Scattering from ZnO Nanorods in an Absorbing Perovskite Layer

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Abstract: Increased light scattering have been found to improve the short-circuit current of photovoltaic devices. In this paper we have tried to optimize the dimensions of ZnO nanorods to achieve this. Scattering efficiency of these nanorods was evaluated by solving Maxwell's electromagnetic equation in the nanorods and surrounding perovskite using COMSOL Multiphysics. For evaluation of scattering parameters the scattered field was integrated on the surface of nanorods. The scattering coefficient was found to increase with increase in radius.

Keywords: ZnO, Nanorods, Solar cells Scattering, Perovskite, $CH_3NH_3PbI_3$.

1. Introduction

The ongoing climate change creates a need for cheap photovoltaic devices. The rapid increase in efficiency of perovskite solar cells achieved in last few years coupled with their low cost of fabrication makes them a promising alternative to popular expensive silicon solar cells. Perovskite solar cells generally employ organic metal halide perovskites as light absorbing material, absorption of light in perovskite results in photogenration of charge carriers. The holes and electrons travel through hole transport layer and electron transport layers respectively to different electrodes and get collected there.[1]

Different architecture involving perovskites have been found to be effective for photovoltaic application, most popular one uses Spiro-O-MeTAD as hole conductor and mesoporous (MS) TiO_2 as electron transport layer. The low mobility of the MS TiO_2 has been found to cause current hysteresis in these solar cells. ZnO nanorods are a good replacement of MS TiO_2 because of their low cost fabrication and higher electron mobility. Various research groups have reported perovskite ZnO nanorod solar cells with efficiency comparable to regular perovskite solar cells.[2] Figure 1 shows the schematic of such solar cells.

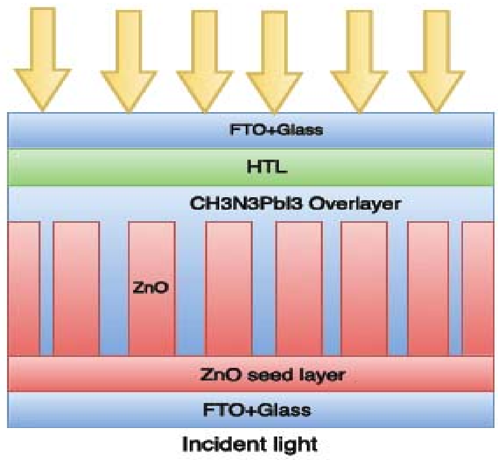

Figure 1. Schematic of a perovskite solar cell with ZnO nanorods.

When light encounters an object of different refractive index a fraction of the incoming light energy may get absorbed in that object while fraction of it may changes its path, resulting in attenuation of incoming beam. This deflection of light is called scattering.[3] Scattering of light in a solar cells increase the path length of light in the device resulting in better absorption and lesser transmission. Different research groups have successfully enhanced the short-circuit current of photovoltaic devices by employing particles and structures which scatter light effectively.[4] For perovskite solar cells scattering due to roughness of perovskite layer have been found to improve the performance of device.[5] Scattering coefficient defined as scattering efficiency per unit cross-section have been used in optical simulation of dye-sensitized solar cells different research groups.

In this paper we have presented scattering efficiency of ZnO nanorods of different radius surrounded by perovskite on all sides. Along with it; effects of presence of ZnO nanorods on different physical quantities in perovskite layer have also been discussed.

2. Theory

Mie scattering theory is the most popular method to calculate scattering parameters due to its simplicity, but its inherent assumption of zero absorption in surrounding medium, renders it inaccurate when the scattering object is surrounded by an absorbing medium.[3] In this paper finite element method (FEM) was used to simulate scattering from the nanorods. Studying scattering of light upon its encountering a finite object, using a numerical technique like Finite difference time domain (FTDT) method or FEM involves calculation of electromagnetic field in a closed area enclosing the scattering entity. This scattered field is then extrapolated to calculate far field (defined as product of electric field and distance vector at infinity) using methods like Stratton-*Chu* formula.

Scattering cross-section of an object is calculated by dividing the integral of scattered electromagnetic power (calculated from the fore-mentioned far field) over an imaginary surface enclosing the object from outside, by the density of incident energy. But in an absorbing medium, this above mentioned far field will be a function of the distance. Hence the rate of scattered energy transferred at the surface is calculated by integrating the Poynting vector of scattered wave normal to the surface at the surface of the object itself by the expression below.[6]

$$W_{sca} = \iint \left[\mathbf{E}_{sca} \times \mathbf{H}_{sca} \right] \cdot \mathbf{n} dS$$

Here, **n** is the normal vector pointing outwards from the nanorod surfaces, and *dS* is infinitesimal surface area. Scattering cross-section was evaluated by taking the ratio of scattered energy and the average of Poynting vector at the incident surface.

Cylinders with length greater than 3-5 times that of diameter acts as infinite cylinder and their scattering cross-sections are rather independent of the length. Hence the scattering parameters were evaluated only for nanorod length 600 nm and the optimization of diameter for this length was assumed to hold for longer nanorods.

