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The mechanical effect and physics properties of ZnO nanoparticles in nanocomposite organic solar cell P3HT:PCBM

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Abstract

Doping particles into composite materials can mechanically stabilize these structure. At nanoscale, doping nanoparticles not only strengthen the material structure but also improve some mechanical and physical properties of materials. In this work, we will investigate the role of ZnO nanoparticles (NPs) doping into the nanocompsite multilayer organic solar cell (OSC) with the active layer composed of P3HT:PCBM. ZnO NPs is an economical ingredient for some applications in organic solar cell devices. They not only enhance significantly the absorption of the incident light but also make the composite nanostructure in OSC more durable. The absorption properties such as the absorption intensity can be explained by Mie scattering theory and studied numerically using finite element method (FEM). The mechanical effects can be illustrated by Young and Bulk modulus.

Keywords: organic solar cell, nanopartiles, nanocomposite, finite element method, Young and Bulk modulus

1. Introduction

A high demand search for the renewable resources has opened a great room for the academic scientists, the industrial companies as well as the investors meeting together. Contributing to the world total energy consumption, renewable energy has rised from 0.02% in 1980 upto 19.4 % in 2013 and an estimated 40GW installed in 2014 [1]. One of the very promising trend in renewable energy demand is the solar harvesting technology including solar cells, solar thermal equipments, so on. One of those, an inorganic solar cells, has been proved to be a good candidate which is able to replace partly the traditional energy such as fossil energy [2]. Unfortunately, the cost and its inflexible properties has limited the inorganic solar cells and make it flat in energy demand recently [3]. From physics side, the physicsts have brought a new idea of the next generation of solar cell into the world of renewable energy devices namely organic solar cells with the light, flexible and economical features which is a potential candidate for the industrial applications and daily use. However, the durability, the stablity in an extreme conditions as well as the low energy conversion efficiency has still challenged the scientists. The reason comes from OSC characteristics itself. The competition between light harvesting and the recombination of charge carrier has set the typical size to the OSC strucutre and limited the efficiency at 11% up to date [4, 5, 6, 7]. Whereas, the critical efficiency for a commerical product should be higher than 20%. One of the solution is to dope the nanostructures such as nanoparticles (NPs). In the presence of NPs will induce the localized surface plasmon resonance. LSPR will increase the cross section of the particles. As the result, the absorption will increase with the cross section. Hence, the performance of organic solar cell as well as the energy conversion efficiency can be improved. For an illustration, we will investigate ZnO nanostructure, i.e. ZnO NPs doping into the active layer in organic solar cell (OSC). Among different conducting blend polymer using for active layer, P3HT:PCBM is highly miscible, exhibits a rapid and unusual interdiffusion and ultimate morphology which relates to the

device efficiency [8, 9, 10]. We will use finite element method simulation to study this system and the mechanical effects such as Young modulus and Poisson coefficient. Our main findings are: the active layer P3HT:PCBM doped with ZnO NPs has a higher light absortion intensity comparing with its counterpart in air. The absorption intensity has increased with the size of nanostrucutre.

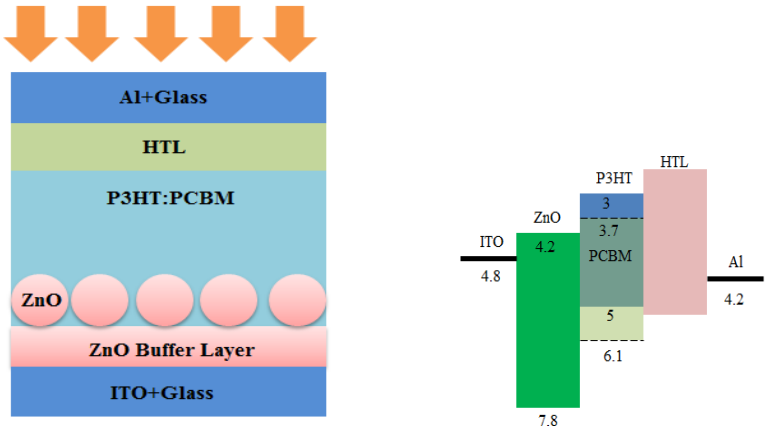
From mechanical perspectives, nano-composite material consists of two or more distinct components at nano-scale which is promising to obtain a new material with better properties. Such components include matrix material and filled materials including fiber, fabric, particles, and so on. The matrix material aims to ensure the linkages among all the composite components, which will resist all external acting on the composite including heating, physical, and chemical loads, while the filled components are used to improve the mechanical properties (stiffness and strength) of the composite [21-23]. The composite reinforcement components typically are composed of fiber, fabric, or particles. The fibers and fabrics play to increase the bearing capacity of the composite structure, while the particles often reduce crack, plastic deformation and increase the waterproofing capacity. Hence, the combination of fiber and particles in the composite material is able to make the composite product more perfect and meet the requirements of modern technology [24,25,26,27]. Recently, the reinforce of polymers using piezoelectric particles, ferromagnetic particles, titanium oxide particles,... not only increases the strength of the material but also makes the composite product own its new physical characteristics. Therefore, the authors are interested in studying the polymer composites reinforced by additional particles in this study [24,25,27]. With composite materials, we need to determine their mechanical and physical properties, and also to find out their elastic module and Poisson coefficient that are the most significant mechanical properties of composite material. Composite with filled particles is often considered as an isotropic homogeneous elastic material, and it has two independent elastic constants, including Young's module (E) and Poisson coefficient. In present, many authors have proposed the different formulas to determine Young's module E of composites. In the article, Dinh et al 2013 [28] empirically tested the modulus E to the polystyrene and titanium oxide particles composite. Recently, many authors have been interested in determining the formula for Young's E modulus of the particles composite [24,25,26]. Here, we can summarize as the follows: there are three approaches for determining the elastic modules of composite material including experiment, inductive methods, and using the mechanical model. The details of each approach are presented as the following:

