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Computational investigation of the effect of metal plasmonic on the hole transport of polymer solar cell --Manuscript Draft--

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Keywords:	ZnS nano-particle; Charge transport, Photons-harvesting, Organic solar cell
Abstract:	<p>Semiconductor organic solar absorber exhibits poor charge transport process because of exciton short diffusion length, short life time, and poor carrier mobilities in the medium. Such transport properties have negatively impacted the performance of organic solar cells (OSC). This article is designed to investigate the effect of solar absorber thickness and metal plasmonicnanoparticles using the most popular polymer blend (P3HT:PCBM) via SCAPS device simulation program. Bulk hetero-junction (BHJ) design of OSC has partially addressed the challenges by increasing inter-facial area of the acceptor/donor (A/D) molecules, which boosts the generation of free charges. However, the collection of these charges hindered due to low carrier mobilities in polymer medium. Significant influence of the Zinc Sulfide(ZnS) metal nanoparticles(NPs) have been observed on the performance of OSC at various concentrations. Thus, we are reporting here the effect of absorber layer thickness and ZnSNPs on the charge transport process in OSC.</p>

Reviewers Comments

Reviewer #1: The paper is about the simulation of a polymer solar cell with various layers. The authors conducted simple modelling, and the results were not discussed enough. I have the following comments.

1. The manuscript's title suggests an "investigation of the effect of metal plasmonics", but the study does not provide any information on the modeling of plasmonic effects. Additionally, the SCAPS software does not account for the phenomenon of local surface plasmon resonance. Instead, the study only involves modelling J-V curves for systems with the ZnS layer, which the authors associate with nanoparticles in some way. It is unclear absolutely how the modelling process took into account the effects, which are described in Section II.

Reply: The authors are grateful for this comment of the reviewer. The authors agree with the fact that SCAPS do not take into account LSPR into the charge transport equations, which the program is based. Our investigation is based on the design of the device architecture to study the effect of plasmonic on the solar cell performances. According to the Fig.2 provided in our manuscript we introduced a thin layer of ZnS just before the hole transport layer of the device to see the effect of the Nano-particles. Despite all the limitation of the SCAPS program, our investigation showed the impact of the ZnS on the transport properties and performance of the solar cell.

2. The authors correlate changes in the parameters of the solar cell (pages 4, 7, and Conclusion) with changes in the shunt resistances and series resistances. Although determining these resistances from the current-voltage characteristics is a standard procedure, the study did not perform it. Therefore, the statement about the influence of resistance appears unsubstantiated.

Reply: The authors agree with the referee's comments. The shunt and series resistance are some of the expected outcomes from the effect of additional factors in the analysis of the device performance of a solar cell. However, the discussion based on R_s and R_{sh} is removed from the conclusion section since they have already been dealt in the body of the results and discussion part of the manuscript.

3. The authors mention real structures several times (on page 2 and in the Acknowledgments for SEM and TEM measurements). However, the study does not present any experimental results for these real structures, specifically with SEM and TEM. Including such results could have potentially confirmed the study's conclusions.

Reply: The authors have included the structural studies of ZnS using TEM in the revised manuscript. Additional discussions are included in section IVc.

4. The purpose of Section IV.B is unclear as it provides general information and several dependencies obtained through SCAPS. The determination of the built-in potential was performed for only one thickness of the absorber layer, and a narrow range of the voltage-capacitance dependence was chosen. It is unclear why the dependence is nonlinear for different voltage ranges, and the magnitude of the built-in potential is not compared to any other value or literature data.

Reply: Authors have re-written this section to remove the ambiguity in this part of the manuscript. The section generally starts with discussion based on the results obtained from

device simulation and then extended the discussion to get more parameters such as capacitance. Authors have made the necessary effort to make the discussion clearer and provided additional justification for extraction device capacitance.

5. All three highlights make the same claim. This indicates that even the authors themselves feel that the results of their work are not very diverse.

Reply: ZnS nanoparticle has wide range of application as indicated in the manuscript. The focus authors attention here is mainly on the impact of ZnS on thin film organic solar cell. However, taking the referee's comment into consideration, authors have improved the highlight of the manuscript in the revised version.

6. According to pages 6 and 7, ZnS has an impact on both absorption and charge collection. However, no explanation or discussion is given regarding how this effect arises. The study's findings consist of SCAPS-calculated dependencies (J-V, C-V EQE-wavelength) for structures with differing absorber layer thicknesses. Most of the text covers familiar material or the dependencies themselves without proper analysis ("what you seeing what you get").

Reply: Authors are grateful for this comment. The impact of ZnS on optical absorption and charge collection has been viewed as follows. In optical absorption ZnS plays the role of electron band to band transition which evident on absorption at low wavelength region. Moreover, ZnS induces light scattering at the interface which increase optical path length in polymer medium that eventually assist light trapping. By improving conductivity between interfaces ZnS enhance collection of charges. We have included supporting discussion and images on ZnS and how it is important on the performance of TFOSC.

Additionally, the paper suffers from poor preparation. Namely,

7. There is no information about other layers of the solar cell besides P3HT:PCBM and ZnS. Table I is extremely inconvenient.

Reply: Additional information on the physical parameters of other layers are provided in revised manuscript.

8. Figure 1b is not relevant to the study - the simulated solar cell does not include a silicon layer with embedded metal nanoparticles.

Reply: Authors are grateful for this comment. The absorber layer is changed to P3HT:PCBM layer. The purpose of this figure is to show the bending of the energy levels at the interface. We have corrected the absorber layer to polymer blend.

9. The scale for most curves in Figure 4 is chosen extremely poorly.

Reply: The scale used in Fig. 4 has suppressed the Voc values which are less than 1. The scale of Fig. 4 is improved in the revised manuscript.

10. The captions for Figures 5 and 10 are incorrect.

Reply: The errors are corrected in the revised manuscript.

11. There is no information on what distinguishes the curves in Figure 5.

Reply: Authors have provided additional information on the Figure 5 and tried to address on the referee's concern.

12. The data in Table II duplicate Figure 4. The same applies to Table III and Figure 11.

Reply: The data in Table II and Table III are not the same. There is close proximity on the data but are not the same. Table II is without ZnS and Table III is with ZnS.

13. On page 3, it is stated that "These results agree with the experimental results found in reference [26]." However, the similarity to the results of [26] is subjective.

Reply: In addition to the reference [26] and now [27] cited earlier, we have added ref[28] reported based on experimental investigations. The results are surprisingly similar with the simulation results provided in the manuscript.

14. On page 4, it is stated that "The maximum power conversion efficiency was found at an absorber layer thickness 200nm as shown in Figure 3." However, this is not visible in Figure 3.

Reply: The statement refers to the J-V curves from which the performance of the devices are drawn. There will be no figure to show on performance of the solar cell except J-V curve.

15. Comparison with the results of [28] is not relevant, as paper [28] does not relate to organic solar cells.

Reply: We apologise for mis quote. This is to mean ref [27].

16. The expected advantages of using ZnS nanoparticles compared to other materials are not specified.

Reply: ZnS is a naturally occurring salt which is the main source of Zn in nature. It is environmentally stable and it has wide range of applications compared to other sulphides such as AgS, CdS and many others. Furthermore, ZnS has high electron affinity and electron mobility which can serve electron transport buffer layer in Polymer solar cell by replacing LiF.

17. On page 6, it is stated that "This performance is much better than that of Pristine." The difference is only 0.6%.

Reply: Yes, it is about 19% change from undoped (Pristine). It is a good performance change in the views of the authors given the high precision of the theoretical calculations.

18. On page 6, it is stated that "It has been observed in many experiments that the large weight of NPs results in poor-performing devices," but corresponding references to these results are not provided.

Reply: The authors have provided the reference [28] and additional image of ZnS which have been used in our previous experimental investigation and cited in the revised manuscript. The word "weight" is replaced by concentration.

19. On page 6, it is stated that "From Figure 5, the 3 nm has the highest maximum power compared to other curves (9 nm to 12 nm)." However, Figure 5 does not relate to structures with different ZnS thicknesses.

Reply: Yes, it is an error from our side. It is meant to refer Fig. 10. It is corrected in the revised version of the manuscript. Figure 10 showed the performance of the devices in terms of J-V curves. All the device parameters are drawn from Fig. 10 and tabulated in Table 3.

20. On pages 6-7, it is stated that "Increasing the concentration of nanoparticles increases the defects in a device material. The defects can poorly affect the photon absorption by the device material." However, these claims are not self-evident. For example, defects often cause additional light absorption and the appearance of additional spectral bands.

Reply: Defect in the manuscript refers to traps that can cause charge recombination and reduce charge collections. Yes, defect that intentionally incorporated like ZnS assists performance as indicated by the reviewers. Additional amendments are given in the revised manuscript.

21. In the Conclusion, it is stated that "The device program works under room temperatures, and allows single or batch calculations at once." However, SCAPS allows calculations to be performed not only at room temperature. Additionally, this information, in my opinion, should not be included in the conclusions of the work.

Reply: Authors do agree with this referee comments. The sentence is removed from the conclusion of the manuscript as suggested.

22. The manuscript requires editing, for instance, it often includes capital letters in the middle of sentences and lowercase letters after periods.

Reply: Authors have made substantial editorial work. All the referee's concerns are corrected in the revised manuscript.

Reviewer #3: In this manuscript, the authors perform a computational study of P3HT:PCBM absorber layer thickness dependence of the performance of organic solar cells (OSC). The computational approach is sound and it is based on the efficient SCAPS simulator, which numerically solves the set of one-dimensional semi-conductor equations. Also the results fairly reproduce some of the experimental evidence already reported in the scientific literature, including the value of the highest efficiency which was found to be of the order of 3-4 %. I have just a few remarks for the authors' attention before the manuscript could be considered acceptable for publication:

1) I recommend a thorough revision of the text for eliminating all the language issues that I noted in the present version.

Reply: The authors are grateful for the referee comments. The manuscript thoroughly edited from language problems and some of the paragraphs even re-written to maintain high standard scientific publishing.

2) There are also other computational approaches which focus on improving the single-polymer properties relevant to the performance of OSCs, see e.g. Computational and Theoretical Chemistry 1070, 14 (2015), Journal of Physical Chemistry A, 125 10593-10603 (2021).

Reply: The authors considered the referee comments and suggestion in the revised manuscript. Some of the recommended references are used.

3) Carrier mobility can also be affected by polymer topology, or morphology of the film, see e.g. Physical Review E, 93, 050501 (2016), Macromolecules, 53, 15, 6151 (2020).

Reply: The authors took into account the referee comments and suggestion in the revised manuscript. Some of the recommended references are used.

Computational investigation of the effect of metal plasmonic on the hole transport of polymer solar cell

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(Dated: May 25, 2023)

Semiconductor organic solar absorber exhibits poor charge transport process because of exciton short diffusion length, short life time, and poor carrier mobilities in the medium. Such transport properties have negatively impacted the performance of organic solar cells (OSC). This article is designed to investigate the effect of solar absorber thickness and metal plasmonic nanoparticles using the most popular polymer blend (P3HT:PCBM) via SCAPS device simulation program. Bulk hetero-junction (BHJ) design of OSC has partially addressed the challenges by increasing inter-facial area of the acceptor/donor (A/D) molecules, which boosts the generation of free charges. However, the collection of these charges hindered due to low carrier mobilities in polymer medium. Significant influence of the Zinc Sulfide(ZnS) metal nanoparticles(NPs) have been observed on the performance of OSC at various concentrations. Thus, we are reporting here the effect of absorber layer thickness and ZnS NPs on the charge transport process in OSC.

