Infrared Harvesting Colloidal Quantum Dot Solar Cell Based on Multi-scale Disordered Electrodes

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ABSTRACT

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Colloidal quantum dot photovoltaics (CQDPV) offer a big potential to be a renewable energy source due to low cost and tunable band-gap. Currently, the certified power conversion efficiency of CQDPV has reached 9.2%. Compared to the 31% theoretical efficiency limit of single junction solar cells, device performances have still have a large potential to be improved. For photovoltaic devices, a classical way to enhance absorption is to increase the thickness of the active layers. Although this approach can improve absorption, it reduces the charge carriers extraction efficiency. Photo-generated carriers, in fact, are prone to recombine within the defects inside CQD active layers. In an effort to solve this problem, we proposed to increase light absorption from a given thickness of colloidal quantum dot layers with the assistance of disorder. Our approach is to develop new types of electrodes with multi-scale disordered features, which localize energy into the active layer through plasmonic effects. We fabricated nanostructured gold substrates by electrochemical methods, which allow to control surface disorder as a function of deposition conditions. We demonstrated that the light absorption from 600 nm to 800 nm is impressively enhanced, when the disorder of the nanostructured surface increases. Compared to the planar case, the most disorder case increased 65% light absorption at the wavelength of $\lambda = 700 nm$ in the 100 nm PbS film. The average absorption enhancement across visible and infrared region in 100 nm PbS film is 49.94%. By developing a photovoltaic module, we measured a dramatic 34% improvement in the short-circuit
current density of the device. The power conversion efficiency of the tested device in top-illumination configuration showed 25% enhancement.

This dissertation work led to the following article:

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LIST OF ABBREVIATIONS

AM1.5 - Air Mass 1.5
CQD - Colloidal quantum dots
EDT – Ethanedithiol
EQE - External quantum efficiency
EM – Electromagnetic
FF - Fill factor
FIB - Focus ion beam
FDTD - Finite difference time domain
IQE - Internal quantum efficiency
IR – Infrared
ITO - Indium doped tin oxide
$J_{sc}$ - Short circuit current density
$J-V$ - Current-voltage characteristics
MoO$_3$ - Molybdenum trioxide
PCE- Power conversion efficiency
PV – Photovoltaic
RMS - Root mean square
$R_s$ - Series resistance
$R_{sh}$ - Shunt resistance
SEM - Scanning electron microscopy
TBAI - Tetrabutylammonium iodide
TEM - Transmission electron microscopy
TiO$_2$ - Titanium dioxide
UV – Ultraviolet
$V_{oc}$ - Open circuit voltage
ZnO - Zinc oxide
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Introduction

1.1 Photovoltaic devices

From the industrial revolution to now, various technologies were applied to generate enough power for ensuring the human activities. The current lifestyle of this generation strongly relies on a continual and stable supply of electricity. Furthermore, with rapid increase of world population, the demands for different resources, like electrical power, must dramatically and continually grow. Although, currently, various fossil fuels are main pillars to power our world, with their finite nature and many environmental issues raised by burning fossil fuel, the development and innovation of renewable energy and techniques are continually and strongly encouraging. From the latest report of National Renewably Energy Laboratory (NREL), in 2013, power production from renewable energy resources accounted for 11.2% of total overall power production in U.S. Solar PV only produced 4% of total electricity generation, but, compared to other renewable energy sources, such as hydropower, wind, biomass, it was the fastest developing renewable electricity generation technology, which the overall installed PV systems grown by about 65% in US [1]. In other regions of the world, such as China and Germy, the increases even were much better [1]. Therefore, solar-generated electricity techniques have a big potential to be one of the most promising candidates to retain enough energy supply for growth of human civilization.

1.1.1 Working Principle
Photovoltaic devices refer to semiconductor devices that have capability to convert solar energy into electrical power through the photovoltaic effect. The photovoltaic effect means that photons from solar radiation excite electrons from ground energy state to higher energy state, which allows excited electrons to contribute to the flowing electric current. In terms of the current generation in solar cells, there are mainly two processes. First one is the creating of electron-hole pairs in active regions. The Electron-hole pairs will be created in photovoltaic devices, provided that the energy of incident photons is greater than the energy of semiconductor band-gap. The photo-generated electrons and holes can only exist for the lifetime of minority carriers. Hence, the second process is to extract the photo-generated electrons to external circuit for powering the loads before recombining [2].

1.1.2 Figures of merit

In order to evaluating the PV performances, there are four figures of merit that are mainly considered, which are the open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF) and the power conversion efficiency (PCE) respectively. A typical solar cell structure can be modeled as an ideal diode in parallel with a current source with losses caused by the series and shunt resistance of the solar cell, $R_s$ and $R_{sh}$. The equivalent circuit model is illustrated by following Figure 1 [1].
Under the dark condition, the diode provides the dark current $J_0$. After shining light on the diode, photons are absorbed and separated in the active materials, which resulting a light generated current. Accordingly the voltage and current are created in PV devices.

The mentioned four key figures of merit can be represented by the following J-V characteristics curve of a solar cell under illuminated conditions.

**Short-circuit current density** ($J_{sc}$): is the current through the unit area of solar cell when the voltage across the device is zero.

**Open-circuit voltage** ($V_{oc}$): is the maximum voltage available from a PV device, and observed at the point of zero net current.

**Fill factor** (FF): is a parameter to determine the maximum output power from a PV device with a conjunction of $J_{sc}$ and $V_{oc}$. It is defined as a ratio of maximum output power of a PV device to the product of the short-circuit current density and the open-circuit
voltage of a PV device. Graphically shown from the figure, the FF measures the squareness of the J-V curve and is the area of the largest rectangle that fit in the J-V curve.

**Power Conversion efficiency (PCE):** is the most common parameter used to evaluate the performance of PV devices, which is define as the ration of maximum generated power from PV devices to the incident power from the light source. The defined equation for PCE is shown as following [2].

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}}$$ (1)

### 1.1.3 Quantum Efficiency

A solar cell’s quantum efficiency main divided into two types, namely external quantum efficiency and internal quantum efficiency, which is used to examine the amount of cell-produced current, when illuminated by a certain wavelength light.