- *The experimental approach*: The advantage of this method is able to determine accurately the elastic modulus of composite. However, the main disadvantage of this method is that it does not reflect the influence of material composition on the composite material because composite is material comprised a variety of components.
- *The inductive methods*: Based on the repeated experiments, the authors can predict the rules and give the formula for determining the elastic module E of the material. This approach is used more effectively with the materials which are surveyed, but less suitable for other materials.
- *The mechanical model*: Based on modeling the mechanical problem, in the mechanical model, the particles are usually the spherical particles. The advantage of this method is easy to determine the relationship between the components of composite materials and elastic modulus. Therefore, we can also calculate and predict their values that is a basis for calculating and optimizing the design of the characteristics for new material. However, the results calculated by the mechanical model depend on the model of calculation and such results may vary according to different composites.

In the next section, we will brieftly introduce the localize surface plasmon resonance (LSPR) effect following by the numerical technique finite element method (FEM). The results and discussion will be placed at the end.

2. Localized Surface Plasmon Resonance In Organic Solar Cell

Figure 1 shows a regular structure of OSC doping with NPs (a) and the energy scheme (b):



(a) (b)

Figure 1. (a) A regular organic solar cell structure: Al and ITO/glass are electrodes, HTL is a hole transport layer, ZnO is a buffer layer, active layer P3HT:PCBM doped with ZnO nanoparticles. (b) The energy scheme of the different layers respectively.

LSPR is well-known phenomenon as the consequence of the interaction between light and medium in the presend of some ingredients at nanoscale such as nanoparticles, nanorods, nanoprisms, nano pyramid, so on. Depending on the nanostrucutre and the properties of the light such as the wavelength and frequency, the physics properties of the medium will be alterned. The metallic NPs such as Au-NPs, Ag-NPs has been claimed to exhibit LSPR in many medium due the collective oscillations of electrons inside metal [11, 12, 13, 14, 15]. Unfortunately, these particles is very costly to produce at the massive quantities. Recently, one has proposed another structure with less expensive cost to replace the metallic particles, namely ZnO. Using Mie scattering theory [16, 17], it is easy to shown that the scattering and absorption cross section as:

$$\sigma_{scat} = \frac{1}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4 |\alpha|^2, \quad \sigma_{abs} = \frac{2\pi}{\lambda}\mathrm{Im}[\alpha] \tag{1}$$

where, α is the polarized coefficient of NPs which depends on the nanoparticle characteristics and the environment surrouding the particles. The absorption properties depends strongly on the cross section, as the results, the change in cross sections has an impact on the absorption intensity. Quantitatively, we can investigate these properties using finite element method which can be described in the next section.