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Keywords: ZnS nano-particle; Charge transport, Photons-harvesting, Organic solar cell

I. INTRODUCTION

Semiconductor polymers have attracted numerous research interests because of its application in photonic devices such organic solar cells (OSCs), organic light emitting diode(OLD), organic sensors etc. The market values organic molecules-based device is continuously growing by the introduction of new technology and applications. This article is trying to discuss some of the challenges of thin film organic solar cell. Organic solar has been under intense investigations for the past three decades due to its potential to generate cheap renewable energy from low cost solar panel. OSC is one of the few emerging solar cell technologies which is evolving to have high power conversion efficiency (PCE) required for mass production [1]. Hence, OSCs are expected to contribute towards renewable energy sector with high potential of reducing cost of device production, light weight, and flexible solar panel [2]. Even though OSCs offer such attractive features but they have drawback in terms of short life time, low efficiency and prone to oxygen and humidity that limits its penetration into energy market [3]. The first Photo-voltaic solar cell was fabricated from crystalline silicon in 1950s at the Bell laboratory. Since then the PCE of silicon based solar cell increases and approaching currently the theoretical limit 30% [4]. On the other hand, organic solar cells were introduced around 1990 [5] and the PCE continuously increasing to nearly 20% from single junction non-fullerene based OSC. The efficiency

of OSCs remains low relative to other emerging and established solar cell technologies due to the poor charge transport processes in organic medium.

Bulk heterojunction is the most successful design of solar absorber in OSC which creates large donor/accepter molecules interfaces for enhanced exciton dissociation [6]. Furthermore, BHJ is allowing an efficient charge dissociation by reducing recombination processes in the photo-active medium. Consequently, the OSCs research gained significant attention because of continuous growth in PCE. However, fullerene based OSC has an efficiency close to 14% because of poor energy band tunability and narrow optical absorption [7]. **One of the challenges in polymer solar cell is the short diffusion length of the excitons, which limits the thickness of the absorber layer to ≤ 200 nm for sufficient charge generation.** In this report, we have investigated the effect of ZnS doped hole transport layer and thickness dependence absorber layer on the performance of thin film solar cells. We employed device simulation program known as solar cell capacitance simulator (SCAPS) which is a one-dimensional device simulation program to investigate the effect of changes on the parameters under investigation. The metal nanoparticles in dielectrics medium exhibits a phenomenon called Local Surface Plasmon Resonance (LSPR) due to the interaction with incident electromagnetic radiation. The excitation of LSPR de-phases through a number of channels including, generation of hot electrons, near field enhancement, charge transfer, energy transfer and light trapping through scattering [8–10]. This investigation takes into account of the advantages of metal nanoparticles on improving charge dissociation and light trapping processes in the functional layers of the solar cell. The article is composed of background theory of metal plasmon, device simulation and discussion of the results.

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II. LOCALIZED SURFACE PLASMON RESONANCE

The interaction between the incident electromagnetic (EM) radiation and metal nanoparticle in dielectric medium leads to the polarization of the surface charge on the metal nano-particles resulting in the excitation of surface charge plasmon resonances. **Figure 1a depicts the electric field component of EM field displaced the surface electron plasma of the metal to one direction creating a dipole moment that oscillate at the frequency of the incident radiation.** This oscillation stores energy that de-phase in the form generating hot electron or other forms energy transfer. The occurrence of LSPR is dependent on the size, shape, position, and the geometry of nano-material [11–14].

The generation of hot electrons exhibited in the form optical absorption whose absorbance can be expressed according to eq(1) derived from Mie theory of classical electromagnetic light scattering. The absorption and scattering cross section are given by [11].

$$C_{abs} = \frac{2\pi}{\lambda} \text{Im}[\alpha], \quad (1)$$

and,

$$C_{scatt} = \frac{1}{6\pi} \left(\frac{2\pi}{\lambda} \right)^4 |\alpha|^2. \quad (2)$$

where λ is the electromagnetic field wavelength, and α is the polarizability of the particle which is given by

$$\alpha = 3V \frac{\omega_p^2}{\omega_p^2 - 3\omega - i\gamma\omega} = 3V \left[\frac{\varepsilon_p/\varepsilon_m - 1}{\varepsilon_p/\varepsilon_m + 2} \right], \quad (3)$$

where V is the particle volume, ε_p is the dielectric function of the particle and ε_m is the dielectric function of the embedding medium.

The excited electrons are sometimes referred as the hot-electrons. These generated hot-electrons will be available for photo-generated current in semi-conductors Figure 1b. Another forms of de-phasing the LSPR excitation is the formation near field which scattered light from the nano-particles into the medium [14]. The scattering of light in the semi-conductor medium increases optical pathlength of the light. This is a processes in which light scatters multiple times within or near the semi-conductor such that the light remain longer in the semi-conductor medium until it is efficiently absorbed by the material.

III. DEVICE ARCHITECTURE AND NUMERICAL SIMULATION

Organic solar cell is composed of layers of different materials for different roles in the function of the

solar cell. The schematic representation of the solar cell structure provided in Figure 2 consists of layers of materials with different thickness. This architecture known as conventional device structure is commonly used in the preparation of thin film organic solar cell experimentally. **Solution processed thin film organic solar cell is fabricated on Indium Tin Oxide(ITO) coated glass substrate followed by a hole transport layer (HTL), photo-active layer, electron transport layer(ETL) and a Cathode.** The photo-active layer used in this investigation is composed of poly(3-hexylthiophene) and [6,6]-phenyl C61-butyric acid methylester (PCBM) blend (P3HT:PCBM). Whereas the charge transport layers are poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (HTL), Lithium Fluoride(LiF)(ETL), Aluminium (Al) as a cathode. The structure remains unchanged for the study of the impact of ZnS in solar cell performances except the insertion of thin ZnS buffer layer. The same device structure is used in all SCAPS simulations.

The device simulation program SCAPS is a one dimensional simulation programme developed at the department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium by a group of researchers listed in references [15–18]. The SCAPS simulator numerically solves the set of one-dimensional transport equations, by firstly discretizing them and uses the Gummel iteration method and Newtons Raphson to solve these equations. Within the bulk of the layers these equations are given by [17, 18].

$$\frac{\partial}{\partial x} \left(\varepsilon \frac{\partial \psi}{\partial x} \right) = -\frac{q}{\varepsilon_0} \left[-n + p - N_A^- + N_D^+ + \frac{\rho_{def}(n,p)}{q} \right], \quad (4)$$

$$-\frac{\partial J_n}{\partial x} + G - U_n = \frac{\partial n}{\partial t}, \quad (5)$$

$$-\frac{\partial J_p}{\partial x} + G - U_p = \frac{\partial p}{\partial t}. \quad (6)$$

Along with the following constitutive equations

$$J_n = -\frac{\mu_n n}{q} \frac{\partial E_{F_n}}{\partial x} \quad (7)$$

$$J_p = -\frac{\mu_p p}{q} \frac{\partial E_{F_p}}{\partial x}. \quad (8)$$

In this set of equations n and p have been used to denote the free carrier concentrations. $-N_A^-$ and N_D^+ represent the charged dopant's concentrations. ρ_{def} is the defect distribution. The electron and hole current densities and denoted by J_n and J_p respectively. The net recombination rates given by U_n and U_p , while the generation rate

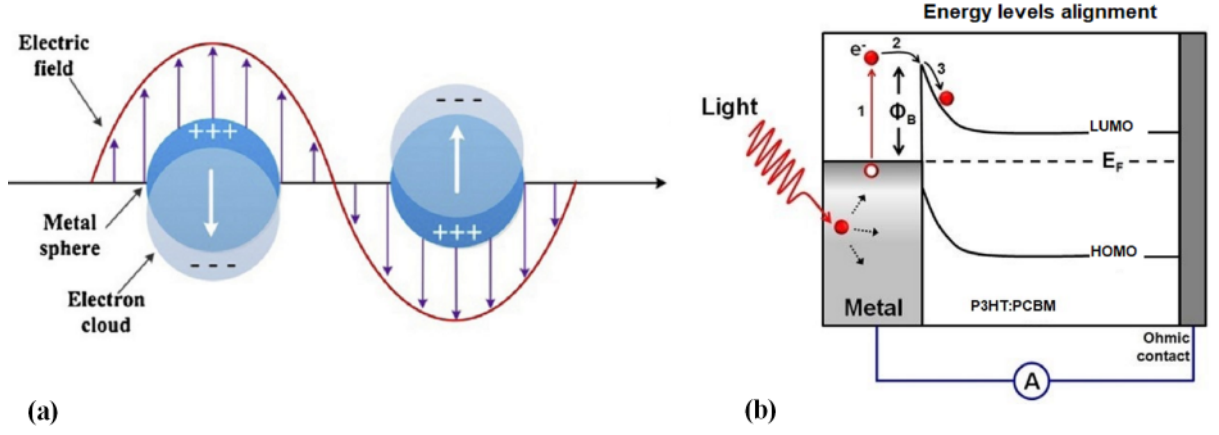


FIG. 1: a) The schematic diagram of LSPR [26], b) Schematic representation of the energy levels alignment and photogenerated electrons injection at metal/semiconductor interface [15]

TABLE I: P3HT:PCBM and ZnS NPs simulation parameters

Parameter	symbol	ITO	PEDO:PSS	P3HT:PCBM	ZnS Nps	units	ref
Thickness	d	80	60	variable	variable	nm	
Energy band gap	E_g	3.6	2.2	1.8	3.5	eV	[19–21]
Electron affinity	χ	4.8	4.4	3.8	3.8	eV	[22]
Di-electric permittivity(relative)	ϵ	8.9	10	3.8	10		[22]
CB effective density of states	N_C	1.1×10^{19}	1×10^{19}	1×10^{19}	1×10^{19}	cm^{-3}	[23]
VB effective density of states	N_V	1.1×10^{19}	1×10^{19}	1×10^{19}	1×10^{19}	cm^{-3}	[23]
electron thermal velocity	v	1×10^7	1×10^7	1×10^7	1×10^7	cm s^{-1}	
hole thermal velocity	v	1×10^7	1×10^7	1×10^7	1×10^7	cm s^{-1}	
electron mobility	μ_n	10	0.001	0.01	160	cm^2/Vs	[21, 25]
hole mobility	μ_p	10	0.0001	0.001	5	cm^2/Vs	[21, 25]
doping concentration of acceptors	N_A	0	0	0	0	cm^{-3}	[22]
doping concentration of Donors	N_D	0	1×10^{14}	1×10^{14}	1×10^{14}	cm^{-3}	[22]

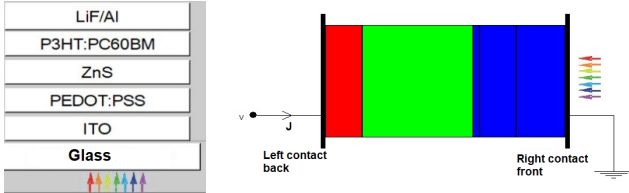


FIG. 2: The conventional solar cell structure in SCAPS

is given by G . The generation rate may be calculated using the following set of equations [7, 8, 18]

$$G(x, \lambda) = \frac{1}{2} c \epsilon \alpha n |E(x)|^2 \quad (9)$$

$$G(x, \lambda) = \frac{\lambda Q(z, \lambda)}{hc} \quad (10)$$

$$G(\lambda) = \int_{1.5G} Q(x, \lambda) d\lambda \quad (11)$$

where c is the speed of light, α is the absorption coefficient, and Q represents the energy dissipation. The physical parameters of the materials given in Table 1 are taken from literatures [19–25].

