Effect of localized surface plasmon resonance from incorporated gold nanoparticles in PEDOT:PSS hole transport layer for hybrid solar cell applications

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Abstract. We report optical and structural properties of poly (3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) incorporated gold nanoparticles capped by citrates (Au-citrates) as hole transport layer for hybrid organic-inorganic solar cell applications. PEDOT:PSS and Au-citrates both are water solution and the mixed are done in 2.378 wt%, 2.978 wt% and 3.144 wt% of Au-citrate. Plasmonic peak in the wavelength area of ~525 nm for Au-citrate is found quite stable after addition of iso-propanol for wettability purpose. In our result, enhanced absorbance spectra of PEDOT:PSS incorporated Au-citrate indicates the effect of localized surface plasmon resonance from Au-citrate and it is estimated to enhance performance of hybrid solar cell efficiency. Optical properties of the thin films in hybrid solar cell device are done in the structure of ITO/ZnO/P3HT:PCBM(active layer)/(PEDOT:PSS:Au-citrate). The complete layer structure shows the enhancement of optical property in all UV-vis region in comparison to that structure without Au-citrate.

1. Introduction

Hybrid organic-inorganic solar cell have recently studied due to simple fabrication processes, large area and flexibility, where the structure integrates the advantage of organic material with high hole mobility and inorganic material with high electron mobility [1]. Ji et al. demonstrated that power conversion efficiency (PCE) is enhanced in hybrid ZnO-polymer solar cell by varied the size and morphology of ZnO nanostructures [2]. In our previous study, we investigated influences of dopant concentrations in sol-gel method derived Al doped ZnO (AZO) layer on the performance of inverted hybrid solar cell. Doping at high concentration produces higher charge carrier density, but not for charge carrier mobility and its electrical conductivity, which may be influenced by the surface morphology [3]. In hybrid solar cell structure, poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) is well known using as good hole transport layer material but water based PEDOT:PSS has a wettability problem when it is introduced on top of active hydrophobic polymer layer by used of spin-coating technique. Modification of PEDOT:PSS through addition of surfactant such as FS-31 successfully reduces the contact angle of PEDOT:PSS on the hydrophobic photoactive layer and the wetting property is sufficiently developed [4].

On the other case, metal nanoparticles such as gold (AuNPs) and silver (AgNPs) have been used in organic solar cells due to strong localized surface plasmon resonance (LSPR) wave, which contributes
to the enhancement of local electromagnetic field and it is believed to be able to improve light absorption and to promote exciton dissociation or charge transfer generation in organic solar cells. The effect of AuNPs incorporated into the active layer of polymer solar cell experimentally and theoretically enhance the light absorption in the active layer because LSPR near field mainly distributes laterally along the active layer [5]. Incorporation of AuNPs or AgNPs in the hole transporting buffer layer of PEDOT:PSS, which is formed on an indium tin oxide (ITO) surface by the spin-coating of PEDOT:PSS-Au or AgNPs composite solution exhibit an 8% improvement in their efficiency due to the enlarged surface roughness of the PEDOT:PSS, which lead to an improvement in the charge collection and in the short-circuit density and fill factor [6].

In this research study, we investigated optical and structural properties of AuNPs, which has capping material of citrates (Au-citrates) incorporated into PEDOT:PSS as hole transport layer (HTL) material for hybrid organic-inorganic solar cell applications. Localized surface plasmon resonance (LSPR) effect from Au-citrates embedded into PEDOT:PSS will be expected to improve charge carrier generation and transport in hybrid solar cell. We studied in detail in how to modify both PEDOT:PSS and Au-citrate solution by used of iso-propanol solvent since it has been known that they are water solution and have wettability problem on hydrophobic layer of active polymer layer in the structure of hybrid solar cell.

2. Experiments

2.1. Preparation of PEDOT:PSS incorporated Au-citrate solution

Au-citrate in water solution with spherical shape and 15 nm of diameter size (Sigma-Aldrich) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) in water solution (Heraeus Clevios GmbH) both were used as received without additional processes. First, 0.0027 mg/ml of Au-citrate were mixed with 50 µl, 100 µl, 200 µl and 500 µl of iso-propanol (IPA) in order to check the stability of Au-citrates in solution. Incorporation of Au-citrate with PEDOT:PSS solution was done by mixed several concentration of Au-citrate (2.378 wt%, 2.978 wt% and 3.144 wt%) into PEDOT:PSS solution and stirred for 60 min at room temperature. Thin film preparation was done by dropping PEDOT:PSS: Au-citrate solution on clean glass substrate and spin-coated at 1000 rpm for 10 s and annealed at 150°C for 15 min.

