

Nanoparticles with Conductive Polymer as Photosensing Applications

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Abstract—In this study, we observed that the electric property of PEDOT:PSS was affected by LSPR effect. LSPR effect was generated by nano gold particles that embedded in PEDOT:PSS films. The high-intensity electric field of LSPR enhances the mobility of carriers. In order to observe this phenomenon, we made some devices. The devices under measurement were composed of ITO glass, thin PEDOT:PSS film, nano gold particles and an Al electrode. In our study, the effect of the devices that were doped with different density of gold nano particles was measured. The higher density of gold nano particles made the lower total resistance of device. The different wavelengths of incident light also made the total resistance of device different. Through those experiments, we validated that the change of electric property of PEDOT:PSS was caused by the LSPR effect from nano gold particles.

Keywords-PEDOT: PSS; gold nano particles; LSPR (Localized Surface Plasmon Resonance).

I. INTRODUCTION

PEDOT:PSS (Poly-3-4-ethyleneoxythiophene/poly-4-sytronsulfonate) is an electro-chemically stable conjugated polymer that is commonly used as the buffer layer and a hole transport layer of organic solar cells and OLED (Organic Light-Emitting Diode), or with the ITO (Indium Tin Oxide) as the anode material. PEDOT:PSS has good light transmission, good conductivity, and can be deposited by either spin coating or ink-jet printing process as a more simpler way to make thin-films. A PEDOT:PSS can be coated on many different substrates, like flexible polymers or ITO glass substrates. These features also show that the PEDOT:PSS can reduce the cost of fabrication [1-3].

A thin film of PEDOT:PSS is a buffer layer of organic solar cells or OLED between the active layer and ITO glass because the surface ITO glass usually has some defects and it is difficult to form a good thin-film active layer on the substrate. The buffer layer of PEDOT:PSS film can modify the surface of ITO glass and can make the film better. A PEDOT:PSS film can also reduce the generation of leakage current [4]. Adding an extra layer in the structure could increase the series resistance of solar cell inevitably. Those extra resistances would reduce the efficiency of components. In this study, the resistance of sample was decreased by LSPR (Localized Surface Plasmon Resonance). The localized surface plasmon resonance was generated by the gold nanoparticles deposited between ITO glass substrate and the PEDOT:PSS film.

The idea of spreading gold nanoparticles between the

substrate ITO glass and PEDOT:PSS film was inspired by the organic solar cell. Lots of studies have validated that the surface plasma induced by metallic nano particles can increase the efficiency of organic solar cell [5].

LSPR effect has already been widely applied to biotechnology, such as surface enhanced Raman scattering (SERS) [6-7]. Those works usually made use of the different incident wavelength to measure the dielectric constant, so that the material type can be inferred then. In this study, we aimed for using the reaction of LSPR effect of the different incident wavelength with conductive polymer as a photo sensor.

PEDOT:PSS is an important material in many photonic devices. In order to prove that the difference of the device resistance was caused by LSPR, DDSCAT was used to simulate the localized surface plasmon resonance spectrum of gold particles [8-10].

In the following paragraphs, simulation methods and the sample preparation are described and explained. After that, experiment result and simulation result are discussed.

II. SIMULATION OF SURFACE PLASMON

Surface plasmon is a phenomenon that surface electromagnetic waves propagate on the interface between metal and dielectric material. Surface plasmon mode is confined near the metal surface to form a highly enhanced near-field. Surface plasmon between the metal and the dielectric material is divided into two types, SPP (surface plasmon polariton) and the LSPR (localized surface plasmon resonance). SPP refers to the surface plasmon on the metal surface in the form of surface wave propagating in the interface of metal and dielectric material. LSPR refers to the highly localized, high intensity electric field resonance that is generated on the surface of metal particle. The electric field resonance would be calculated by Maxwell's equations and boundary condition under Quasi-static approximation [11].

$$\begin{aligned} \Phi_{in}(r, \theta) &= \text{Arcos } \theta & (r < a) \\ \Phi_{out}(r, \theta) &= -E_0 r \cos \theta + \frac{B}{r^2} \cos \theta & (r > a) \end{aligned} \quad (1)$$