IV. DEVICE SIMULATION RESULTS

A. The effect of absorber layer thickness

Photo-generated exciton has short diffusion length in polymers blend solar absorber medium, and consequently, the absorber layer thickness plays a critical in the performance of TFOSC. A number of device simulations were conducted in this investigation using P3HT:PCBM solar absorber layer of the solar cell. The absorbers thickness were varied from 120 nm to 300 nm to study the device performances. The simulations were carried out under a 1 Sun illumination (1000 W m^{-2}) A.M.1.5G and with the neces-

sary physical parameters of the different functional layers of the solar cell (Table 1). Consequently, Figure 3 represents the simulations results of the J-V curves for activelayer thicknesses ranging from 120 nm to 300 nm. The main solar cell parameters found from the device simulation are pro-

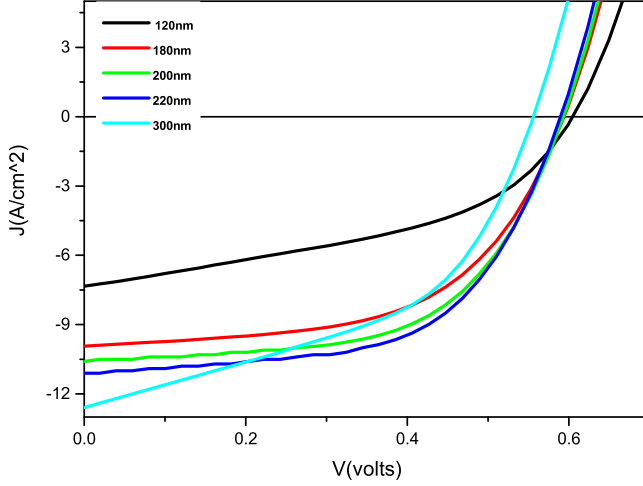


FIG. 3: The J-V curves of P3HT:PCBM at different absorber layer thickness

vided in Table 2. These device parameters agree with the experimental results found in reference [27, 28]. According to the results given in Figure 3, the photo-current found from the device with absorber thickness 120 nm was lower than the other devices. It is in fact generated the least power conversion efficiency (see Table 2), which is attributed to low optical absorption and significant amount of incident light escaped unnoticed by semitransparent absorber film. But, as the thickness increases the power conversion efficiency also increases because of the enhanced photo-current and more photons absorptions. The maximum power conversion efficiency found in the simulation was at an absorber layer thickness 200 nm. This variations of absorber layer thickness in the devices basically affected almost all device parameters such as J_{sc} , FF and PCE. The highest performance of P3HT:PCBM based solar cell is observed at the thickness ranging from 180 nm to 220 nm, which is consistent with best OSC fabricated in the laboratory using same polymer blend. The variations in device parameters with thickness of the active layer are given in Figure 4. The FF rose from the minimum 48 % at 120 nm to 52 % at the thickness of 220 nm. The short current density increases from 7.336 mA cm^{-2} at the thickness of 120 nm to 10.89 mA cm^{-2} at the thickness of 220 nm. This improvement is due to the increased photons absorption which resulted in enhanced photo-generated current.

According to the results provided in Figure 4 the

V_{oc} slightly varied from 0.5615 V -0.6052 V for both simulated and experimental results [29]. This is due to the fact that the V_{oc} is mostly dominated by the difference in energy levels of lowest unoccupied molecular orbital (LUMO) of the acceptor material and the highest occupied molecular orbital (HOMO) of the donor material [29] as well as the work function of the electrode. However, significant growth in V_{oc} is

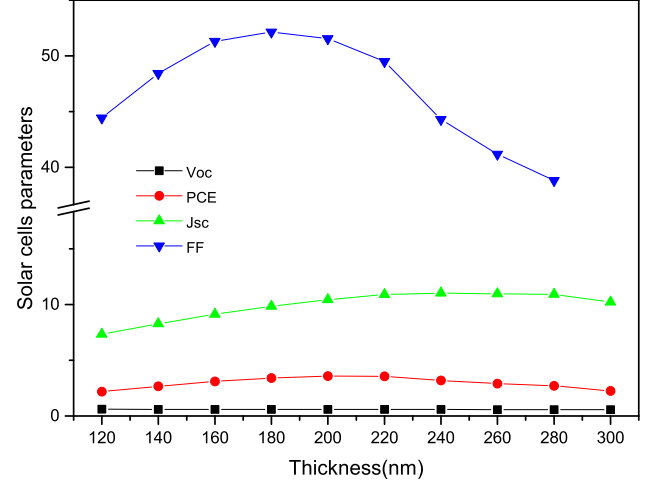


FIG. 4: The solar cell parameters derived from device simulation plotted against absorber layer thickness

recorded at thickness $> 220 \text{ nm}$, which has contributed to best power conversion efficiency 3.57%. All the device parameters are decreasing as the thickness increases beyond 220 nm, including the V_{oc} , FF, and J_{sc} , confirmed by device simulation results (Table 2). The V_{oc} decreases from 0.5925 V to 0.56227 V, and similarly, the Fill Factor drops from 52 % to 35 %, which is attributed to the changes in series resistance and shunt resistance of the devices. The shunt resistance prevent the leakage through the current pathways. The shunt resistance decreases with increasing thickness while the series resistance increases with thickness [29] because the polymer medium become more resistance to current flow as polymer medium get thicker. **Furthermore, the life time of photo-generated excitons is low because of it's short diffusion length in polymer medium, and hence, optimum layer thickness is necessary to balance sufficient optical absorption and exciton life time. Therefore, increasing absorber thickness means high the series resistance which reduces the value of the FF. The short current density is also affected by generation, recombination rate and built in electric field [29]. As it can be seen from Poisson's continuity equations eq(7) and eq(8), the solution of the current $J(v)$ explicitly depends on the recombination and**

generation coefficients. Large thickness results in the high recombination [29–32] of carriers thus carriers lose energy in the form of heat. Increasing thickness decreases the built in electric field, which therefore leads to an exciton dissociation failure, since the exciton is separated by the electric field at donor-acceptor interface[29]. The quantum efficiency of the simulated solar cells, which is defined by the ratio of the number of collected charge carriers divide by the number of incident photons is given in Figure 5. The EQE is calculated for different thickness of the active layers (120 nm, 220 nm, 300 nm), which has significant conversion yield from 350 nm to 650 nm wavelengths of the incident photons. This is mainly determined by the absorbency of the P3HT:PCBM blend. Thus, the EQE yield is dependent on the absorber thickness which shows maximum yield at 300 nm (blue) and followed by minimum at 120 nm layer thickness. The maximum EQE peak recorded in

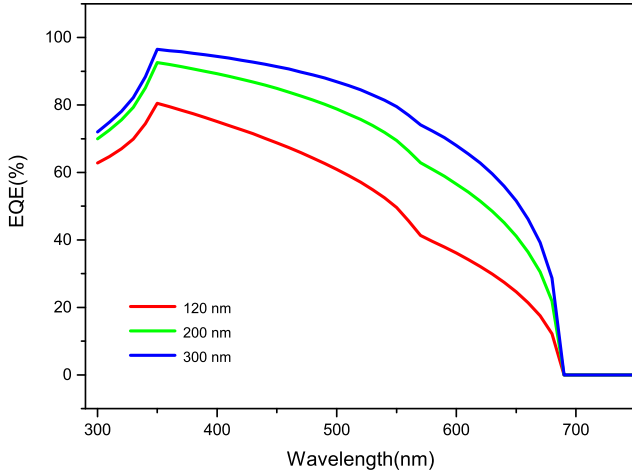


FIG. 5: The External Quantum Efficiency plotted against the incident light wavelengths

the simulations was found to be at 360 nm incident wavelength, where 80 %, 90 % and 95 % are measured at 120 nm, 220 nm, and 300 nm, respectively.

TABLE II: Device parameters of P3HT:PCBM based solar cell at various thickness of active layer

Thickness (nm)	V_{oc} volts	J_{sc} mA/cm ²	FF %	η %
120	0.6051	7.3366	44.43	2.19
180	0.5959	9.8484	52.13	3.40
200	0.5955	10.437	51.54	3.57
220	0.5925	10.895	49.49	3.55
300	0.5621	10.214	35.30	2.25

B. Capacitance Voltage plot of the devices

The interfaces between the active layer and electrodes is the region of interest when looking at the built in potentials as well as capacitance generated due to the accumulation of charges at the interface [34, 36]. Indeed, TFOSC has very thin inter-facial buffer layers which can diffuse into active layer in the process of device fabrications. The accumulation of space charge at the interfaces produces capacitance at the metal/semiconductor contact, which is an important parameter to understand the inter-facial conditions in solar cells (Fig. 1b). The information extracted from capacitance in response to applied voltage or frequency is affected by built-in potential and doping density (in C-V plots). The capacitance is defined by equ (12) [32]

$$C = \frac{\epsilon_0 \epsilon_r A}{w} \quad (12)$$

where ϵ_0 and ϵ_r are the permittivity of free space and dielectric medium. whereas A is inter-facial area while w is the width of depletion region, which can be expressed by an equation of the form :

$$w = \sqrt{\frac{2\epsilon_0 \epsilon_r (V_{bi} - V)}{qN}} \quad (13)$$

where V_{bi} is built in voltage, V is bias voltage, q is the elementary charge, and N is the doping concentration given in equ (16) [31].

$$N = \frac{N_A N_D}{N_A + N_D} \quad (14)$$

According to the calculated results on device capacitance presented in Figure 6, the capacitance is decreasing in a forward bias condition while it is increasing in reverse bias voltages of the solar cell [35]. This is expected from the fact that more charges are crossing the interface in the forward bias, because smaller depletion width, than the reverse bias condition. Furthermore, the capacitance of the devices decreases with thickness of the absorber layer, which is an indicative of the low concentrations of charges at the interfaces in thick polymer active layers. In other words, as thickness of the active layer gets larger, it increases the width of the depletion region, which results in charge recombination hence the capacitance gets reduced in thick layers (see equ(12)). Similarly, there is a possibility of either the photon-generated charges are collected by the electrodes or neutralised by recombination processes. This agree with the fact that thick active