2.2. Preparation of hybrid solar cell layers

Thin films for hybrid organic-inorganic solar cell application was prepared on indium tin oxide (ITO) glass which were consisted of ZnO/P3HT:PCBM/PEDOT:PSS: Au-citrate layers. ITO glass was cleaned in ultrasonic bath by de-ionized (DI) water and continued by used of mixed iso-propanol and aceton and finalized by ethanol. ITO glass was dried by N2 gas before used. Next, ZnO layer was prepared by following our previous study (sol-gel method) [3] in which 0.0878 g of zinc acetate-dihydrate (Zn(CH3COO)2.2H2O, Merck) was dissolved in iso-propanol as solvent and stirred for 15 min at temperature of 60°C. Next, diethanolamine (HN(CH2CH2OH)2, Sigma-Aldrich) as stabilizer agent was gently added into zinc acetate (Zn-Ac) solution and kept stirring for additional 12 h in room temperature. Deposition of Zn-Ac on ITO glass was done by used spin-coating technique at 4000 rpm for 10 s and the film was pre-heated at 300°C for 10 min. This process was repeated for 3 times and then post-heated at 500°C for 60 min to form ZnO film. Active layer was prepared by mixed poly(3-hexylthiophene) (P3HT, Sigma-Aldrich) and phenyl C61 butyric acid methyl ester (PCBM, Sigma-Aldrich) with weight ratio of 1:1 in chlorobenzene and stirred at 35°C for 12 h. Deposition of active layer on ZnO thin film was done by spin-coated at 2000 rpm for 10 s. PEDOT:PSS with and without incorporated Au-citrate was prepared as explained in section 2.1.

2.3. Measurements

Optical properties of Au-citrate, PEDOT:PSS incorporated Au-citrate including thin films in hybrid solar cell structure were characterized by used of Ultra Violet-visible spectrometer (UV-vis Agilent Technologies 8453). Chemical structures of PEDOT:PSS incorporated Au-citrate was investigated by
used of Fourier Transform Infrared spectrometer (FT-IR Prestige 21 Shimadzu, Japan). Information of morphology and thickness of PEDOT:PSS thin film was recorded by used of Scanning Electron Microscope (SEM Hitachi Model SU3500).

3. Results and Discussions

3.1. Optical properties of PEDOT:PSS incorporated Au-citrate

In figure 1, typical plasmonic peak of Au-citrate solution is appeared clearly at wavelength of 525 nm together with sharpen peak shape, which is indicated distribution of particles size is relatively homogenous around 15 nm in diameter as shown also in our previous work for synthesis of Au-citrates [7]. In this study, 0.027 mg/ml of Au-citrate in water solution is quite stable with addition of 50 μl, 100 μl and 200 μl of IPA as shown in absorbance spectra in comparison to the spectrum of Au-citrate in water solution as reference. A small broadening peak is found in the 500 μl addition of iso-propanol into Au-citrate solution indicated the particle starts to aggregate.

![Figure 1. UV-Vis spectra of Au-citrate in water and iso-propanol.](image)

Figure 2(a.2)–(a.4) shows solution of PEDOT:PSS in water mixed with 2.378 wt%, 2.978 wt% and 3.114 wt% of Au-citrate compare to the PEDOT:PSS solution without addition of Au-citrate (figure 2(a.1)). This result indicates that Au-citrate is quite stable in PEDOT:PSS solution. Moreover, UV-vis spectroscopy result as shown in figure 2(b) suggests that the enhancement of the absorbance peaks in the region of PEDOT:PSS spectra caused by LSPR effect of Au-citrate. In our experiment, we investigated the enhancement of absorbance peaks at LSPR peak position for Au-citrate as indicated by black dash line in the figure 2(b). The absorbance peak intensities are found much enhanced for PEDOT:PSS solution contain 2.378 wt% and 2.978 wt% of Au-citrate. In case of incorporation 3.114 wt% Au-citrate in PEDOT:PSS solution, the increased intensity is not significant, which indicated Au-citrate starts to aggregate even though the precipitate does not appear yet in the solution (figure 2(a.4)).
Figure 2. (a) PEDOT:PSS solution incorporated Au-citrate (1) 0 wt%, (2) 2.378 wt%, (3) 2.978 wt% and (4) 3.144 wt% and (b) Absorbance spectra of PEDOT:PSS incorporated Au-citrate in solution.