3. Finite Element Method

In order to investigate different structure, finite element method (FEM) [18] is a good choice since FEM can create a smooth mesh for these structures. Comparing to other techniques, i.e. FDTD technique [19], FEM is a better choice for a complex problem. The main step in simulation is to map our problem into a set of the independent ordinary differential equations by using the mesh generated by FEM. An example of a FEM grid for a nanoparticle is illustrated in Figure 2 below

We should note that a mapped mesh has to satify the following rules: firstly, the two different elements only share their boundaries. This condition will rule out the overlap between the two elements. The boundary can be the points, the lines as well as the surfaces. Secondly, the set of these elements forms a shape similar to the original one. In other words, the good grid can capture the most feature of the original system. This condition tries to avoid the empty space between the elements. For a symmetry structure, the simulation can be done in a piece of structure which incorporate all properties of the systems. The higher the symmetry is, the lower computer consumption is.

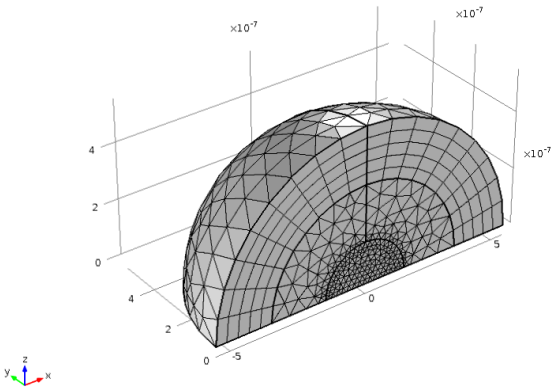


Figure 2. A regular structure of OSC, the nanoparticles are illustrated with the spheres with the same radius. The nanoparticles are blend inside the active layer P3HT:PCBM

4. Results And Discussion

4.1. Physics properties

We will start with a light absorption spectrum of ZnO NPs doping into P3HT:PCBM active layer for an illustration. In order to investigate the LSPR effect of ZnO NPs, we will compare its absorption spectrum in two different environments: a pure air and P3HT:PCBM. We have used the ZnO dielectric constants at different wavelengths for our investigation as written in Table 1

Table 1. The real and imaginary part of the ZnO dielectric constant at the different wavelengths

Wavelength λ (nm)	ε' (real)	ε'' (imaginary)
300	3.99	2.281
400	4.48	0.023
500	4.08	0.037
600	3.85	0.093
700	3.75	0.103
800	3.63	0.101

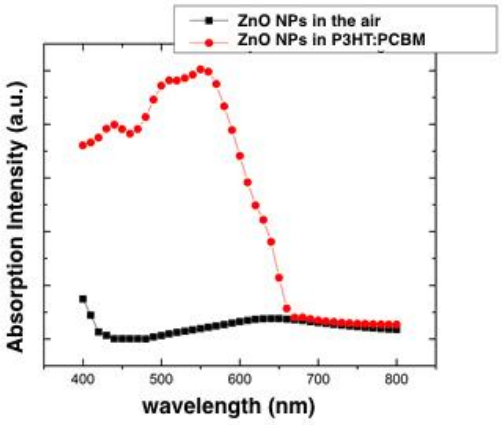


Figure 3: The absorption intensity of ZnO-NPs versus the wavelength in two environments: in air (black filled squares) and in P3HT:PCBM (red filled circles)

Figure 3 shows the absorption spectrum of ZnO-NPs in air (black filled circles) and ZnO-NPs in P3HT:PCBM (red filled circles). The two curves are obviously different. ZnO-NPs in air has a smooth curve and a very weak peak in the infrared range whereas ZnO-NPs in P3HT:PCBM has a strong peak around the two wavelengths $\lambda = 500nm$ and $\lambda = 580nm$. We should note that ZnO NPs in the pure

air has absorption peak in the UV spectrum. Obviously, the NPs has turned the absorption from the UV to the visible light of P3HT:PCBM. This is important since the most energy stored in light coming from the Sun has been located in the visible spectrum. We conclude that ZnO-NPs has induced an additional absorption peak in the visible spectrum. This can be explained simply using the LSPR theory: exciting ZnO-NPs with the invisible light induces the multi-oscilations, on other hand this will lead to the defraction as well as the absorption of light. Moreover, P3HT:PCBM owns the $\pi-\pi$ bindings in its polymer chain which causes the stronger absorption. This makes P3HT:PCBM become a better absorption environment. A calculation for ZnO NPs has shown a similar feature. Interestingly, the peak in NPs case has shown a larger effect of LSPR by 25% than NPs absorption peak. It means that the NPs has a stronger LSPR effect in P3HT:PCBM and therefore it is better to dope NPs into the active blend layer in OSC. The LSPR effects of ZnO-NPs in P3HT:PCBM could be illustrated through the distribution of the electromagnetic field at different weavelengths.

