CuPc thin layer, the plasmonic enhancement effect could be extended to a broader optical spectrum. The effects of different NPs shape on light absorption in CuPc thin films have been presented. It is shown that the absorption enhancement and $(J_s)$ with cylinder Ag-NPs are generally higher than that with the other Ag-NPs merely inside the active layer. The results show that the NP shapes have the potential effects on visible light scattering and absorption enhancement in CuPc thin films. The achievement of 66.854% enhancement in photocurrent, could be ascribed to light-trapping in the case of cylinder Ag-NPs. This study can also be useful for all types of organic sensors, thin films, and flexible solar cells to further improve their performances.

REFERENCES

ATWATER, H. A. & POLMAN, A. 2010. Plasmonics for improved photovoltaic devices. Nature materials, 9, 205.

BAFFOU, G. & QUIDANT, R. 2014. Nanoplasmonics for chemistry. Chemical Society Reviews, 43, 3898-3907.

CATCHPOLE, K. & POLMAN, A. 2008. Design principles for particle plasmon enhanced solar cells. Applied Physics Letters, 93, 191113.

CHEN, X., JIA, B., SAHA, J. K., CAI, B., STOKES, N., QIAO, Q., WANG, Y., SHI, Z. & GU, M. 2012. Broadband enhancement in thin-film amorphous silicon solar cells enabled by nucleated silver nanospheres. Nano letters, 12, 2187-2192.

DJURIŠIĆ, A. B. 2019. Organic Optoelectronic Devices Materials, Desine Rules.

DUCHE, D., TORCHIO, P., ESCOUBAS, L., MONESTIER, F., SIMON, J.-I., FLORY, F. & MATHIAN, G. 2009. Improving light absorption in organic solar cells by plasmonic contribution. Solar Energy Materials and Solar Cells, 93, 1377-1382.

GU, M., OUYANG, Z., JIA, B., STOKES, N., CHEN, X., FAHIM, N., LI, X., VENTURA, M. J. & SHI, Z. 2012. Nanoplasmonics: a frontier of photovoltaic solar cells. Nanophotonics, 1, 235-248.

GWAMURI, J., GUNEY, D. & PEARCE, J. 2013. Advances in Plasmonic Light Trapping in Thin-Film Solar Photovoltaic Devices. Solar cell nanotechnology, 241-269.

LEZNOFF, C. & LEVER, A. Phthalocyanines: Properties and Applications (VCH, New York, 1989). Google Scholar.

LI, X., CHOU, W. C., HOU, L., XIE, F., SHA, W. E., DING, B., GUO, X., LI, Y., HOU, J. & YOU, J. 2012. Dual plasmonic nanostructures for high performance inverted organic solar cells. Advanced Materials, 24, 3046-3052.

MAIER, S. A. & ATWATER, H. A. 2005. Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. Journal of applied physics, 98, 10.

NIESEN, B., RAND, B. P., VAN DORPE, P., CHEYNS, D., TONG, L., DMITRIEV, A. & HEREMANS, P. 2013. Plasmonic efficiency enhancement of high performance organic solar cells with a nanostructured rear electrode. Advanced Energy Materials, 3, 145-150.

PALK, E. 1991. Handbook of Optical Constants of Solids. University of Maryland, College Park, U.S.A., Academic Press.

QADIR, R. W., AHMAD, Z. & SULAIMAN, K. 2014. Effect of the shapes of nanostructures on the light absorption in organic thin films. Journal of Modern Optics, 61, 636-640.

QU, D., LIU, F., HUANG, Y., XIE, W. & Xu, Q. 2011. Mechanism of optical absorption enhancement in thin film organic solar cells with plasmonic metal nanoparticles. Optics Express, 19, 24795-24803.

SHAMJID, P., ANJUSREE, S., AMEEN, M. Y. & REDDY, V. 2017. Performance enhancement of polymer solar cells by incorporating Ag nanoparticles at an indium tin oxide/MoO3 buffer layer interface. Semiconductor Science and Technology, 32, 065010.

SIEGERT, B., DONARINI, A. & GRIFONI, M. 2016. Nonequilibrium spin crossover in copper phthalocyanine. Physical Review B, 93, 121406.

WANG, H., LIU, Y., LI, M., HUANG, H., XU, H., HONG, R. & SHEN, H. 2010. Multifunctional TiO2 nanowires-modified nanoparticles bilayer film for 3D dye-sensitized solar cells. Optoelectron. Adv. Mater. Rapid Commun, 4, 1166-1169.

YANG, L., XUAN, Y. & TAN, J. 2011. Efficient optical absorption in thin-film solar cells. Optics express, 19, A1165-A1174.

YANG, X., LIU, W., XIONG, M., ZHANG, Y., LIANG, T., YANG, J., XU, M., YE, J. & CHEN, H. 2014. Au nanoparticles on ultrathin MoO3 sheets for plasmonic organic solar cells. Journal of Materials Chemistry A, 2, 14798-14806.

ZHANG, D., CHOW, W. C., XIE, F., SHA, W. E., LI, X., DING, B., ZHANG, K., HUANG, F. & CAO, Y. 2013. Plasmonic Electrically Functionalized TiO2 for High-Performance Organic Solar Cells. Advanced Functional Materials, 23, 4255-4261.

ZHANG, Y., OUYANG, Z., STOKES, N., JIA, B., SHI, Z. & GU, M. 2012. Low cost and high performance Ag nanoparticles for broadband light trapping in Si wafer solar cells. Applied Physics Letters, 100, 151101.