External quantum efficiency (EQE) is defined as the ration of output current to the number of incident photons, which is used to quantify the charges extraction efficiency and illustrate the solar cell performances. Particularly, the external quantum efficiency can be expressed as a function of energy of incident photons, which is useful to examine the wavelength dependence of charge extraction. The EQE equation is shown as following:

$$EQE = \frac{electrons \cdot s^{-1}}{incident \ photons \cdot s^{-1}}$$ (2)
Compared with EQE, the internal quantum efficiency (IQE) is defined as following:

\[ IQE = \frac{\text{electrons s}^{-1}}{\text{absorbed photons s}^{-1}} \] (3)

1.1.4 Absorption coefficient

The absorption coefficient decides that how deep into a material light of a particular wavelength can penetrate. The amount of radiation that a material absorbs depends on the thickness of the material. In terms of a material with a low absorption coefficient, the light is poorly absorbed, if this material is thin enough, it will become transparent to that wavelength. The absorption coefficient is employed to compare the optical property between different materials. The Beer-Lambert Law describes the relationship between the thickness and absorption coefficient of materials.

\[ T = e^{-\alpha l} \] (5)

Where \( T \) represents the percent of transmitted light, \( l \) describes the thickness of materials and \( \alpha \) represents the absorption coefficient [2].

1.1.5 Charge separation and transportation

An electron-hole pair is created after that the active material absorbs an incident photon. The light-generated charge carriers must be separated to correct contacts for contributing into the light-generated current. In the depleted heterojunction structure that is widely used in CQD solar cell after 2010, the charge carriers will drift over the whole depletion region with the assistance of electrical field generated in the depletion region. In order to extract the charge carriers, the carriers have to
travel certain distance in materials, which is called extraction length. The extraction
length is defined as $W_{\text{dep}} + L_{\text{diff}}$, which the $W_{\text{dep}}$ is the width of the depletion region
and the $L_{\text{diff}}$ is the minority diffusion length [4]. However, because of the existence of
trap states in the material that can sever as recombination centers, it is possible that
the light-generated charge carriers will recombine. This process will result in a loss
of electrons, and accordingly reduce the $J_{\text{sc}}$. Generally, the longer extraction length
leads a higher recombination probability of carriers. Hence this places a upper limit
on the thickness of CQD film, as the charge extraction will become difficult, when
thickness of CQD film exceeds the extraction length [4].

1.2 Colloidal quantum dots

1.2.1 Applications to solar cell

Solar-based power generation techniques have motivated great research
enthusiasm, because of their sustainable and green characteristics. First generation
solar cells are silicon based solar cells, including single-crystalline and multi-
crystalline, which already achieved 25% [12] power conversion efficiency and been
manufactured in industrially scales. The thin film solar cells are regarded as second-
generation solar cell technology, which contains CdTe with 17.3%, Cu(InGa)Se$_2$ with
20.3% in mass production scales [12]. Although the costs of solar-generated
electricity have significantly reduced by technology advancement and manufacture
management, compared with traditional power generation techniques, it still very
high. Therefore, the commercialization capability of currently solar generation techniques is limited.

In order to further reduce the cost of solar power generation techniques, many researchers focus their attentions on the third generation solar cell technology, which contains colloidal quantum dot solar cell (CQDSC), dye-sensitized solar cell (DSSC), and Polymer solar cell (PSC) [12]. Colloidal quantum dot solar cells are solution processing solar cells, which mainly use PbSe and PbS CQDs to form light absorbers with compelling features of low-cost, and tunable band-gap.

CQDs are nanometer-scale semiconductor crystals, which are synthesized in the solution phase. The tunability of their band-gaps is the most attractive property of CQD materials. The radius of quantum dots is reduced to the size that smaller than the exciton Bohr radius, the quantum confinement effects give rise to an increase of band-gap energy, which is illustrated by Figure 2a [13]. For the efficiency of single junction solar cells, the limit of Shockley-Queisser is 31% [12]. In terms of silicon materials, the bang-gap energy of 1.1eV is not easily modified, and this bulk band-gap energy restricts the theoretical efficiency of silicon-based PV device to 29% [12]. But CQDs materials offer a potential to reach the efficiency limit of Shockley-Queisser for single junction solar cell, even break it through the tunability of band-gap. For example, PbS CQDs in large scale have bulk band gap energy of -0.38eV; we can increase their bang-gap to 2eV through simply tuning physical size of particles, which encompassing the optimal band-gap energy of 1.34eV for single junction solar
cells [12]. By utility of this unique property, the optimal bang-gap could be found for solar cells design. Therefore, tunable capability of bang-gap of CQD materials associates with features of low cost and solution processibility can show that the CQDs are very promising material for high performance PV application.

![Solar spectrum](image)

**Figure 2** The absorption in CQD materials can be varied via the tunability of CQD materials. Through changing the CQD size, the quantum confinement is affected and subsequently their band-gap. [13]

As mentioned before, CQDPV experiences a rapid development over period from 2005 to now. Before 2009, the simple Schottky junction solar cell structure, transparent conductive oxide/CQD film/metal electron (TCO), was mainly concentrated on. During those days, indium tin oxide (ITO) was developed as the TCO layer, which played role as the substrates and constructed the Ohmic contact with CQD film. Many types of metal, Ca, Mg and Al, had been tried as the electrodes,
and contacting with p-type CQD films to form Schottky junction. Through those efforts, the efficiency of Schottky junction based devices exceeded 1% in 2008, and further reached 3.6% in 2009[4]. But the $V_{oc}$ of ideal Schottky junction limits performances of such device, which is $0.67E_g$. In practical cases, the $V_{oc}$ is usually lower than that in ideal situations. In addition, for short current density $J_{sc}$, as the absorption will start at the side of TCO, the photo-generated electrons have to pass through the whole region of CQD film. It is unavoidable to stop the carriers recombination behaviors, since many unknown trap states exist in the CQD film region, which leads to the decrease of $J_{sc}$ [4].

Heterojunction structures started to be used in 2009, as researchers realized the deficiencies of Schottky junction structures [4][12]. The typical heterojunction architecture is transparent conducting oxide/n-type oxide/p-type CQD/metal electrodes. The p-n junction structure is the core part of this device architecture, which is a depletion region with built-in electric field that is responsible for charges separation. Heterojunction based solar cells well solved the mentioned limitations of Schottky junction based solar cells. The $V_{oc}$ was increased by reducing the interfacial defects between oxide layers and CQD films; and further improved by maximizing the shunt resistance, which can increase the fill factors (FF). Furthermore, as the charge carriers were usually generated near the junction region, the electrons transport length decreased and the extraction efficiency improved, the $J_{sc}$ finally shown some increases. In the following years, with assistance of band alignment
engineering and further study of ligands in CQD solar cells, the newest certified efficiency in 2015 reached 9.9% [4][12].