In these two equations, 'a' is the radius of the metal particle. Those equations and boundary condition (equation 2 below) could be used to simulate the LSPR effect on a single particle. With the boundary condition, A and B in equation 1 can be solved accordingly.

$$\begin{aligned} \Phi_{out}(a, \theta) &= \Phi_{in}(a, \theta) \\ \varepsilon E_{out} \hat{n} &= \varepsilon_m E_{in} \hat{n} \end{aligned} \quad (2)$$

Then assuming an ideal dipole that can be described as $\vec{P} = \varepsilon \alpha E_0 e^{-i\omega t} \hat{Z}$. The electric field of incident electromagnetic wave is $\vec{E}_{inc} = E_0 e^{-i(kx - \omega t)} \hat{Z}$.

We can use the above equations to calculate the extinction cross section (C_{ext}) and scattering cross section (C_{sca}).

TABLE I. THE SIGNIFICANCE OF VARIABLES

variables	significance
ϕ	Electric Potential
ε	Dielectric constant
A, B	Constant
E_0	Electric field magnitude
\vec{p}	Dipole moment
α	Polarizability

But, to simulate a metal particle array just with those equations would be very difficult [12]. For this purpose, DDSCAT is used to simulate the effect that LSPR is generated on the surface of gold nanoparticles. DDSCAT, a FORTRAN code for calculating scattering and absorption of light by irregular particles, has been jointly developed by Bruce T. Draine and Piotr J. Flatau [8-10].

Based on the discrete-dipole approximation, DDSCAT simulated the electric field around the particles by Maxwell's equations. The discrete-dipole approximation (DDA) is a flexible approach for calculating scattering and absorption properties of arbitrary continuum targets, usually a finite geometry of polarizable points. The local electric field induces dipole moments that could be acquired by the points. The dipoles influence each other through their electric fields as well. Therefore the DDA is sometimes called discrete dipole approximation.

DDSCAT is well-developed simulation software. There can get the source code of DDSCAT on the internet [10]. After compiling the source code, we have an executable file. There are other two files, ddscat.par and diel.tab, that are used to control the executable file.

For building the boundary condition to process DDACAT, it would be crucial to enter the dielectric constant of gold nano particles and the dielectric material (PEDOT:PSS and ITO glass) to the file (i.e., diel.tab) of DDSCAT. The particle radius and other boundary condition were entered into another file (i.e., ddscat.par). We could then simulate the scattering and absorption of incident light by different wavelengths on gold nano particles. In this study, DDSCAT was used to simulate the absorption of the incident light between 300 nm and 800 nm and gold nano particles with 20nm diameter. The data of simulation would be

compared with the experiment results in the following section.

III. SAMPLE PREPARATION

Samples were fabricated with PEDOT:PSS (Baytron P VP Al 4083), gold nano particles (gold colloid SI-G1652) and ITO glass substrates (15 ohm/square). The patterned ITO glass substrates were placed into the ultrasonic cleaners for removing the surface dirt. Then the ITO glass substrates were washed by oxygen plasma for 20 minutes in order to make the PEDOT:PSS easy to form on substrates. After being cleaned by oxygen plasma, the surface of ITO glass would be changed to hydrophilic. We took PEDOT:PSS out from the refrigerator and put it aside until it returned to room temperature. After that, filtering PEDOT:PSS twice by target syringe filters with pore size of 0.45um.

After finishing the preparation of PEDOT:PSS, we mixed the solution of gold nanoparticles and ethylene glycol at one to one and one to two ratio (The concentration of gold nanoparticles is $3.9 * 10^{-5}$ g/ml and $2.6 * 10^{-5}$ g/ml). Next, we coated the solution that contained gold nano particles on the ITO glass substrates by 1000 rpm for 10 seconds and 2000 rpm for 20 seconds. We baked the samples after coating at 180 °C for 3 minutes to dry those residue of ethylene glycol. Then, those nano gold particles spread on the ITO glass substrate. The distance from particle to particle was about 100 nm. We then coated PEDOT:PSS on the ITO substrate with and without gold nano particles by 3000 rpm for 30 seconds. Baking those prepared sample at 180 °C for 5 minutes [13]. PEDOT:PSS covered gold nano particles and formed a 30nm film. The thickness of PEDOT:PSS films were 30nm with and without gold nano particles. Finally, we deposited 120 nm of aluminum on the sample as the electrode by thermal evaporator. The samples are illustrated in Figure 1.