Optical property of PEDOT:PSS:Au-citrates thin film is presented in figure 3, which indicates similar phenomena to the sample solutions. The increased of absorbance peak in the wavelength area of ~300 nm for PEDOT:PSS : Au-citrate (2.978 wt%) in comparison to the absorbance peaks of PEDOT:PSS without Au-citrate indicates the strong effect of LSPR from Au-citrate.

Figure 3. Absorbance spectra of PEDOT:PSS with and without incorporated Au-citrate in thin film.

3.2. Structural properties of PEDOT:PSS incorporated Au-citrate

Chemical structures of PEDOT:PSS incorporated Au-citrates was investigated by used of FT-IR spectroscopy. The samples were prepared by dried-up the solution of PEDOT:PSS with and without Au-citrate in room temperature and mixed with potassium bromide (KBr) to form a pellet. The differences in FT-IR peaks of PEDOT:PSS with and without Au-citrate are shown in figure 4. The peaks related to C-C, C-O, S-H and C-S bonds. Peak of C-S at wavenumber 831 cm⁻¹ in PEDOT:PSS are reduced drastically in the PEDOT:PSS: Au-citrate, whereas C-O-C bond at
wavenumber of 1388 cm\(^{-1}\) is disappeared. These results indicate that the changes intensities are caused by new bonding formation in the sample especially between PEDOT:PSS and citrates capping of Au nanoparticles. The shifted of peak intensity in FT-IR spectra to higher and lower frequencies are still in our investigation which could be caused by the effect of LSPR from Au-citrates.

![FTIR spectra of PEDOT:PSS and PEDOT:PSS:Au-citrates.](image)

**Figure 4.** FTIR spectra of PEDOT:PSS and PEDOT:PSS:Au-citrates.

Morphology of PEDOT:PSS:Au-citrate thin film on glass substrate resulted from spincoating technique at 1000 rpm for 10 s is clearly shown in figure 5(a) and its cross section view shows the thickness around \(~174\) nm. Annealing process at 100°C after spin-coated process is important to eliminate the solvent and to form homogenous thin film.

![SEM images of thin film PEDOT:PSS:Au-citrate on glass substrate.](image)

**Figure 5.** SEM images of thin film PEDOT:PSS:Au-citrate on glass substrate (a) on top view and (b) cross section view.

3.3. **Layer by layer optical properties of fabricated hybrid solar cell**

In order to investigate more detail of the LSPR effect from Au-citrates in PEDOT:PSS as hole transport layer in hybrid solar cell applications, we measured optical properties layer by layer structure in hybrid solar cell by used of UV-vis spectroscopy. Figure 6 shows typical absorbance spectra from each layer structure of ITO as cathode, ZnO as electron transport layer (ETL), P3HT:PCBM as photoactive layer and PEDOT:PSS as hole transport layer (HTL) with and without Au-citrates. Complete layers structure of hybrid solar cell incorporated Au-citrates shows enhancement of absorption in all UV-vis region compared to structure without Au-citrates. All enhancement of optical
properties which are suggested by the effect of LSPR from Au-citrates is expected to be improved the efficiency of inverted type hybrid solar cell.

![Absorbance spectra of layer by layer hybrid solar cell structure incorporated Au-citrates.](image)

**Figure 6.** Absorbance spectra of layer by layer hybrid solar cell structure incorporated Au-citrates.

4. Conclusions
Optical properties of PEDOT:PSS incorporated Au-citrates with concentration of 2.378 wt%, 2.978 wt% and 3.144 wt% were investigated by use of UV-vis spectroscopy. Enhanced absorbance spectra of PEDOT:PSS incorporated Au-citrates in solution and thin film are caused by the effect of localized surface plasmon resonance (LSPR) from Au-citrates. In this case, we conclude that Au-citrates is quite stable, when it is embedded into PEDOT:PSS and iso-propanol solution. FTIR characterization confirm that there are peaks intensity changes and peaks shifted between PEDOT:PSS and PEDOT:PSS incorporated Au-citrates due to chemical bonding between PEDOT:PSS and citrates from Au nanoparticles. In our result, enhancement of optical properties in complete layer structure of hybrid solar cell incorporated Au-citrates in all UV-vis region can explain that the generation of LSPR is expected to be improve the efficiency of inverted type hybrid solar cell.

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