1.2.2 Limitations

Compared with theoretical efficiency limit of single junction solar cell, the CQDPV still has a potential to be further improved. The function of photovoltaic devices aims to capture solar radiation and convert into electrical power. Naturally, for increasing their efficiency, it is preferred to maximize the absorption of incident light in solar cells. To achieve light absorption of greater than 90%, in terms of commonly used CQD materials, such as PbS and PbSe, the thickness of films at least needs to be 1\mu m. Once the light is absorbed, the charge carriers need to be extracted out for powering external load. But in typical CQD solar cells, the drift length that decided by doping density and dielectric constant is in the range of 100-200nm, and the diffusion length, which depended on mobility and lifetime of photo-generated carriers, is about 50-100nm [4][5-7]. Additionally, the longer transport distance leads to more defects inside the CQD active layers, which means more carriers recombination is prone to happen. It will further reduce the photocurrent density and limit the device performances. So based on this understanding, an upper limit is placed on the thickness of CQD absorbing layers. The typical solar cells with optimal CQD active layer thickness can only absorb roughly 30%-40% of incident light [7-10]. This can be further confirmed by following external quantum efficiency figure.
Compared with EQE in blue region, the EQE of longer wavelength is significantly lower.

To balance these two aspects, high light absorption and efficiently collecting carriers, which are both significant for the CQD solar cell performance. Several ways were tried to address this issues. Tandem cell structures were studied to overcome mentioned limitations \([6]\). The tandem cell structures are multiple-junctions devices, which serially connect different band-gap materials for absorbing different parts of light spectrum to achieve higher power conversion efficiency. However, in the design of tandem cell structures, some factors, such as current match and intervening layer design, must carefully take into considerations for ensuring performance of tandem solar cell, which are not easy to achieve. Alternative way to promote light absorption at the given thickness of the CQD active layer is to apply photonic techniques. This can be achieved by application of mental nanoparticles, nanostructured metal electrodes, which are able to trap light into CQD active layers through plasmonic effects \([14]\).

### 1.3 FDTD simulation

#### 1.3.1 Fundamental theory

Finite-difference time-domain (FDTD) method is a numerical analysis technique to investigate the propagation of electromagnetic field in various materials. Based on
the Maxwell’s equations, in particular for Ampere’s Law and Fraday’s law, they indicate that the change in electrical fields in time is dependent to the change in magnetic fields in space, which leads to the basic FDTD time-stepping relationship. The idea behind the FDTD simulation is to simply discretize the Maxwell’s equations in time and space with the central approximation. For better introducing the fundamental theory of FDTD simulation, we begin with 1-D case. In this one-dimension case, Maxwell’s equations are written in following form with assuming the free space as the propagation medium:

\[
\frac{\partial E_x}{\partial t} = \frac{1}{\varepsilon_0} \frac{\partial H_y}{\partial z} \tag{6}
\]

\[
\frac{\partial H_y}{\partial t} = \frac{1}{\mu_0} \frac{\partial E_x}{\partial z} \tag{7}
\]

Where the z represents the wave propagation direction.

With applying central difference on the derivatives, the \(E_x\) and \(H_y\) will shift by half a step both in time and space. Hence the equations (1) and (2) can be rewritten in following form:

\[
\frac{E_x^{n+\frac{1}{2}}(k) - E_x^{n-\frac{1}{2}}(k)}{\Delta t} = -\frac{1}{\varepsilon_0} \frac{H_y^n \left( k + \frac{1}{2} \right) - H_y^n \left( k - \frac{1}{2} \right)}{\Delta z} \tag{8}
\]

\[
\frac{H_y^{n+\frac{1}{2}} \left( k + \frac{1}{2} \right) - H_y^n (k + 1)}{\Delta t} = -\frac{1}{\mu_0} \frac{E_x^{n+\frac{1}{2}}(k + 1) - E_x^{n+\frac{1}{2}}(k)}{\Delta z} \tag{9}
\]
The left part of equation (5) shows the derivative of E field at n\Delta t can be expressed as the difference between the value at \((n - \frac{1}{2})\Delta t\) and the value at \((n + \frac{1}{2})\Delta t\). The right side shows the derivative of H field at space point \(k\Delta z\) can be represented in terms of the H field value difference between points of \((k - \frac{1}{2})\Delta z\) and \((k + \frac{1}{2})\Delta z\) [16].

1.4 Objectives

This thesis aims to design, modeling, fabricate and characterize a new type of solar cell, based on disordered nanostructures prepared through electroplating process.

The outline of this report is as following. The chapter 2 will begin to present results with describing the FDTD setup. Then the simulation models and results of FDTD analysis will be presented. The second part in Chapter 2 concentrates on the nanostructures fabrication, including the electrical deposition method optimizing, for the nanostructures growth. Subsequently we will characterize the prepared electrodes made from different fabrication conditions. The section 4 and 5 will develop a photovoltaic module based on this disorder metallic electrode architecture and device characterization. The chapter 3 will briefly discuss several issues encountered in the experiments and the further work for future research.
Results

2.1.1 FDTD setup

In this project, we performed massive simulations to confirm experimental results, analyze the behavior of light in our device and the details of energy localization on the metallic nanostructure. The FDTD method was used for studying the behavior of light interaction with nanostructured metal and light propagation in nanostructured device. All the numerical FDTD simulations were performed through our NANOCPP Maxwell solver (www.primalight.org). NANOCPP is a two/three dimensional FDTD Maxwell code based on a parallel implementation of the Yee FDTD algorithm.

In order to accurately model the disorder surface structure, the surface profile of the gold electrode was generated using a number $z_u(x)$, that Gaussian distributed random number convoluted with Gaussian [17]. N.Garcia had applied the technique to model a random rough surface in his Monte Carlo calculation before [17]. The surface corrugation function $D(x)$ is shown as following:

$$ D(x) = HL^{1/2} \pi^{-1/4} \int_{-\infty}^{+\infty} \exp \left[ -\frac{(x-x')^2}{2L^2} \right] z_u(x') dx' \quad (10) $$

Where the $c_L^2 = 2L^2$.