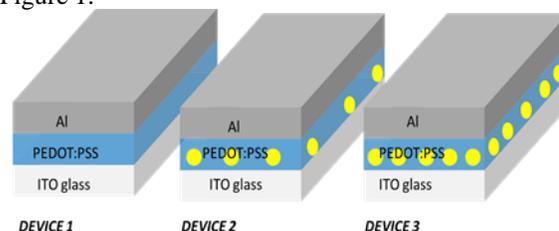


Figure 1. The structure of device 1 without add PEDOT:PSS, device 2 with gold nanoparticles $2.6 * 10^{-5}$ g/ml, device3 with gold nanoparticles $3.9 * 10^{-5}$ g/ml.

The measurement was performed by using Keithley 2400 to record the IV curve. PL-2100 COOL LIGHT SOURCE was light source, and we measured the current density of devices with bias voltage 1V under illuminating of different wavelength incident light from QE-III (Enlitech). The measurement setup is shown in Figure 2.

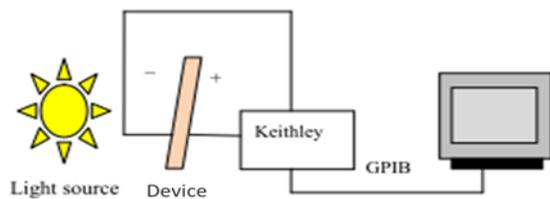


Figure 2. The measurement setup diagram

IV. EXPERIMENTAL RESULTS

Figure 1 shows the sample structure. The top aluminum is the cathode and the bottom of the ITO is the anode. Light source was incident from the side of ITO, and we used Keithley 2400 to record the current value from 0V to 1.5V. Figure 3 is the comparison of the two samples with and without gold nanoparticles. In Figure 3, it shows that the current density of the sample with gold nano particles was higher than the sample without gold nano particle at the same bias voltage. We also observed that if the density of gold nano particles was higher, the current density was higher too. In other words, the sample with gold nanoparticles has lower total resistance than the sample without gold nanoparticles when those sample are exposed to incident light irradiation [14- 15].

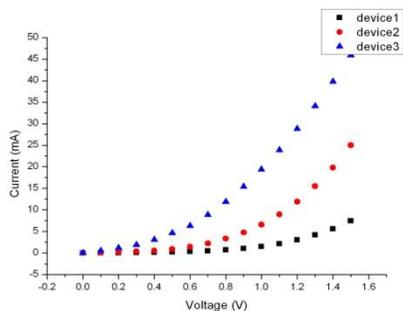


Figure 3. The sample current varies with voltage, device 1 (black square), device 2 (red circle), device3 (blue triangle).

Although the performance of device 3 is the best, the low repeatability and stability of device 3 is the reason that we focus our discussion on device 2 and device1. Figure 4 shows the IV-curve of device 2 (with gold nanoparticles between ITO glass and PEDOT:PSS film) that was under illumination and not under illumination. In this figure, it can be found that when the bias voltage was the same, the current value of device 2 under illumination was increased significantly than device 2 without being exposed to incident lights. When the bias voltage was 1.5 volts, the current density of device2 under illumination was increased from 15 mA to 25 mA. But if there were no bias voltage, the current density would be the same no matter the sample was under illumination or not. Therefore, this result can prove that the increase of current density was not caused by the excess

carrier generation. We believe the overall resistance was decreased because of the incident light.

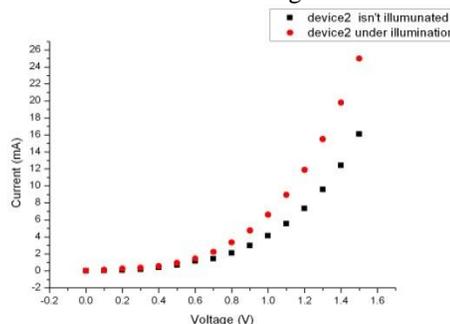


Figure 4. The device2 current density varies with voltage that is illuminated and isn't illuminated.