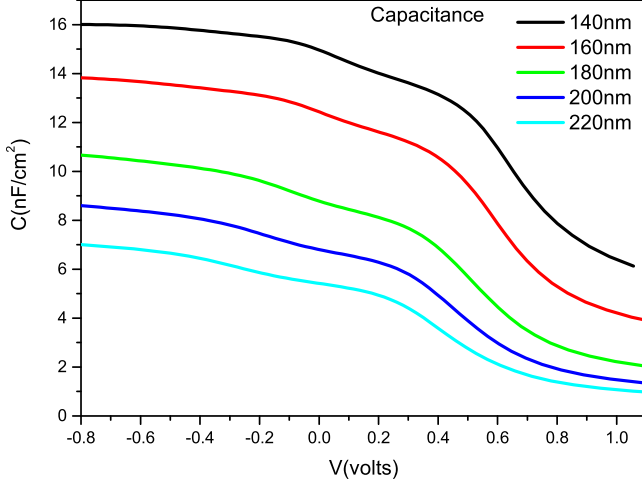


FIG. 6: The capacitance voltage plot of the Pristine with various absorber thickness

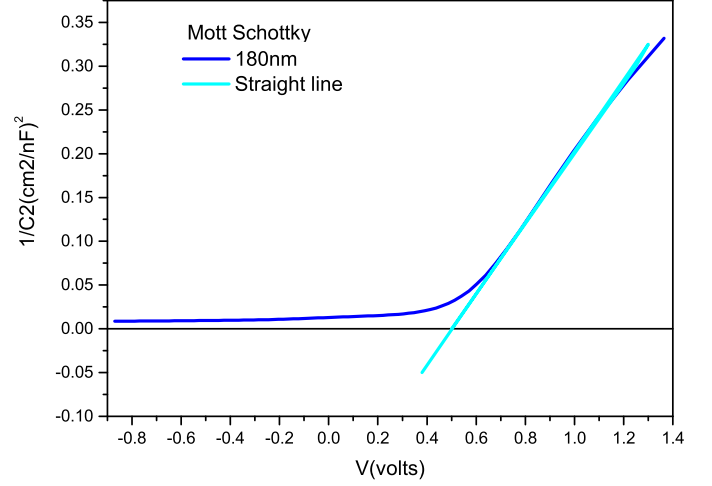


FIG. 8: The Mott Schottky plot of a pristine layer at 180 nm thickness

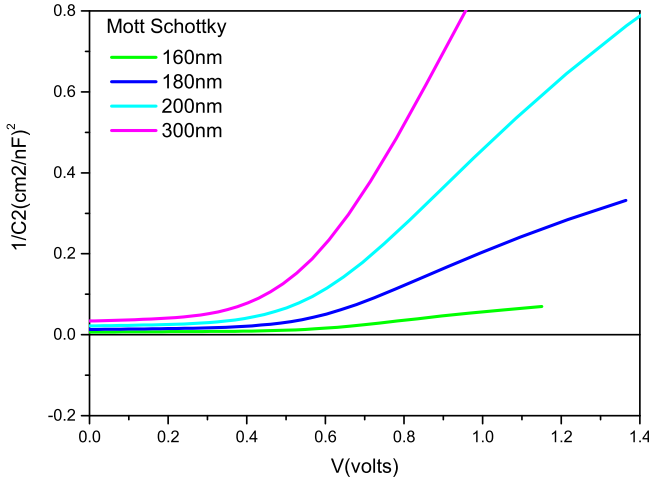


FIG. 7: The Mott Schottky plot of the P3HT:PCBM based active layer with the thickness varied from 160 nm to 220 nm

layers are better performing in terms of producing high power conversion efficiency.

In an effort to determine the built in potential from the simulation data, Mott Schottky plots are drawn as provided in Figure 7. The plots are defined by the inverse square of the capacitance equation, which is often referred as the Mott Schottky equation and expressed by equ (15) [37]. The built in potential can be determined by drawing a straight line tangent to the curves that cross the horizontal axis. For instance, using a data from 180 nm thick layer device a built in potential is determined by extrapolating the line to the horizontal axis

(Figure 8). Hence, the x-intercept of the straight line is found to be $V_{bi} = 0.5$ V. This value is a reasonable estimate of the built in potential, which is comparable to the open circuit voltage of P3HT:PCBM based solar cells.

$$C^{-2} = \frac{2(V_{bi} - V)}{\epsilon_0 \epsilon_r A^2 q N} \quad (15)$$

N_A and N_D being the doping concentration of acceptor and donor impurities, respectively. The inverse square of the capacitance gives a linear relationship with the voltage [36]. It's slope is used to find the doping concentration while the x-intercept is used to determine the built in voltage [36]. In some literatures, it is reported about the inadequacy of Mott Schottky plot to determine the built in potential and the doping density. However, the result found in the current calculations is not far from the expected.

C. The impact of ZnS NPs on device performance

The effect of ZnS on the performance of thin film polymer solar cell is investigated using device simulation program. At the moment, the SCAPS program, which uses transport equations for device simulation, is not able to include LSPR effect into fundamental bases. However, the approach used in this investigation is to introduce a very thin layer of ZnS between the photo-active layer and hole transport layer as depicted in Figure 2 to study its impact on device performance. All the functional layers of the device structure are kept at a constant thickness and absorber layer thickness used is 180 nm. **However, the ZnS layer thickness is allowed to vary with view to change the concentrations of NPs**

in the device structure. The ZnS NPs were chosen because of their broad application areas such as blue lighting emitting diodes, solar cells and field emission devices [38]. Our group have successfully used ZnS, as dopant in absorber layer of P3HT:PCBM blend, which has produced an improved performance [28]. ZnS exhibited optical absorption due to electron band to band transition which is evident on absorption at low wavelength region [28]. Moreover, ZnS induces light scattering at the interface which increase optical path length in polymer medium that eventually assist light trapping. Furthermore, by improving conductivity between interfaces ZnS enhances collection of charges. The morphology of ZnS powder, as presented in Figure 9, is taken using high resolution tunnelling electron microscopy (TEM). The TEM image shows a highly crystalline microstructures with crystal spacing 0.31 nm, which an important property for charge transport across the layers. Several studies suggest that metallic NPs play important roles at different functional layers TFOSC [8–10]. In this work, ZnS thickness was

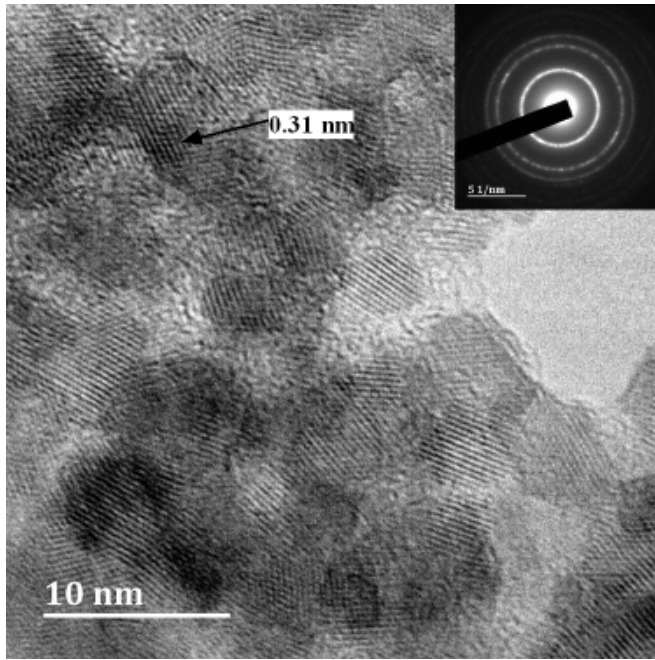


FIG. 9: The TEM image of ZnS powder

varied from 3 nm to 12 nm, and consequently, several calculation was conducted to determine performance of the devices. The J-V curves provided in Figure 10 shows the impact of ZnS concentration in the device structure. The best performance is found to be at 3 nm ZnS thickness. The power conversion efficiency reaches to the maximum value of 4.06 %, the FF = 61.56 %, Jsc = 10.24 mA cm⁻², and the Voc = 0.5800 V (as shown in Figure 10 and Table 3). This performance is much better than that of the devices without ZnS layer. Therefore, device improvements

are recorded in both optical absorption and collection of charges, consequently, the PCE grew by 19%. Generally, all the device parameters are enhanced by the incorporation of ZnS NPs in the device structure compared to devices without ZnS. The optimum thickness of the ZnS layer for efficient device performance is 3 nm, which exceeds almost all device parameters (see Table 3). Ac-

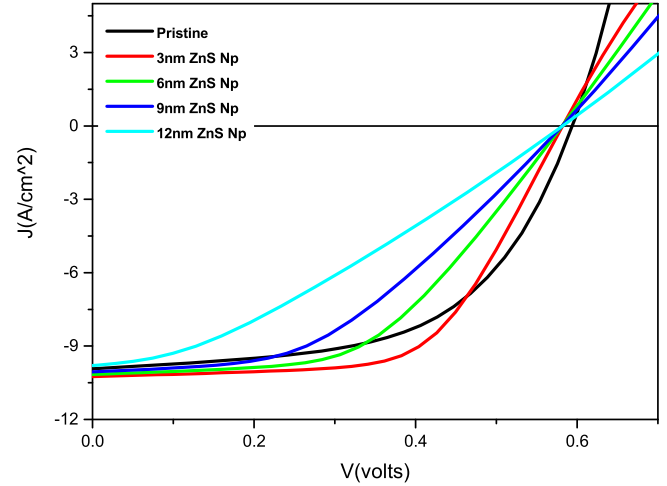


FIG. 10: The J-V curves of P3HT:PCBM + ZnS Nps at different thickness of ZnS Nps

cording to the observed results, increasing the ZnS NPs thickness(beyond 6nm) is unfavourable for device performances. Especially, when the band gap of the ZnS layer is beyond 2.5 eV. It has been observed in many ex-

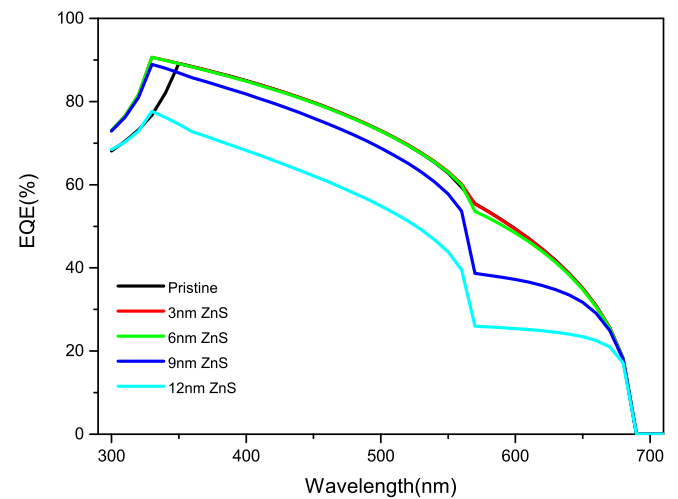


FIG. 11: The External Quantum efficiency plotted against the ZnS Np thickness

periments [1–3], that the large concentration of NPs in absorber layers result in poor performing devices [8, 9]. This is attributed to the generates unwanted defects concentration at high doping level of nano-particles in a device that can promote charge recombination and leading to poor device performance. Furthermore, high concentration of NPs increases the series resistance and lowers the shunt resistance, which limits the maximum power that can be drawn from the device.