Here H is scaling factor of surface disorder, which can be regarded as the average height of the nanostructure features. The $c_L$ is the correlation length of surface roughness.
Through employing such a method to model the random rough surface, we can construct expected nanostructured electrodes with precisely varying disorder level via simply adjusting the correlation length and height.

### 2.1.2 Simulation models

Through applying the equation of (10), we can create the simulation model close to the experimental structure through fine adjusting the correlation length and average height. Figure 3 illustrates the tendency of the roughness of metallic surface as functions of both height and correlation. We generated the stimulated models that corresponding to the nanostructured cases made from 13mM solution with respectively 180 seconds, 360 seconds and 600 seconds in NANOcpp code. Since we expect to that all the absorption improvement is a result from energy harvested by the disorder metallic nanostructure rather than increasing the thickness of CQD layers, we should maintain the total volume of active layer as constant. The equation of (10) is able to help us generate a disorder profile at the interface between metal layer and active layer with an average height of 0. So the peak parts in metal nanostructure can compensate the increased valley parts of CQD volume, which can result in a constant CQD volume.

### 2.1.3 Simulation results

To theoretically investigate the impact of disorder metallic nanostructure on the absorption behaviors, the massive simulations were performed using FDTD. The TiO$_2$ is a non-absorbing dielectric layer for visible region and infrared region, so there is no absorption happen in this layer. When we were designing the simulations, the impact of
this layer was ignored. In terms of the thickness of TiO$_2$, we will experimentally discuss it in the experiment section.

Through precisely controlling the correlation length and average height in equation of (10), we generated simulation models, which matched to the features profiles of experimental models made from 13mM HAuCl$_4$ solution with 3 minutes ($L_c$ =20 nm), 6 minutes ($L_c$ = 40 nm) and 10 minutes ($L_c$ = 50 nm) exposure time. To verify that how the thickness of CQD films influences the impact of nanostructured Au electrodes, we stimulated 100 nm and 300 nm thick CQD films over different levels of roughness of nanostructured Au electrodes. Figure 4a,b summaries our simulated absorption results.
Compared Figure 4a,b with Figure 11a,c, for both 100 nm and 300 nm thick CQD cases, we observed a great agreement with our simulation results. The resonance peaks in simulation data also appear at the wavelength of 590 nm for 100 nm thick CQD films case, and the wavelength of 590 nm and 790 nm for 300 nm thick CQD films case in planar structure. With increasing the disorder of surface roughness, the resonance peaks were gradually flattened, which can be attributed to that the disorder nanostructure can prevent the forming of standing waves. For both two kind of thickness CQD cases, the most nanostructured electrodes with correlation length = 50 nm and average height = 35 nm, show the near flat absorption curves, keeping a consistent with then experimental results. Comparing with the absorption results of thinner and thicker CQD films cases with different level of roughness, the absorption enhancements of the thinner CQD cases are much more aggressive, since the thicker CQD films could weaken the impact on broadband absorption improvement from nanostructured Au electrodes. More interestingly, we can observe the impressive absorption enhancement in the infrared region of 720 nm -1100 nm. Figure 1c provides us details on the energy localization on interface between disorder metallic surface and active films. We considered the most nanostructured Au electrode with correlation length = 50 nm and average height = 35 nm, subjected to the monochromatic incident light at wavelength of 790 nm. As our expectation, the localized energy distribution plot demonstrates that light energy at wavelength = 790 nm gets accumulated very efficiently on the interface between disorder metallic surface and the surface of CQD films. In this set of simulations, we reproduce the same level of broadband light absorption enhancement, corresponding to our related experimental results, which means the nanostructured gold electrodes with highest
disorder level can harvest biggest amount of energy. In principle, it offers us a big possibility to transfer such big absorption enhancement into the improvement of current density of PV devices.

From Figure 4a,b we note that, for roughest surface cases, the absorption curve still have a potential to improve through optimizing our disorder metallic nanostructure. Hence we carried on perform some extra simulations to find out the optimum combination of correlation length and average height. In order to approaching near unit absorption curve, we directly generated extremely disorder metallic nanostructures, which means each
feature of metallic nanostructure is very spiky. The results in Figure 5 further confirmed that our assumption has a good agreement with theory. The highly disorder cases exhibit the near-flat absorption curve (>90%) in the whole visible and infrared region, which means that the highly disorder metallic nanostructure have a very excellent capability to effectively harvest energy from broadband.

![Figure 5 FDTD results of highly disorder metallic nanostructure and planar structure](image)

Additionally, we know that the entire slab achieved such high absorption, including the active layer and the metallic layer. For deeply understanding the detailed absorption behaviors in different layers, we performed a series of simulations to clarify the absorption contributions from different layers. Figure 6a,b summaries the results. We generated simulation models with fixed correlation length \( L_c = 15 \) nm and average height \( H = 100 \) nm covered with different thickness of CQD films. The results illustrate an increasing tendency of absorption in CQD films with increasing the thickness of CQD.
films, conversely the absorption in metal layer decreased in the visible spectrum. Figure 3c shows that the capability to capture electromagnetic energy from the broadband of such disorder metallic nanostructures keeps almost the same. In comparison, in the thinner cases, the parasitic absorption of gold is dominant, which will limit the absorption of active films. But we can redistribute the harvested energy by simply adjusting the thickness of active layers, which would be able to make absorption in active films dominate.

Figure 6 FDTD analysis of varying CQD thickness. (a) CQD absorption results of disorder Au electrodes with Lc = 15nm and H = 100nm covered by varying CQD thickness. (b) Metal absorption results of disorder Au electrodes with Lc = 15nm and H = 100nm covered by varying CQD thickness. (C) Total absorption results of disorder Au electrodes with Lc = 15nm and H = 100nm covered by varying CQD thickness.
2.1.4 Summary

In this section, the simulation results agree well with our experimental results, which the roughest metallic surface yields the highest amount of energy trapping. We designed another series of simulations to determine the optimum combination of correlation length and average height of nanostructure profile, which can achieve the near-unit absorption curve in both visible and infrared region. This would be very helpful to offer a direction to further optimize the nanostructure fabrication in future experiments. At last, we investigated that how the harvested energy to be separately absorbed by the active films and the gold layer through performing the thickness study of CQD in simulations. These results would provide us with help to design the real PV devices in following chapter.
2.2 Sample fabrication

2.2.1 Electro-deposition Process

To fabricate realistic metallic electrodes with controllable disorder features, we decided to employ the electrochemical deposition method, which has been successfully applied in biological sensing applications for the production of multiple scale disorder with high surface ratio [18-20]. This is first time to apply this method in the energy-harvesting context. Electro-deposition process is to employ the electric current to reduce the metal ions in solution for growing a coherent metal layer on the conductive electrode. For this project, a three-electrode setup was considered, which Figure 7 shows.