3. Use of COMSOL Multiphysics

The Electromagnetic Waves, Frequency Domain User Interface of Wave optics module of COMSOL Multiphysics was used for results presented this paper. The nanorods were assumed to be surrounded by perovskite on all sides, which is slightly different from the actual device structure. In an actual device the nanorods are most likely to be deposited on ZnO seed layer. But in a working device a very small fraction of light energy is assumed to reach the layer beneath ZnO nanorods. Hence we expect, thin film layer the bottom would not much affect the magnitude and pattern of scattering. COMSOL Multiphysics has a model in model library to study both far field and near field scattering from a gold nanoparticle. In that model, a background planer electromagnetic field has been defined inside an imaginary surface enclosing the scattering nanoparticle from outside. A relative electric field or scattered field was calculated at mesh points inside that surface by solving the Maxwell equations.

$$\nabla \times \mu_r^{-1} \left(\nabla \times \mathbf{E} \right) - k_0^{\,2} \left(\varepsilon_r - \frac{j\sigma}{\omega \varepsilon_0} \right) \mathbf{E} = 0$$

The imaginary surface was surrounded by spherical perfectly matched layer (PML). This PML is an artificial layer which effectively truncates computational regions of numerical methods like FEM by completely absorbing wave incident on it to avoid any interference due to reflection of wave from the boundaries.

Furthermore the outer boundaries of PML were defined as scattering boundary condition. Scattering boundary conditions when applied make a boundary transparent to both the excited plane wave and the scattered wave and hence sum of them as given below.

$$\mathbf{E} = \mathbf{E}_{sc} e^{-jk(\mathbf{n} \cdot \mathbf{r})} + \mathbf{E}_0 e^{-jk(\mathbf{n} \cdot \mathbf{r})}$$

In a uniform non absorbing media in absence of any disturbance, the total electric field will be the excited field itself. But absorption in surrounding medium will result in a finite electric field distribution relative to the excited plane wave being observed even in the absence of any change in refractive index, as clear from figure 2; which presents z component of relative electric field in perovskite excited by an electric field. The outer layer with negligible electric field is a PML layer.

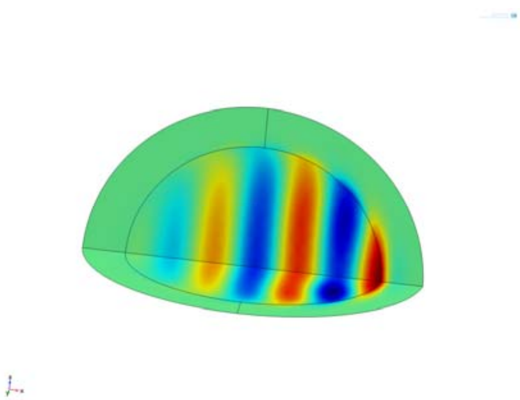

Figure 2. z-component of relative field in the absence of a scattering.

This non-zero relative field clearly indicates that if Maxwell's equations are solved for relative field in presence of a scattering entity, the solution obtained would be a result of both, the absorption in the surrounding medium and scattering from the scattering entity. To study the variation of electric field caused by the presence of scattering entity, independent of the effect of absorption in surrounding medium a different approach was used in this paper.

Transverse electric (TE) light wave was excited in a rectangular slab of perovskite using an active port at one of the faces as shown in figure 3.

$$\mathbf{E}_{\mathbf{inc}} = \left(0\ ,\ \mathbf{E}_0 e^{-jkz}\ ,\ 0\right)$$

This excited wave was absorbed by a passive port defined at the opposite face. This whole rectangular slab and ports were surrounded by Cartesian PML on all sides. The relative field was then calculated using the previously calculated values of electrical field as background field and solving the Maxwell's equation as for the simulation setup shown in figure 3.

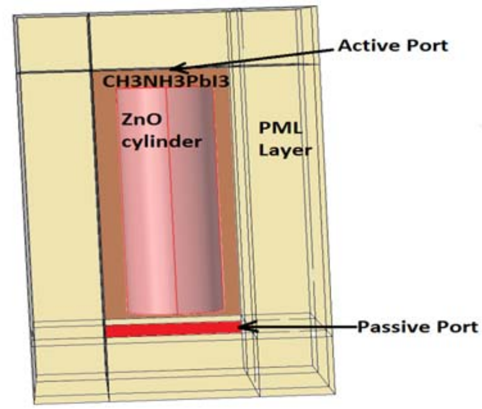

Figure 3. Simulation setup used in this paper.

For perovskite the refractive index of Methyl ammonium lead iodide perovskite ($CH_3NH_3PbI_3$) was taken from published literature and so was refractive index of ZnO.

4. Results

Greater electrical energy density was observed in surrounding perovskite compared to ZnO nanorods, as clear from figure 4. This better electrical density in perovskite will lead to more photo-generation of charge carriers.