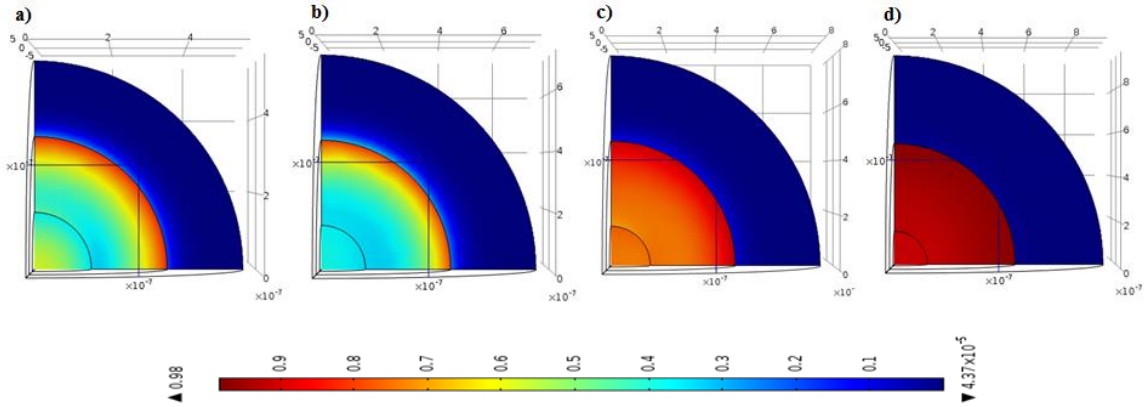


Figure 4. The distribution of the electromagnetic field of the ZnO-NPs in P3HT:PCBM with different incident wavelengths: a) λ =400 nm, b) λ =580 nm, c) λ =650 nm, d) λ =800 nm

Figure 4 shows that the LSPR at the wavelengths $\lambda = 400nm$ and $\lambda = 580nm$ has stronger effects than LSPR in the infrared region, i.e. $\lambda = 650nm$ and $\lambda = 800nm$. As we can see, the red-shift of the incident light reduces the LSPR effect. It means that the defraction as well as the absorption of ZnO-NPs responses weakly to the incident light with a large wavelength, i.e. the infrared light. A similar enhancement effects of ZnO nanorods has been observed experimentally in the recent publication [20].

4.2. Mechanical properties

Doping NPs has been applied for several OSC . In this section, we will investigate the Young module as well as the Poisson coefficient of P3HT:PCBM active layer doping ZnO NPs as follows:

From Einstein and Guth, we have the Young modulus as:

$$E_E = E_m\left(1+1,25\xi_a\right) \tag{2}$$

And, Guth later has a better formula which has incorporated the non-linear effect:

$$E_G = E_m(1+2,5\xi_a+14,1\xi_a^2) \tag{3}$$

Moreover, Kerner has developed the formula to include the Poisson coefficient as:

$$E_K = E_m\left[1+\frac{15\xi_a\left(1-\nu_m\right)}{\left(1-\xi_a\right)\left(8-10\nu_m\right)}\right] \tag{4}$$

where ν_m is Poisson ratio of matrix material. Interestingly, Quemeda have also proposed a formula for Young modulus as:

$$E_Q = E_m \frac{1}{\left(1-0,5k\xi_a^2\right)} \tag{5}$$

In which, $k = 0,25$ has been chosen for a fiting reason. Recently, Thomas has found a formula which takes into account the higher order term:

$$E_T = E_m\left[1+2,5\xi_a+10,05\xi_a^2+0,00273\exp\left(16,6\xi_a\right)\right] \tag{6}$$

Kristensen also claimed that there is a new form of Young modulus:

$$E = \frac{9\overline{K}_E\overline{G}_E}{3\overline{K}_E+\overline{G}_E} \tag{7}$$

where:

$$\overline{G}_E = G_m\left[1-\frac{15\left(1-\nu_m\right)\left(1-\frac{G_a}{G_m}\right)\xi_a'}{7-5\nu_m+\left(8-10\nu_m\right)\frac{G_a}{G_m}}\right];\quad \overline{K}_E = K_m+\frac{\left(K_a-K_m\right)\xi_a'}{1+\left(K_a-K_m\right)\left(K_m+\frac{4G_m}{3}\right)^{-1}} \tag{7'}$$