TABLE III: P3HT:PCBM + ZnS solar cells parameters

ZnS thickness (nm)	V_{oc} volts	J_{sc} mA/cm^2	FF %	η %
0.0	0.5959	9.8484	52.13	3.40
3	0.5800	10.244	61.56	4.06
6	0.5790	10.146	51.87	3.39
9	0.5799	10.033	42.59	2.75
12	0.5804	9.8725	34.79	2.22

The quantum efficiency of the devices with ZnS layer is calculated and given in Figure 11, which shows a distinct changes in the values of the calculated EQE with the thickness of ZnS layer. The EQE drops drastically as the ZnS thickness is increased from 6 nm to 12 nm, which signifies the occurrence of charge recombinations in the photoactive layer. Even the high energetic photons are less absorbed when the the ZnS NPs has the thickness of 12 nm. Similarly, the EQE drops to below 80 % as the thickness is increased from 9 nm to 12 nm.

V. CONCLUSION

With the aid of device simulation programme, appreciable solar cell parameters were recorded from the study of absorber layer thickness dependence and the effect of ZnS on the performance of OSC. The thickness of the photo-active layer (P3HT:PCBM blend) was varied from 120 nm to 300 nm, in device simulation, to see the role of thickness on device performance. The results clearly suggested that absorber thickness indeed affected device performance because of the short diffusion length of the exciton in polymer medium. However, lowering the thick-

ness too much is not favourable either, and thus, the optimum absorber thickness found in the study were from 180 nm to 220 nm. The highest efficiency achieved in P3HT:PCBM blend absorber was 3.57 % at 200 nm thick layer, which agrees with the experimental results. As the thickness of P3HT:PCBM exceeds beyond the optimum range all the device parameters dropped and device performances gets lower. Therefore, the thickness of active layer plays an important role in designing OSC devices. Another independent investigations conducted, by employing ZnS nano-particles in the device structure, with the view to increase performance and charge transport processes. This study has demonstrated that ZnS layer is indeed influenced the device performance of P3HT:PCBM based solar cell. However, the high concentration of ZnS in the device structure negatively impacted the solar cell parameters. Therefore, the maximum efficiency recorded in this study was 4.06 % at the thickness of 3 nm ZnS NPs, which is 19% growth in PCE from solar cells without ZnS. The improvement is attributed to the occurrence of LSPR and light scattering by the presence of ZnS NPs in the device structure. These results suggest that ZnS NPs can be used as a mechanism to trap light in polymer medium and improve the conductivity between the PEDOT:PSS and P3HT:PCBM interfaces. It can also be used as acceptor material due to it's high electron affinity, which can assists in exciton dissociation in polymer.

Declaration of competing interest

The authors declare that they have not known any competing financial interests or personal relationships that could have influenced the work reported in this paper.

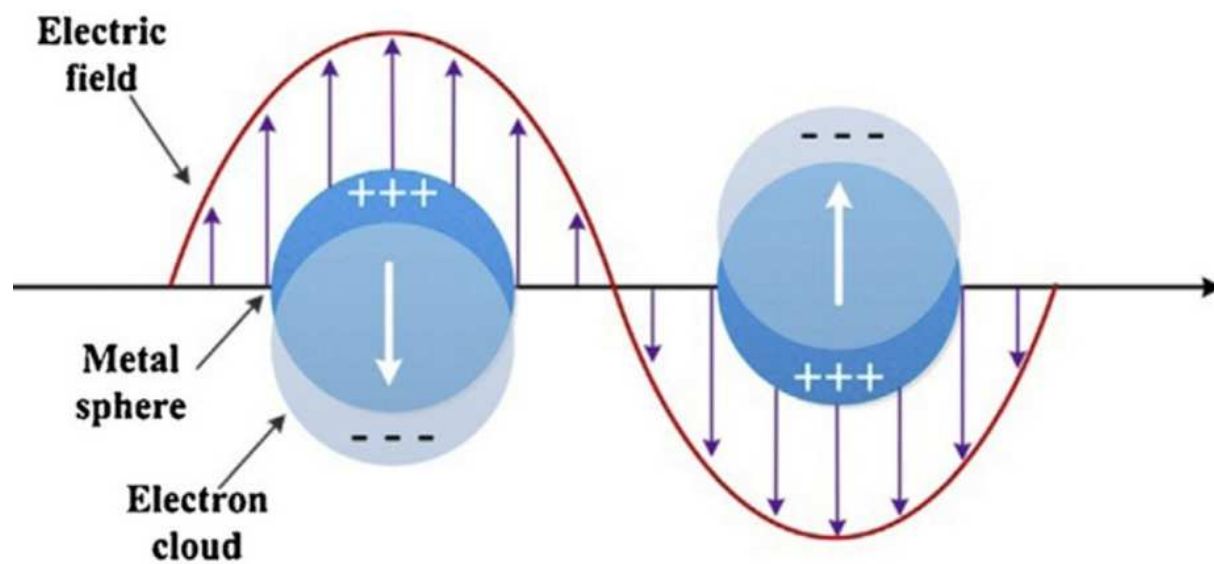
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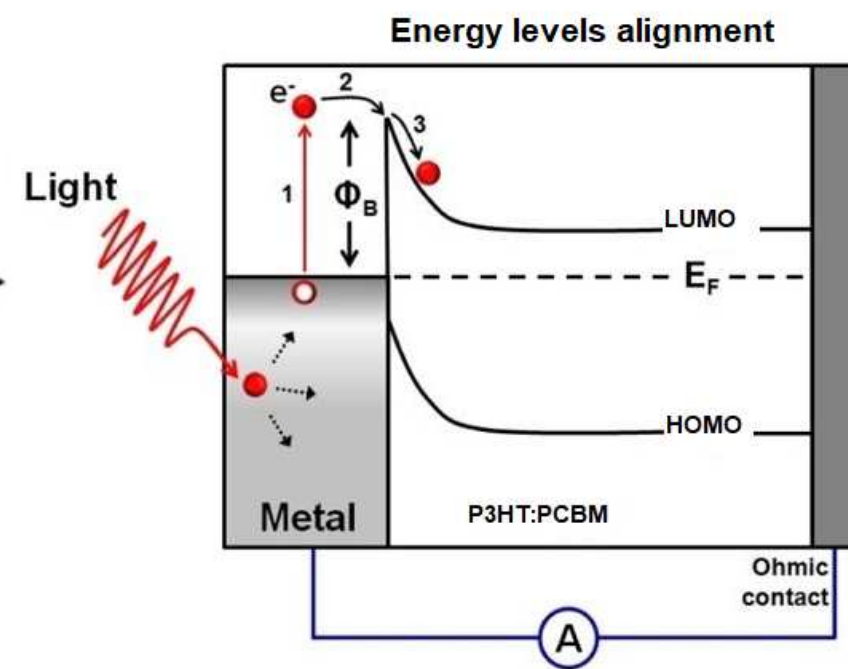
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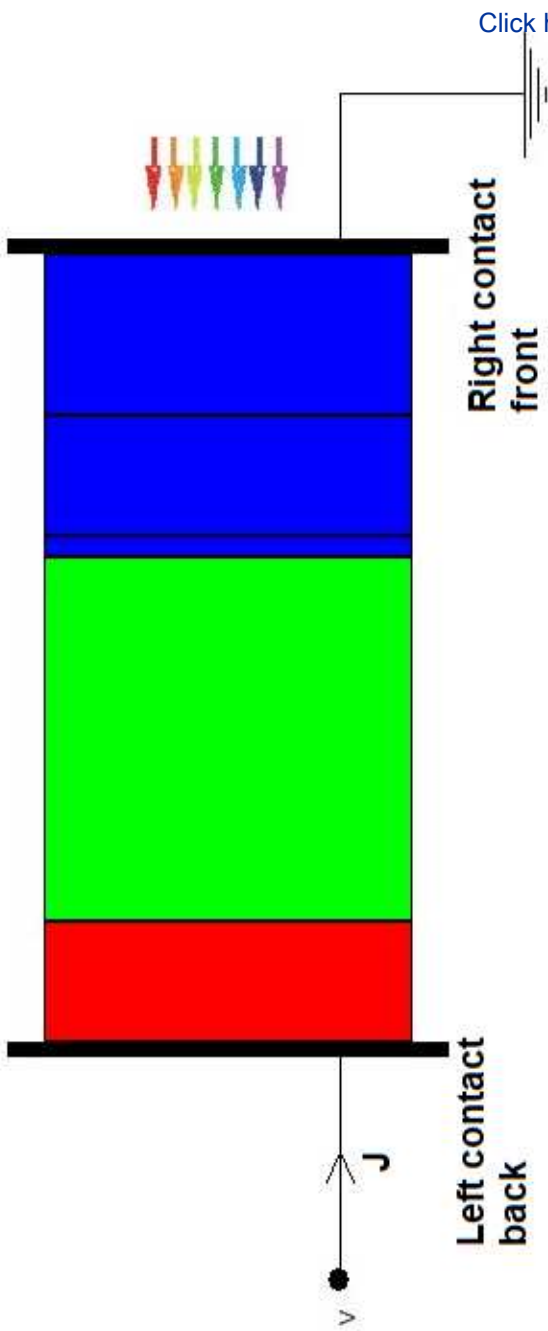
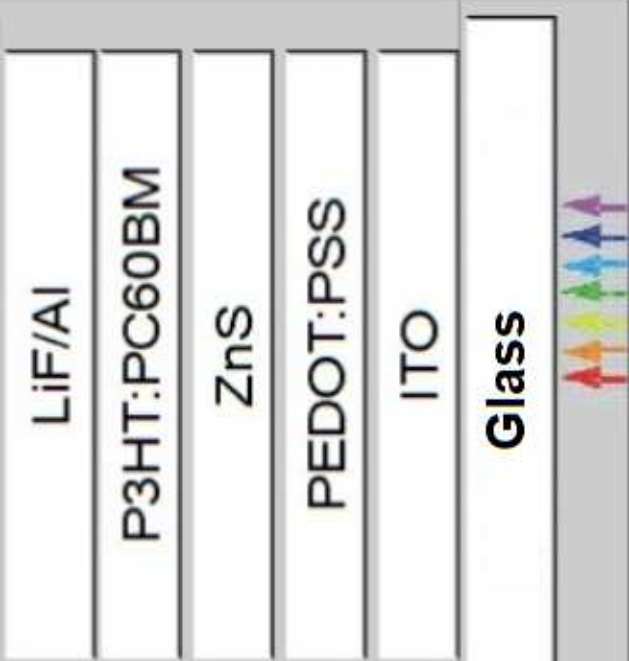