![Electrodeposition System Diagram](image)

**Figure 7 Schematic of electrodeposition system for disorder nanostructure growth**

The three-electrode setup has three electrodes, which are a counter electrode, a reference electrode and a working electrode respectively. In this case, we chose platinum mesh as
the counter electrode, which does not participate in chemical reaction, but allowing the current to flow between counter electrode and working electrode. The reference electrode has a stable and known potential point, which is used as a reference point of potential control and measurement in an electrochemical process. The working electrode is the place where the reduction reaction happens. The electrons are supplied to the metal ions in solution from the working electrode, resulting in that the material is deposited on the working electrode. In terms of this project, the HAuCl₄ with HCl is used as counter ions for gold electro-deposition. The relevant reactions in this electrochemical process are shown as follow.

On the working electrode, the gold chloride is reduced by:

\[ 2HAuCl_4 + 6e^- \leftrightarrow 2Au + 2HCl + 3Cl_2 \]

On the counter electrode, the oxidation of water occurs as:

\[ 2H_2O \leftrightarrow 2O_2 + 4H^+ + 4e^- \]

2.2.2 Nanostructured Gold Substrates

Embedding nanostructured gold substrates into CQD film is promising architecture for improving light absorption, which is able to localize the much more infrared energy into the CQD material through the plasmonic effects, compared with using a planar gold substrate. The degree of absorption enhancement is determined by the surface roughness of gold nanostructure. Hence it is important to control the growth of nanostructure.
Gold-coated glass substrates with a titanium adhesion layer were used as a base for growing nanostructures. In terms of procedure preparing the substrates, initially, two sonication steps were essential to clean gold substrates, starting with acetone and followed by isopropanol. Then cleaned substrates need to be quickly dried through nitrogen after each clean step. Then oxygen plasma processing is sequentially carried out for 10 minutes at the condition of 100 mTorr before growing nanostructures.

We prepared the nanostructured substrates using the HAuCl₄/HCl material system. The size of nanostructured gold features can vary as a function of the solution concentration, deposition potential, and deposition time. Hence the disorder control over the gold substrate surface can be achieved. Accordingly, this provides a possibility to tune the plasmonic property of disorder gold substrates.

During the electro-deposition process, the simplest way to increase the surface roughness...
is to adjust the deposition time and keep rest of parameters consistent. To achieve this purpose, we designed experiments using a 13 mM solution of HAuCl₄ with deposition times of t=180 seconds, 360 seconds and 600 seconds. The SEM images from (a), (b) and (c) in Fig. 8 clearly show the surfaces roughness increased as function of deposition time, which respectively corresponding to the correlation lengths $l_c = 20\text{nm}$, $40\text{nm}$, $50\text{nm}$ and the average features heights $h_{\text{ave}} = 10\text{ nm}$, $25\text{nm}$, $35\text{nm}$. The feature sizes of nanostructures vary in the range of 10 nm to 500 nm.

The solution concentration is another important parameter in the process of preparing nanostructured Au substrates. In order to further investigate how the solution concentration impacts the nanostructure growth, we prepared nanostructured Au substrates through varying the solution concentration. The SEM images in Figure 9a-c show clear differences in nanostructure configuration among cases of (a), (b) and (c). In terms of the same exposure time condition of t=360s, with increasing solution concentration, we observed the surface structuring with progressive growth of micron-scale Au features, which has the feature size about $\sim 2 \mu\text{m}$ in length. In terms of highest solution concentration $[\text{HAuCl}_4]= 40\text{mM}$, the density of micron-scale features is approximately 100 per $10 \mu\text{m} \times 10 \mu\text{m}$ area, coexisting with random nano-scale structure features, which have spatial scale across around 100nm or less. All of those nanostructured Au electrodes exhibit very interesting absorption behaviors. We will further discuss absorption behaviors of those samples in following section.
Figure 9 Top view SEM images of nanostructured An electrode fabricated by using HAuCl₄ with (a) 13mM; (b) 26mM; and (c) 40mM applied for t=360s exposure.
2.3 Absorption Measurement

In order to investigate the impact on broadband absorption from nanostructured Au electrodes with varying levels of disorder, we prepared nanostructured Au electrodes respectively using \([\text{HAuCl}_4] = 13\text{mM}\), \([\text{HAuCl}_4] = 26\text{mM}\) and \([\text{HAuCl}_4] = 40\text{mM}\) for exposure time \(t = 3\) minutes, 6 minutes and 10 minutes. Then we prepared fixed 50 nm thick films of lead-sulfide (PbS) on each of nanostructuring cases using dip-coating process. Samples were automatically manipulated using a medium-sized KSV NIMA multi-vessel dip-coater. Samples were first dipped into a 30 mL beaker containing 15 mL of 7.5 mg/mL PbS quantum dots in hexane for 30 seconds, and left to dry for 180 seconds. Samples were then dipped into a 30 mL beaker containing 15 mL of 0.2% MPA in methanol solution (solid-state exchange) for 3 seconds followed by 120 seconds drying (or 15 mL of 10 mg/mL TBAI in methanol solution for 10 seconds followed by 120 second drying). And finally the samples were rinsed in a 50 mL beaker containing 25 mL of pure methanol for 5 seconds and dried for 120 seconds. This process was repeated for 4 cycles for optimal results.