In order to confirm that the effect of resistance decrease was caused by gold nano particles, we compared the current increases under illumination between device 1 (the sample with only PEDOT: PSS) and device 2 (the sample with gold nano particles) in Figure 5.

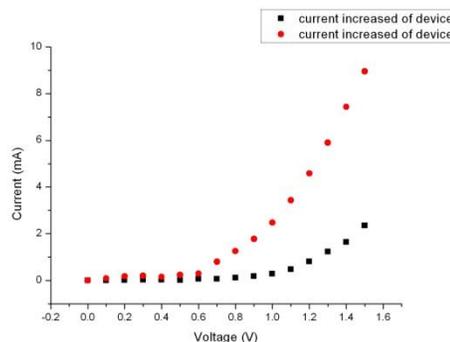


Figure 5. The increase of current density while device2 (red square) and device 1 (blue diamond) were exposed to incident light

Even though the current density of device 1 also increased while the sample was illuminated, the value of increased current density was far less than that of device2. Therefore, it can be claimed that the phenomenon of the resistance reduce was due to the gold nano particles within the sample irradiated by light.

The reason of that is considered that the LSPR generated by gold nanoparticles reduces the resistance of the junction of PEDOT:PSS films and ITO glass substrate

The highly localize, and high-intensity electric field resonance of LSPR in the junction causes the transmission of those carriers (holes) easily, as shown in Figure 6. Due to the existence of the gold nano particles, the gold nanoparticles is in the dashed area. This increase the electric field gives electric holes an attractive force and make the mobility of electric holes be increased.

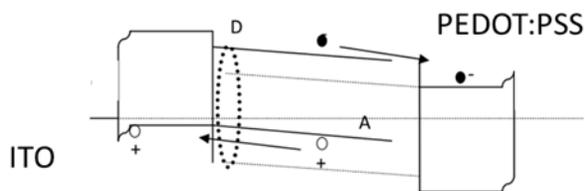


Figure 6. Schematic drawing of device with nano gold particles, where A is acceptor, and D is the donor. The dashed area is gold metal cluster surface plasmon resonance.

To further confirm the relationship between resistance and LSPR, the device 2 was exposed to visible light irradiation with the wavelength from 350 nm to 750 nm. We measured the current density with bias voltage, as shown in Figure 7. We used DDSCAT to simulate the absorption spectra of gold nano particles, 20nm diameter, from 300 nm to 800 nm, and compare it with experimental results. The simulation results are shown in Figure 8.

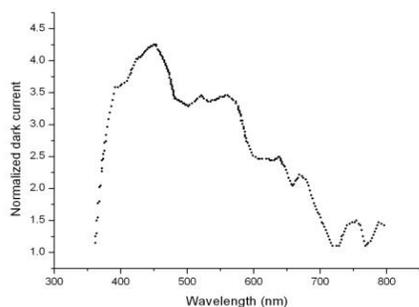


Figure 7. Current density (device 2) versus the wavelength of incident lights, normalized with the dark current density.

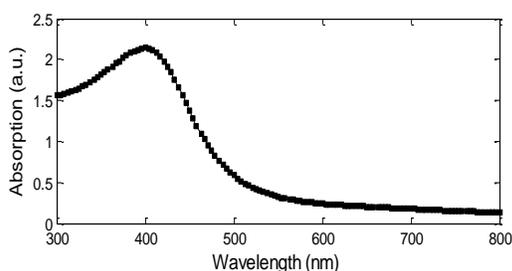


Figure 8. The absorption rate of 20nm gold particles versus incident wavelength by DDSCAT simulation.

Comparing Figure 7 and Figure 8, it can be observed that the shape of those curve are very consistent with each another. Although the curve of experiment result was 20-30nm shift to longer wavelength, we believed that reason of red shift is that not all the diameter of gold nano particles is actually 20nm. In our simulation the diameter is set to be 20nm, since the average diameter of the gold nano particles used in the experiment is 20nm. However, those gold nano

particles with diameter larger than 20nm may affect the waveform. But it was still within measurement tolerance. This result still directly proved that the effect of LSPR was the main cause of sample's resistance decrease.

As shows in Fig. 7, the device with gold nano particles are measured different current density while the wavelength of incident light is changed. We can use device 2 to recognize the wavelength of incident light by the measurement setup as shown in Fig. 2. This feature makes the device as a wavelength sensor.