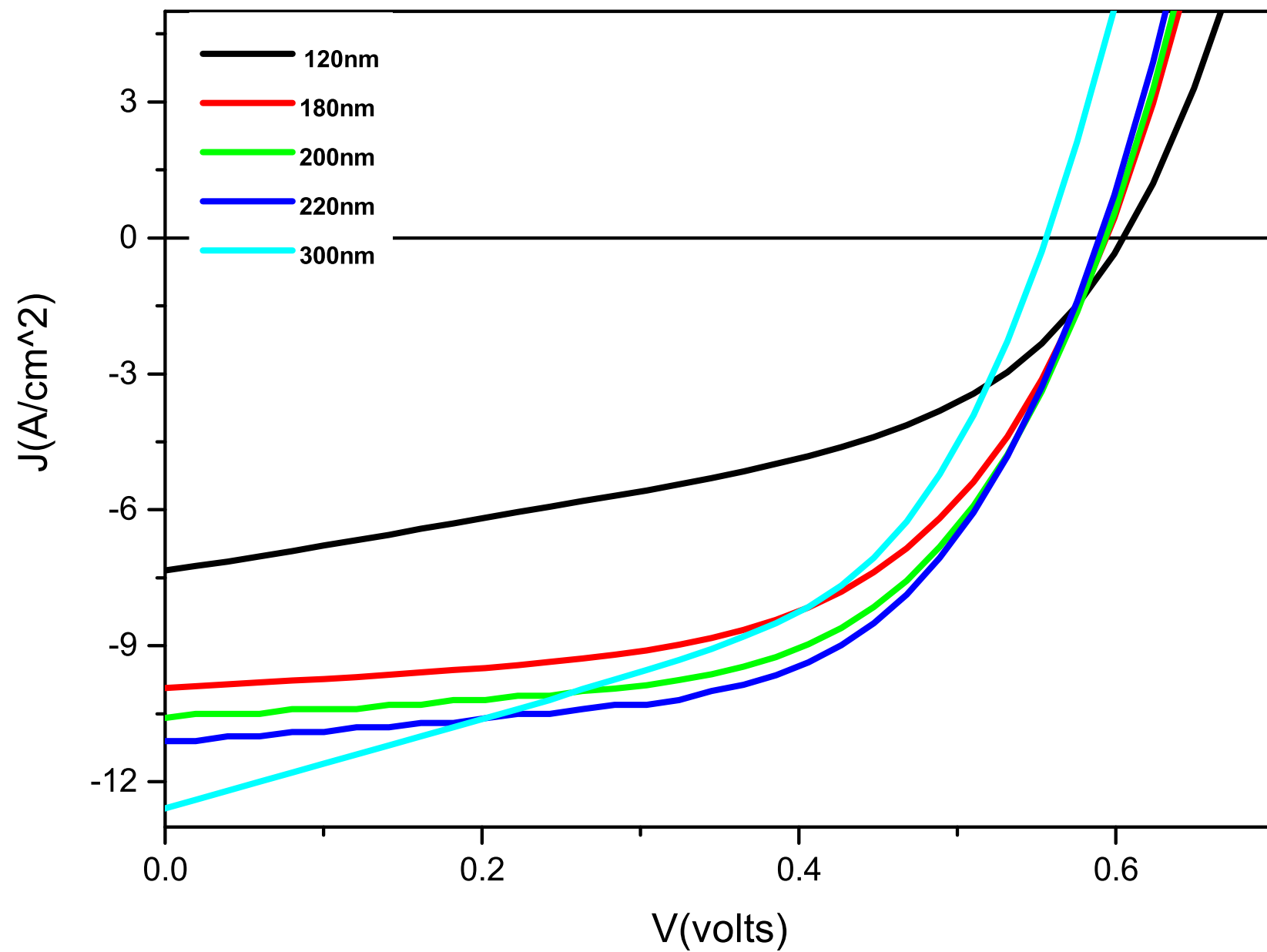
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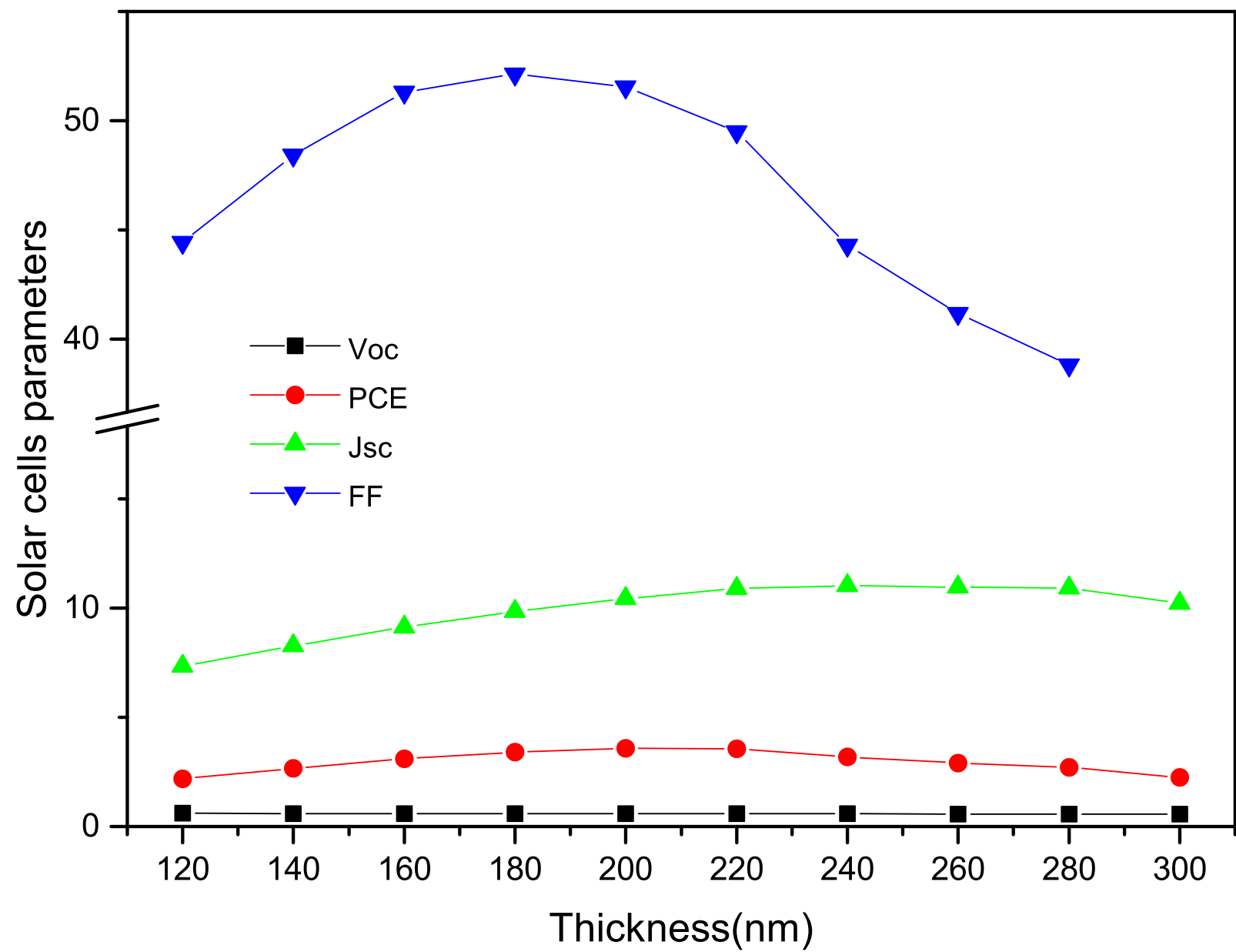