Recently, Vanin- Nguyen Dinh Duc, 1996 [24,27] has found the new formula for Young modulus which can be simply written as:

$$E = \frac{9\overline{K}\overline{G}}{3\overline{K}+\overline{G}} \tag{8}$$

Where:

$$\overline{K} = K_m\frac{1+4\xi_a'G_mL\left(3K_m\right)^{-1}}{1-4\xi_a'G_mL\left(3K_m\right)^{-1}};\ \overline{G} = \frac{1-\xi_a^{'}\left(7-5\nu_m\right)H}{1+\xi_a^{'}\left(8-10\nu_m\right)H} \tag{9}$$

Here, $L = \dfrac{K_a-K_m}{K_a+\frac{4G_m}{3}}$; $H = \dfrac{\frac{G_m}{G_a}-1}{8-10\nu_m+\left(7-5\nu_m\right)\frac{G_m}{G_a}}$

In the equations from (2) to (8), the terms E_m, ν_m, K_m G_m, G are Young modulus, the Poisson coefficient, volume module and shear modulus of matrix material, respectively. The subscript "a" belong to the NPs characterization. We should note that Eqn (7) and (8) are different from the others since we have taken into account the coupling between the NPs and the host layer. It has been applied to calculate the elastic modulus of TiO2 in MEH:PPV [28]

In the formula from (2) to (6), ξ_a is the mass ratio of particle. Other while, ξ_a' in the formulas (6) and (7)-(8) is volume ratio of particle. In our formula (7)-(8) [24, 27], we have taken into account the interaction between particle and matrix material. The values ξ_a' and ξ_a is according to volume ratio and mass ratio, which are determined as below:

$$\xi_a^{'} = \frac{V_a}{V_a+V_m} = \frac{\frac{m_a}{\rho_a}}{\frac{m_a}{\rho_a}+\frac{m_m}{\rho_m}} = \frac{1}{1+\frac{m_m\rho_a}{\rho_m m_a}} = \frac{1}{1+\frac{\rho_a}{\rho_m}\left(\frac{1}{\xi_a}-1\right)} = \frac{\rho_m}{\rho_m+\rho_a\left(\frac{1}{\xi_a}-1\right)}$$

$$\xi_a = \frac{m_a}{m_m + m_a},\ \frac{1}{\xi_a} = 1 + \frac{m_m}{m_a} \Rightarrow \frac{m_m}{m_a} = \frac{1}{\xi_a} - 1 \tag{10}$$

We have the correlation between the volume ratio and mass ratio as below:

$$\xi_a^{'} = \frac{V_a}{V_a + V_m} = \frac{\rho_m}{\rho_m + \rho_a \dfrac{m_m}{m_a}} \tag{11}$$

Where, V_m and V_a are the volumes of P3HT:PCBM matrix and ZnO NPs; ρ_m and ρ_a are the density of P3HT:PCBM matrix and ZnO nano-particles, respectively. In this manuscript, we have chosen the parameters for P3HT:PCBM and ZnO NPs as: in case of P3HT:PCBM, E= 6.2 GPa, *v*=0.35 and ZnO NPs: E=127GPa, *v*=0.3. Figure 5 sumarizes our finding:

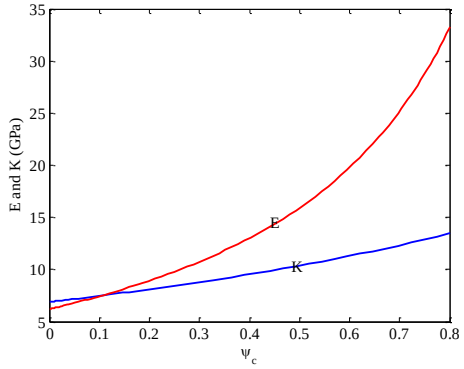


Figure 5. The dependence of elastic modules E (red line) and K(blue line) on volume fraction ψ_c of P3HT:PCBM

Obviously, we can make a conclusion that the more ZnO NPs are, the higher elastic modulus. In particular, Young modulus E increase significanly with the density of ZnO NPs

5. Conclusion

In this manscript, we have investigated the effects of ZnO NPs doping into the active layer P3HT:PCBM in OSC. We have shown that on the power conversion efficiency can be improved by using NPs through the LSPR effects which has enhanced the visible light absorption in OSC. We have found that the absorption intensity peak incuded by NPs doping in P3HT:PCBM has been increased about 20% more than NPs in the air. The electromagnetic field of ZnO-NPs has also illustrated to show the LSPR effects in OSC. The mechanical effects based on our investigation of the elastic modulus such as Young modulus and Poisson coefficient has shown that these quantities increase with the density of ZnO NPs. Hence, NPs are suggested to dope into OSC application for a better energy conversion efficiency as well as the stability of the devices.

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