The absorption measurements were done by use of a Perkin Elmer Lambda UV-Vis-NIR equipped with integrating sphere. Samples were placed inside the integrating sphere and measured while angled at 20 degree versus the incident beam. Except from the port for the incident beam, the rest of ports were closed for capturing the total transmission and reflection. Then the absorption can be calculated as \(100\%-T\%(\text{Transmission})-R\%(\text{Reflection})\). An empty sphere was used for the 100% baseline measurement.
The absorption results are reported in Figure 8. The absorption for all cases dramatically increases with longer deposition time, but the increase rate of absorption has a decreasing trend with increasing the solution concentration. Combining with the Figure 3a-c, we clearly note that the higher concentration leads to more spiky gold features, accompanying with appearance of micron size features. The results illustrate that the more spiky gold features have better capability to capture more energy from the infrared region. In addition, Figure 6d shows saturation effect, which the absorption for cases of 13mM, 26mM and 40mM with 600s exposure time approaches a saturated value over spectrum of 300 nm to 1200 nm. The absorption behaviors mainly depend on the density of Nano-scale gold structures and shapes. In terms of micro-scale features (1μm − 2μm), 50 nm CQD films would not cover them conformably; hence the contribution of absorption should be negligible.
Figure 10 Absorption results. (a) Comparison absorption results of planar case and 13mM with exposure time of \( t = 180s, t = 360s \) and \( t = 600s \); (b) Comparison absorption results of planar case and 26mM with exposure time of \( t = 180s, t = 360s \) and \( t = 600s \); (c) Comparison absorption results of planar case and 40mM with exposure time of \( t = 180s, t = 360s \) and \( t = 600s \);

Additionally, for experimentally characterizing the impact on broadband absorption enhancement of disorder nanostructured Au electrodes covered by different CQD thickness, we experimentally carried on the CQD thickness study. First of all, we used \([\text{HAuCl}_4] = 13\text{mM}\) solution with exposure times of \( t = 3 \text{ minutes} (L_c = 20\text{nm}), 6\text{minutes} (L_c = 40\text{nm}) \) and 10minutes \( (L_c = 50\text{nm}) \) to fabricate the nanostructured Au substrates. We used layer-by-layer spin-coating process to deposit 100 nm and 300 nm lead-sulfide
(PbS) CQD films on the top of three levels of surface roughness and the Au planar control. In terms of each layer, the CQD solution (50mg/mL in octane) was deposited on Au electrodes and spin-cast for 10s at 2500 RPM. Then 1% MPA was used to soaking the film for 3 seconds prior to spinning dry for 10 seconds at the RPM of 2500. At last, the methanol was used twice to wash the unbound ligands.

Absorption spectra of nanostructured Au with a 100 nm CQD film are compared for all levels of nanostructured substrates, which is illustrated by Figure 9a. We can clearly observe the dramatic absorption enhancement over the 600 nm to 1200 nm. In particular, at $\lambda = 850 \text{nm}$, that a typically poorly absorbed wavelength for 1.3eV PbS films, we measured absorption values of 13%, 18%, 39% and 60%, which are respectively for planar case, $L_c = 20$ nm, $L_c = 40$ nm, and $L_c = 50$ nm nanostructured Au electrodes. The most disorder case ($L_c = 50$) showed the impressive enhancement of light absorption, compared with planar case. For better presenting the impact of nanostructured disorder on PbS film absorption, we plot the relative enhancement for each nanostructured substrate versus the planar control, illustrated by Figure 9b. From Fig. 9b, we can observe, for $L_c = 20$ nm case, the most significant enhancement happened at the $\lambda = 600 \text{nm}$, with 20% more absorption. In terms of $L_c = 40$ nm and $L_c = 50$ nm cases, wavelengths that the maximum absorption happened, have a slight shift. The maximum enhancement is observed at $\lambda = 655 \text{nm}$ for $L_c = 40$ nm case and at $\lambda = 700 \text{nm}$ for $L_c = 50$ nm, with more increases of 50% and 65%. More interestingly, we observed the impressive increase at the most weakly absorbing wavelength $\lambda = 850 \text{nm}$ for all three nanostructured cases. From Figure 9b, it respectively shows improvement of 5%, 26%
and 47% for $L_c = 20$ nm, $L_c = 40$ nm, and $L_c = 50$ nm cases versus the planar case. Compared with the most nanostructuring case and least nanostructuring case, there is a 9-fold relative enhancement. Additionally, in terms of the infrared region, the most disordered case shows a constant of 40% absorption increase, which is impressive and interesting.

The absorption spectra and relative enhancement for 300 nm CQD films are reported by Figure 9c. Compared with 100 nm CQD cases, we observe a great absorption for planar case from 600 nm to 800 nm, with apparent Fabry-Perot resonance effects. The absorption, at $\lambda = 850$ nm, is about 17%, 42%, 61% and 75% for the planar, $L_c = 20$ nm, $L_c = 40$ nm and $L_c = 50$ nm cases respectively. Obviously, the most disorder case generates the highest light absorption. Figure 9d reports the absorption enhancement of each nanostructuring substrates versus the planar case. Comparing the absorption enhancement between the least nanostructured case and the most nanostructured case, with thicker CQD films, we note that the enhancement for $L_c = 50$ nm case is approximately 2-fold greater than that for $L_c = 20$ nm case. This result demonstrates the role of disordered nanostructure electrodes on the absorption of PbS films. In terms of thinner active films, the much more significant absorption enhancement is observed from the roughest electrode, which indicates to the improved impact of near-field effects on overall absorption enhancement.
Figure 11. Absorption results. (a) Comparison absorption results of 100 nm thick CQD films on varying degrees of disorder of nanostructured Au electrodes. (b) Relative enhancement for each nanostructured electrode (each level of disorder) compared to the planar control (for 100nm CQD film). (c) Comparison absorption results of 300 nm thick CQD films on varying degrees of disorder of nanostructured Au electrodes. (d) Relative enhancement for each nanostructured electrode (each level of disorder) compared to the planar control (for 300nm CQD film).
2.4 Design and fabrication of the photovoltaic module

More importantly, how to transform such huge absorption shown in Figure 11a-c into practical current enhancement in photovoltaic context is concerning question, which can be used to develop a novel solar cell that has a big potential to harvest huge energy from infrared region. We developed a test device in a top illuminated configuration shown in Figure 12. A layer of gold (planar or nanostructured) was put atop glass as the bottom electrode, then a certain thickness TiO$_2$ layer was grown atop the prepared Au electrode by RC magnetron sputtering or ALD method, and treated with TiCl$_4$; 10 layers (~300 nm) films of 1.3 eV PbS CQD was grow on the TiO$_2$ layer through spinning coating method; finally a certain thickness ITO (tin-doped indium oxide) was sputtered consequently as the transparent top-contact.
Several nanostructure Au electrodes were investigated in the above section. From the absorption results in Figure 8 and 9, in principle, the higher light absorption will lead to better current density enhancement; hence the large and spiky features probably are most expected. However, from the device standpoint, as the CQD film thickness is relative thin (~300nm), the film would be impaled by those 1 – 2μm large spikes, which caused electrical shorting of solar cells (Figure 11). Hence we decided to focus on the nanostructured Au electrodes that made from 13mM solution with 360s and 600s exposure time.
Nanostructured CQD photovoltaic devices were developed atop a layer of titanium dioxide (TiO$_2$), which play a role as the n-type window layer to form the depleted heterojunction. Hence, currently, the layer of TiO$_2$ is necessary for developing such photovoltaic module. However, the absorption enhancement mainly is attributed to plasmonic effects introduced by rough metallic surface, which can localize a big amount of energy from infrared region at the metal-dielectric interface, like energy hot spot with certain radius. As such, introducing of a TiO$_2$ layer between CQD films and nanostructured Au electrode reduced the overlap between localized energy spots and active layers, leading lower current enhancement. Hence we experimentally determined the optimal thickness of TiO$_2$ layer (Table 1).
Table 1 reports the relationship between thickness of the TiO$_2$ layer and the performances of devices. We noted that the performances of tested devices dropped dramatically, when the thickness of TiO$_2$ was smaller than 50 nm. In terms of TiO$_2$ thickness, the 25 nm and 12.5 nm cases shown dramatic decreases in the $V_{oc}$ and $J_{sc}$, accordingly, the PCE reduced. The reason behind results is that the thinner TiO$_2$ is not able to provide enough charge carriers to completely deplete the CQD layer, which caused the deficient band separation, leading to lower $V_{oc}$. Combination with the consideration of maximizing overlap area between localized energy spots and active layers, 50 nm TiO$_2$ layer is the optimal thickness for our nanostructured Au electrode photovoltaic module.

Another important issue we need to consider for developing a top-illuminated architecture is the design of top transparent contact. The thicker top contact provides better conductivity, but at the expense of higher absorption. The compromise between absorption and conductivity of top contact is a crucial issue for PV devices [24].
To experimentally determine the optimal ITO thickness for our top-illuminated architecture, we fabricated device on planar Au substrates with varying thickness of ITO. The following table 2 shows the varying thickness ITO and corresponding performances of devices.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>PCE(%)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm</td>
<td>-0.51</td>
<td>10.3</td>
<td>2.0</td>
<td>31</td>
</tr>
<tr>
<td>200 nm</td>
<td>-0.51</td>
<td>11.6</td>
<td>2.3</td>
<td>35</td>
</tr>
<tr>
<td>300 nm</td>
<td>-0.52</td>
<td>12.6</td>
<td>2.6</td>
<td>41</td>
</tr>
<tr>
<td>400 nm</td>
<td>-0.54</td>
<td>11.3</td>
<td>2.4</td>
<td>41</td>
</tr>
</tbody>
</table>

A clear tendency from Table 2 shows that increasing thickness of ITO leaded to decreasing series resistance ($R_s$), which accordingly result in an enhancement in FF with increase of $J_{sc}$. Subsequently, an overall improvement is observed in PCE with increasing thickness of ITO. From the case of 400 nm ITO, we noted the FF saturated at the value of 44, with the decreasing short-circuit current density, since the thicker ITO reduces the transmittance. Hence, we experimentally chose 300 nm as the optimal ITO thickness.

After determining the nanostructure profile, TiO$_2$ thickness and ITO thickness, we considered testing device with integrating our nanostructured electrode. The cross-sectional SEM pictures in Figure 12 a-b clearly illustrate the stack configuration of testing photovoltaic devices. We prepared nanostructured Au electrodes using 13mM
solution with 10 minutes ($L_c = 50$ nm) and 6 minutes exposure time ($L_c = 40$ nm). For both of two cases, we sputtered 50 nm TiO$_2$ atop Au electrodes with treatment of TiCl$_4$, then 10 layer 1.3 eV PbS CQD films (300 nm) was fabricated on the top TiO$_2$ layer through the spinning coating method. At last, the 300 nm ITO (tin-doped indium oxide) was grown atop CQD films as the top transparent contact.

Figure 14 Cross-sectional SEM of the nanostructured Au photovoltaic device illustrating the various layers. (a) 600 seconds nanostructured case. (b) 360 seconds nanostructured case.
2.5 Efficiency Measurement

We measured external quantum efficiency and current-voltage data for our photovoltaic devices. A monochromatic light source (400 W xenon lamp source filtered through a monochromator) that passed through an optical chopper operated at 220 kHz was employed to measure the external quantum efficiency. A white light that approximated solar illumination was applied to test photovoltaic devices. Newport 818-UV and Newport 818-IR power meters were used to measure the monochromatic light power. The current response was measured by a Stanford Research Systems lock-in amplifier under short-circuit condition. The accuracy of the EQE measurements was ±8%.

In terms of current-voltage measurement, we employed a Keithley 2400 source meter to measure all fabricated devices under the condition of N₂ flowing. The solar spectrum at condition of AM 1.5 was simulated to within A specification (less than 25% spectral mismatch). A xenon lamp and filter were used as the light source. The source intensity was measured employing a Melles-Griot broadband power meter through a 4.9 mm² circular aperture and confirmed using a calibrated reference solar cell (Newport, Inc.). The accuracy of the measurement was ±5%.

Figure 13a reports external quantum efficiency spectra of a planar Au electrode device and nanostructured Au electrode devices, which shows a similar tendency as the absorption data presented in Figure 10a. Clearly, we observed that the tendency of improved external quantum efficiency is a function of electrode roughness, which was directly beneficial from absorption enhancement. From the Figure 15a, we note that the
enhancement of EQE with any level nanostructured Au electrode was broadband. Explicitly, for the more disorder case (with 10 minutes exposure time, $L_c=50\text{nm}$), we can observe more obvious improved response for $\lambda > 750\text{nm}$. At the wavelength of $\lambda = 840\text{nm}$, the EQE response is improved by a relative 41% for the 10-minutes nanostructured case ($L_c=50\text{nm}$). At the exciton peak ($\lambda = 980\text{nm}$), compared with 6-minutes nanostructured case and planar case, the EQE response of the 10-minutes nanostructured case is enhanced by a relative 10% and 57%.