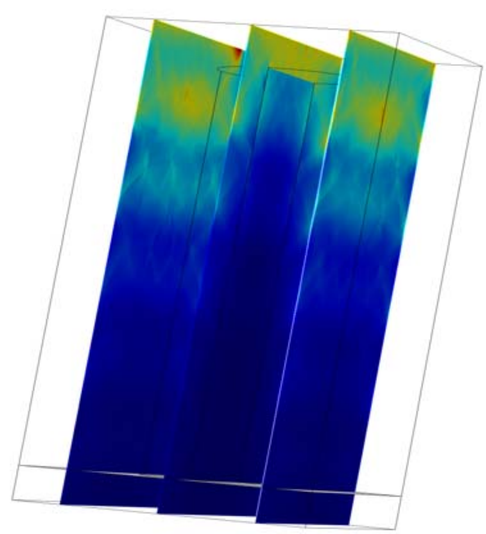

Figure 4. Electric energy density in perovskite and ZnO nanorods.

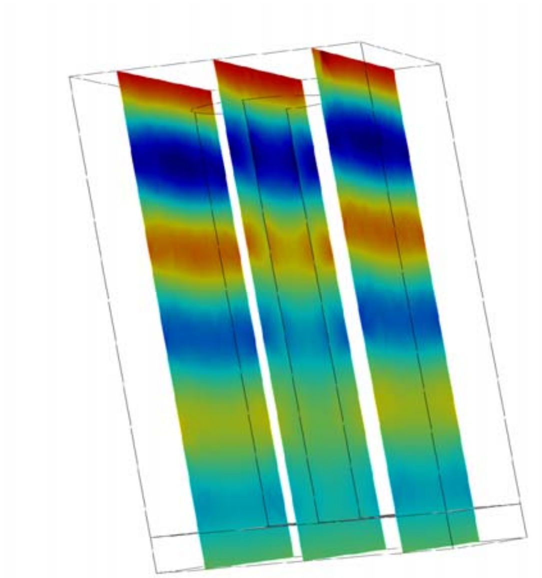

Figure 5. y component of total electric field in perovskite and ZnO nanorods.

Figure 5 shows total electric field which is sum of incident and scattered field. Magnitude of electric field clearly is lower in the ZnO nanorods compared to the surroundings.

$$\vec{\mathbf{E}}_{tot} = \vec{\mathbf{E}}_{inc} + \vec{\mathbf{E}}_{sca}$$

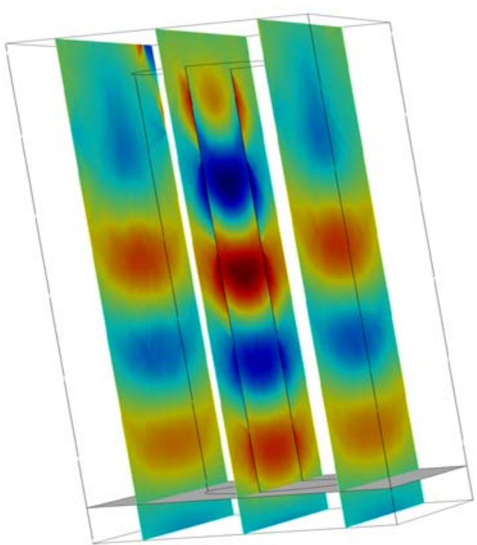

Figure 6. Relative electric field y component in perovskite and ZnO nanorods.

Like total electric field relative field was also found to reduces gradually towards the bottom as it would have been expected due to absorption in the perovskite layer.

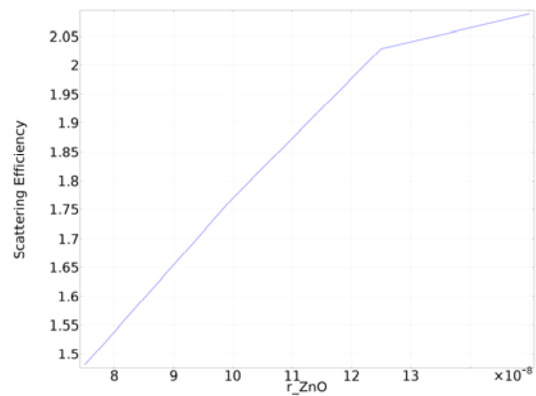

Figure 7 Scattering efficiency of ZnO nanorods as a function of radius.

The ZnO nanorods were found to be weakly scattering, the scattering efficiency obtained for the nanorods were less than half of scattering coefficient for spherical TiO_2 400nm particles, which are commonly used as scattering layer in Dye sensitized solar cells for performance enhancement. But these nanorods have the length of the whole active layer rather unlike spherical particles who have the thickness about one third of the active layer. Hence we expect an increase in performance of solar cells because of scattering by these ZnO nanorods.

5. Conclusions

Increasing diameter of nanorods was found to improve scattering, the improvement gradually reducing with increase in diameter. However the increase in diameter may affect electron transport properties. Increasing the diameter will also decrease the interface area between perovskite and ZnO decreasing the interface defect density. All these will affect the performance of the solar cells. Hence a complete optoelectronic simulations of the device will be required to optimize the diameter for better photovoltaic performance.

6. References

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