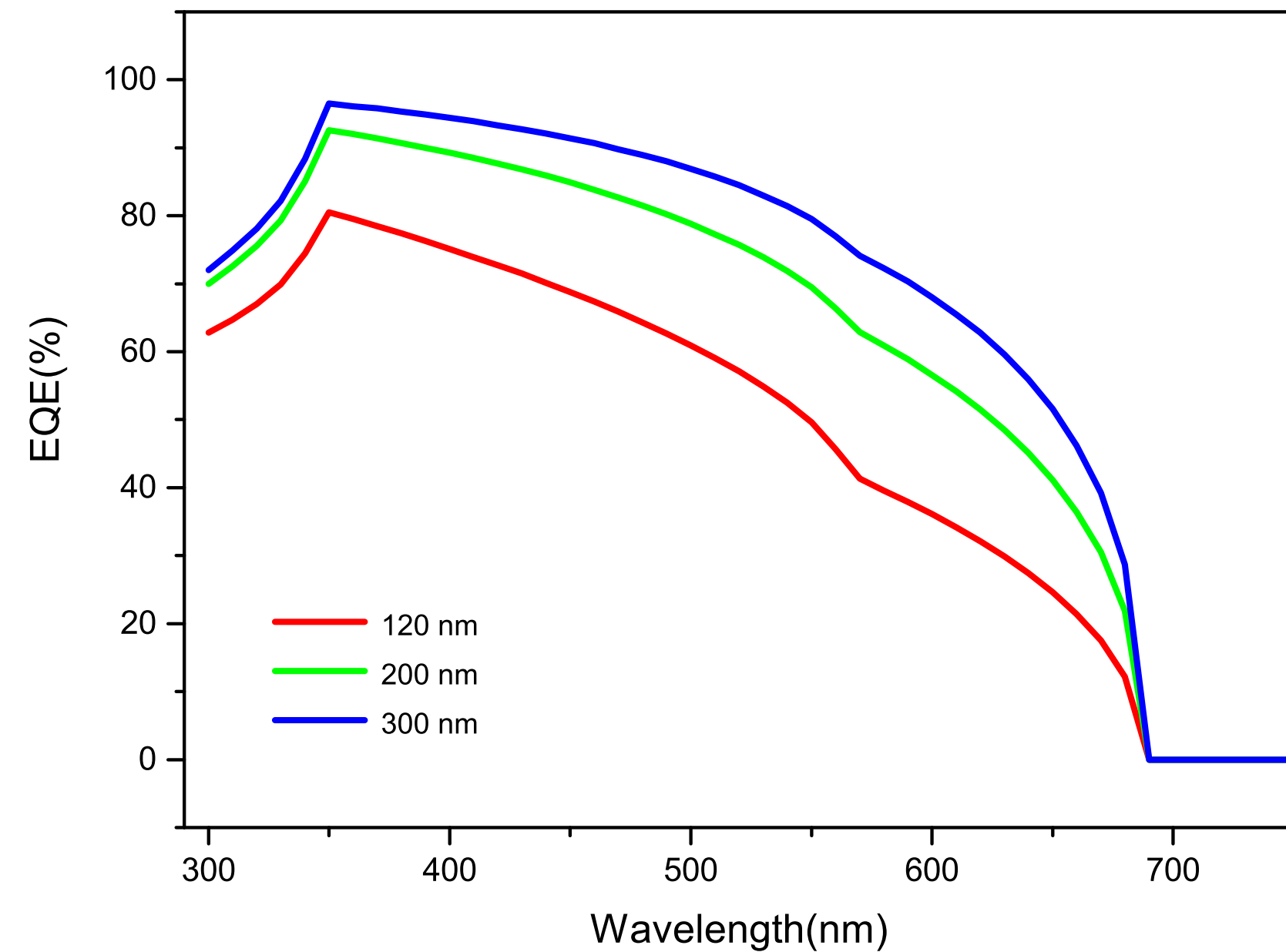
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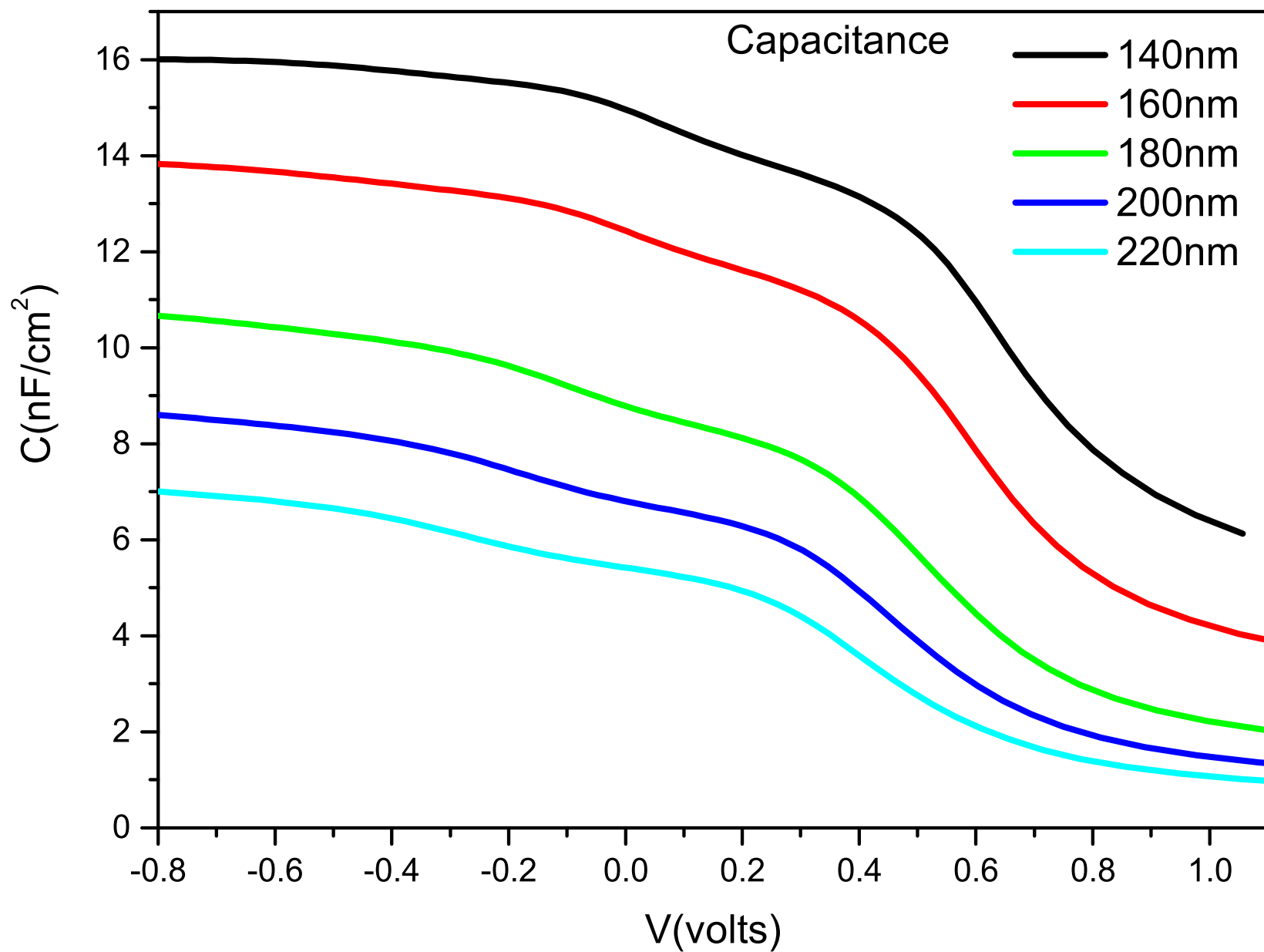
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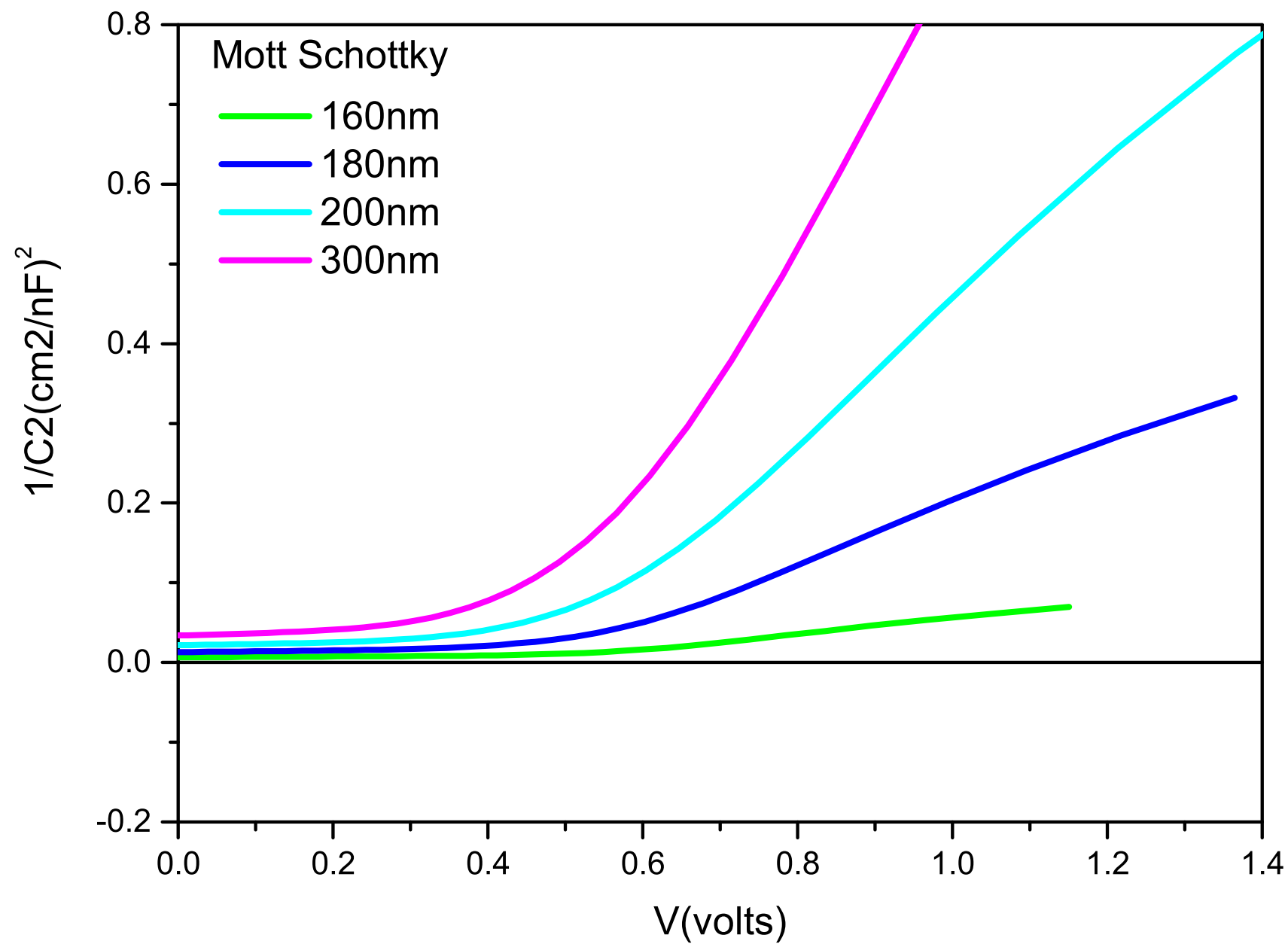