Figure 15b reports the current-voltage (J-V) of developed photovoltaic devices. We can clearly observe that the 10-minutes nanostructured case exhibits the highest current density, leading to highest 3% power conversion efficiency (PCE), as compared to 2.6% for 6-minutes nanostructured case and 2.4% for planar case. In the relative terms, the most disorder case shows a gain factor of 15% above less disorder case and 25% enhancement compared to planar control. More importantly, all of three cases show the similar open circuit voltage ($V_{oc}$), that approximate -0.5 V, which indicates that almost all enhancement results from improved short-circuit current density. Explicitly compared with planar control case and 6-minutes nanostructured case, 10-minutes nanostructured case respectively shows 34% and 19% enhancement in short-circuit current density ($J_{sc}$). The exceeding 30% improvement in short-circuit current density is real an impressive achievement in addressing the absorption-extraction compromise of CQD thin-film solar cells.
Figure 15 (a) External quantum efficiency (EQE) of planar, $t = 6$ minutes and $t = 10$ minutes nanostructured Au photovoltaic cells, demonstrating improved QE as a function of electrodes disorder. (d) Input-Output I-V curves for planar, $t = 6$ minute and $t = 10$ minutes nanostructured Au photovoltaic cells, again showing proportional improvement in the output photocurrent $J_{sc}$ (and also PCE) as a function of electrode disorder, with approximately 34% improvement in $J_{sc}$ over the planar film for the highest level of disorder.
Discussion

In this project, we demonstrated that the significantly improved broadband light absorption, particularly for the infrared region, is resulted from the multi-scale disorder metallic electrode. In the tested top-illumination photovoltaic prototype, we also proved that the 10-minutes nanostructured case shows 25% increase in power conversion efficiency over the planar control device, which almost all the enhancement was from the increase of short-circuit current density. To maximize the value of this approach to photovoltaic devices, the advances of inverted architecture are desirable. In the tested solar cell architecture, basically, the space layer of TiO2 between active films and metallic electrodes reduced the plasmonic effects, which indicates that a portion of improved absorption could be not localized into active layer. Hence the promising way to address this issue is to develop inverted architecture with n-type window layer fabricated on the top of CQD layers, which can make active films directly contact with disorder metallic electrodes. However, to achieve this, a strategy of surface treatment is required to be developed to ensure the adhesion of the active layer on the Au electrode. For the transparent top-contact ITO, although it shows excellent optoelectronic properties when it was grown on the glasses, we note some degradation of optoelectronic properties while it were directly deposited on the CQD layers. To obtain better device performances, we would expect that the ITO top-contact maintain >90% transmittance for the spectrum of 400-1200nm and the sheet resistance should keep below 10Ω/cm.
Additionally, the configuration of nanostructured gold electrodes still has potential to be further optimized. Combining with simulation results in Figure 5 and SEM top view images in Figure 9, we note the nanostructured gold electrodes shown better absorption performance, especially in the infrared region while the nanostructure features are spikier, meaning the lower correlation length and higher average height. But the spikier nanostructure features were observed in the micron-scale range, which are too big to integrate into thin film photovoltaic devices. Hence, to harvest the maximum energy from infrared region, how to more precisely grow spikier nanostructure features in nano-scale would be another way to maximize the value of this strategy. Material study is also an interesting part in the future work. In this project, we focused on the gold, which is well known that it is very expensive material. If we can expand the scope of materials, such as from gold to silver, aluminum etc., which will dramatically reduce the cost of this approach. With above amendments of device architecture, nanostructure configuration and materials, we could properly enhance the IQE of the solar cell, globally increase the power conversion efficiency and reduce the cost of device fabrication. Compared with a standard planar depleted heterojunction cell with similar PbS film thickness, with the advances of architecture, electro-deposition method and materials, we predict that this approach could lead to impressive enhancement in record-efficiency CQD photovoltaic devices and decrease of fabrication cost.
**Conclusion**

It is well known that near half amount of energy of solar spectrum resides in the infrared region. If the part of energy could be effectively harvested and transfer into active layer of solar cells, it is will be very promising way to approach the high performance and low-cost CQD solar cells. In addition, the compromise between absorption and extraction are demonstrated as a critical step to further advance the CQD photovoltaic device performances [25]. In this project, with consideration for both two aspects, we propose a strategy, that disorder nanostructured metal electrode, to localize more energy from infrared and overcome absorption/extraction compromise.

We adapted a chemical electro-deposition technique for fabricating the disorder nanostructured gold electrodes with control the disorderness of electrode surface through varying the solution concentration and exposure time. We experimentally demonstrated that the proper nanostructured gold electrodes shown the impressive broadband absorption enhancement, in particular for improvement from the infrared region. Then we further modeled the disorder nanostructure through FDTD simulation and illustrated the existence plasmonic effects caused by the disorder nanostructures. Furthermore, we obverse that the enhanced plasmonic effects and increased absorption are a function of surface roughness of prepared nanostructures. We further valid our results using thinner CQD films, which clearly
supported that the large portion of energy was harvested using disorder nanostructured gold electrodes and was transferred into active films. In order to approve the practical value of this stratagem, we finally applied it into the real photovoltaic context. We developed a CQD photovoltaic prototype with top-illuminated architecture, which using the disorder nanostructured gold substrate as the bottom electrode. Then compared with the planar control, we demonstrated the improvement of the multi-scale metal electrode based CQD solar cell, including EQE, short current density and power conversion efficiency as a function of the increasing disorderness of the nanostructured electrodes.

Our strategy and the developed infrared photovoltaic prototype open an avenue for the infrared energy harvesting and ultra thin film solar cells. The current inverted architecture still has some space to be improved for maximizing the value of this approach. In future work, we plan to keep optimizing the configuration of metal nanostructure, developing the more appropriate inverted architecture and investigating metal materials. With those progresses, we believe that this strategy could generate impressive improvements in CQD record-efficiency. More importantly, it provides a big potential to further reduce the thickness of active layer without considering the compromise between absorption and extraction, meanwhile the cost of solar cell fabrication could dramatically decrease.
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