V. DISCUSSIONS

According to the experiment and simulation, we get the following two results. First, the resistance of devices is reduced by gold nanoparticles. Besides, this effect is strong when gold nanoparticles are illuminated. Second, the magnitude of absorption of gold nanoparticles is consistent with the current density of device.

From the two results, it is validated that LSPR from gold nano particles is the reason why the current density of device is increased.

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REFERENCES

- [1] G. Greczynski, Th. Kugler, and W. R. Salaneck, "Characterization of the PEDOT-PSS system by means of X-ray and ultraviolet photoelectron spectroscopy "Thin Solid Films 354, pp. 129-135 (1999)
- [2] J. Luo and W. Tang, "Influence of PEDOT with Different Conductivity on the Performance of Polymer Photovoltaic Cells", Journal of Guangdong University of Technology Vol. 25 No. 3, pp. 6-9, (2008)
- [3] Nurdan D. Sankir, "Selective deposition of PEDOT/PSS on to flexible substrates and tailoring the electrical resistivity by post treatment" , Circuit World Vol. 34 · Number 4, pp.32-37(2008) .
- [4] J. Ouyang, C.-W. Chu, F.-C. Chen, Q. Xu, and Y. Yang, "High-conductivity poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) film and its application in polymer optoelectronic devices", Advanced Functional Materials Vol. 15, Issue 2, pp. 203-208, (2005)
- [5] S.-S. Kim, S.-I. Na, J. Jo, D.-Y. Kim, and Y.-Ch. Nah, Plasmon, "Plasmon enhanced performance of organic solar cells using electrodeposited Ag nanoparticles", APPLIED PHYSICS LETTERS 93,pp. 073307-073309 (2008)
- [6] Jeffrey M. McMahon, Anne-Isabelle Henry, Kristin L. Wustholz, Michael J. Natan, R. Griffith Freeman, Richard P. Van Duyne ,and George C. Schatz, "Gold nanoparticle dimer plasmonics: finite element method calculations of the electromagnetic enhancement to surface-enhanced Raman spectroscopy" , Vol. 394, Number 7, pp.1819-1825 (2009)
- [7] Qiuming Yu and Greg Golden, "Probing the Protein Orientation on Charged Self-Assembled Monolayers on Gold Nanohole Arrays by SERS", Langmuir, 23 (17), pp 8659-8662 (2007)
- [8] Draine, B.T. and Flatau, P.J., "Discrete dipole approximation for scattering calculations", J. Opt. Soc. Am. A, 11, pp.1491-1499 (1994)

- [9] Draine, B.T. and Flatau, P.J., "User Guide to the Discrete Dipole Approximation Code DDSCAT 7.1", <http://arXiv.org/abs/1002.1505v1> (2010)
- [10] Draine, B.T. and Flatau, P.J., "Discrete-dipole approximation for periodic targets: theory and tests", *J. Opt. Soc. Am. A*, 25, pp.2593-2703 (2008)
- [11] Stefan A. Maier, "Plasmonics: fundamentals and applications", Springer Verlag, pp.65-75 (2007)
- [12] N. W. Ashcroft, and N. D. Mermin, "Solid State Physics", Harcourt (2000)
- [13] Vishal Shrotriya, Gang Li, Yan Yao, Tom Moriarty, Keith Emery, and Yang Yang, "Accurate Measurement and Characterization of Organic Solar Cells", *Adv. Funct. Mater.*, 16, pp.2016-2023 (2006)
- [14] Y.H. Zhou, F.L. Zhang, K. Tvingstedt, Sophie Barrau, F.H. Li, W.J. Tian, and Olle Inganäs, "Investigation on polymer anode design for flexible polymer solar cells", *APPLIED PHYSICS LETTERS* 92, pp.233308-233310 (2008)
- [15] S.W. Tong, C.F. Zhang, C.Y. Jiang, G. Liu, Q.D. Ling, E.T. Kang, D.S.H. Chan, and Chunxiang Zhu, "Improvement in the hole collection of polymer solar cells by utilizing gold nanoparticle buffer layer", *Chemical Physics Letters* 453, pp.73-76 (2008)