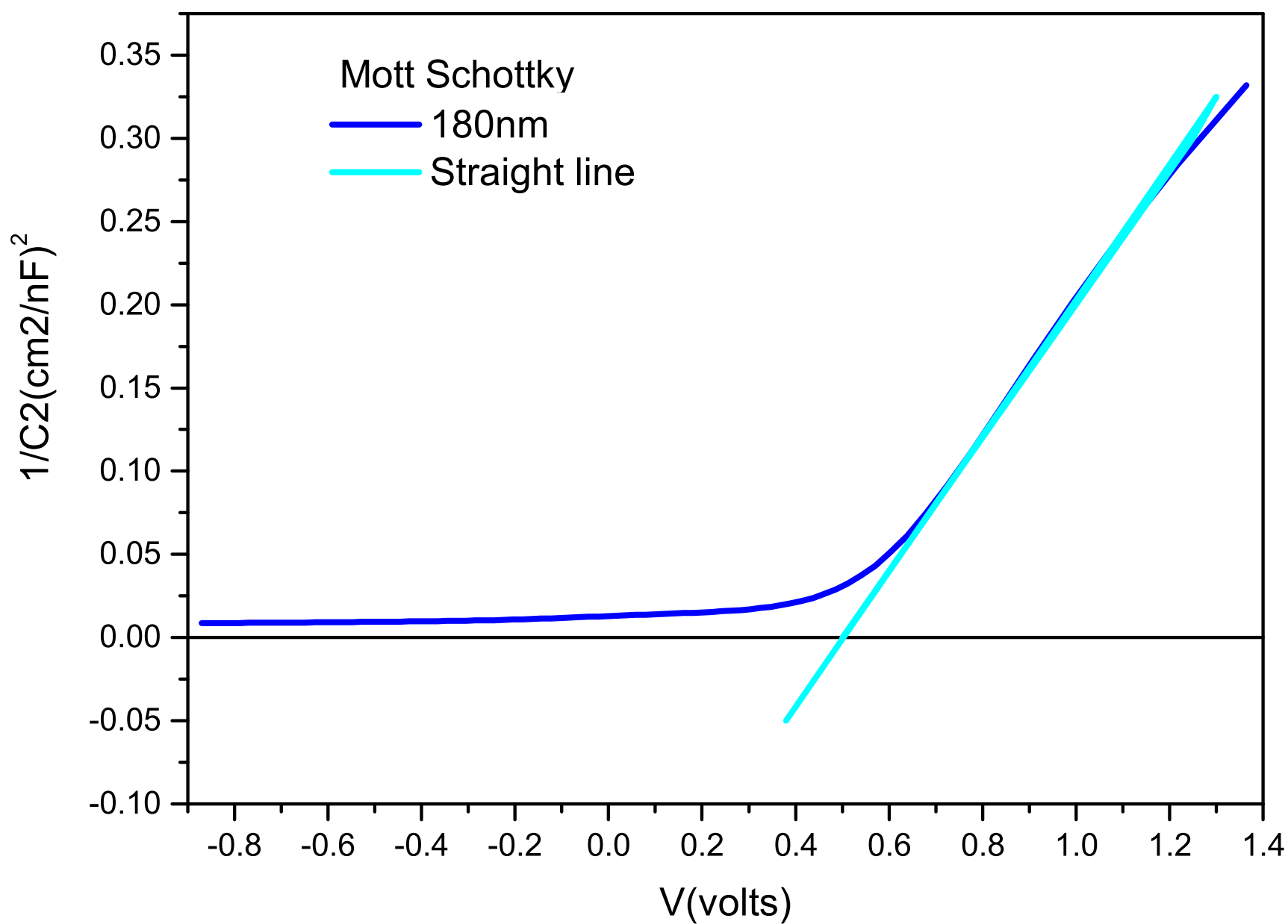


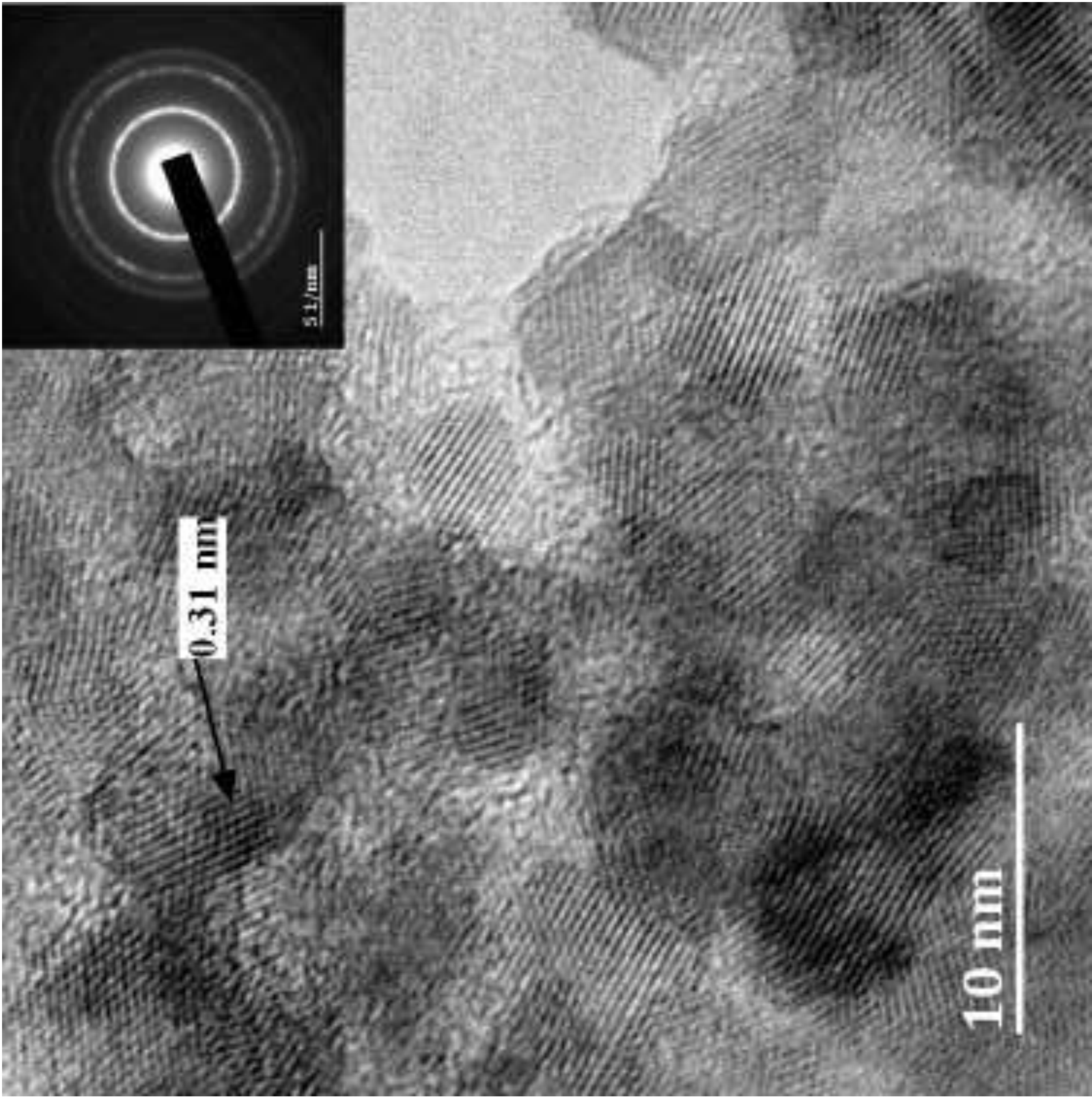


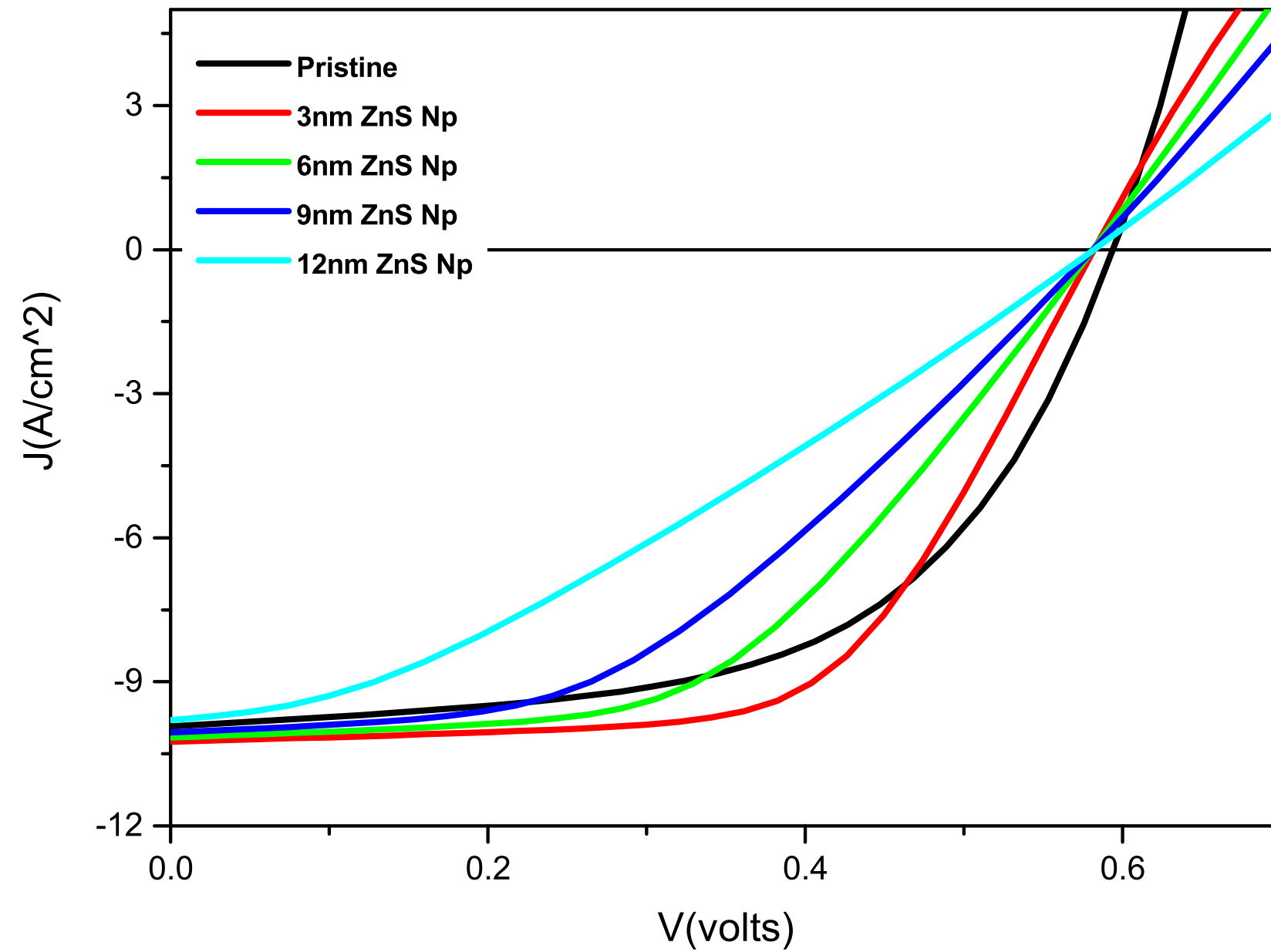


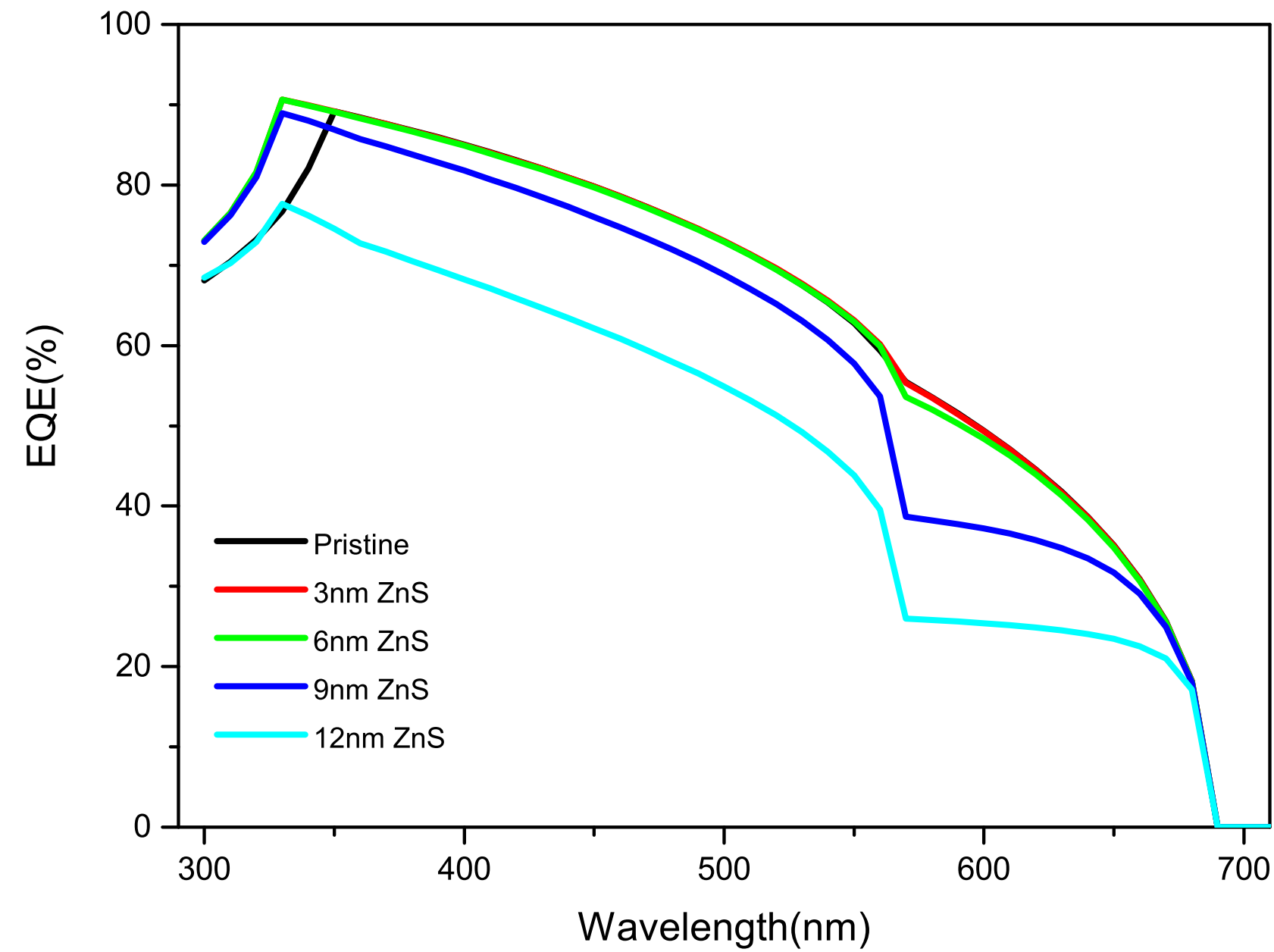












Highlights

- Polymer solar absorber thickness has significant impact on the performance the solar cell
- ZnS nano-particle is an effective mechanism to improve charge transport process in polymer solar cell.
- ZnS nano-particle can reduce charge recombination at the metal/polymer interfaces.

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: