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Near Infrared Shielding Properties of PEDOT:PSS with Different Additives

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Abstract. We have investigated the near Infrared (NIR) properties of shielding effect and transparent character nanocomposite films. In this work, we prepared composite films of Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) with various additives such as concentration of single wall carbon nanotube (SWCNTs), modified SWCNT (t-SWCNT) and poly(ethylene glycol) (PEG) on substrates by simple mixing and coating process. The modified SWCNTs were prepared by acid treatment method, which were exhibited the distinct peak of functionalized SWCNT surface by Raman spectrometer. The degree of distribution in PEDOT:PSS/t-SWCNT films closely were related with visible light transmittance by UV-Vis/NIR. As the acid treatment time increases (6 and 24 h), SWCNT length is decreased and transmittance increased in visible range over 75, 92 %, respectively. Both PEDOT:PSS/SWCNTs and PEDOT:PSS/PEG system films appeared unusual Infrared shielding tendency as their additives concentration. Particularly, in case of PEDOT:PSS/PEG system film was found to have the best IR shielding capability up to 10 % at 1000 nm. These facts indicates that the interaction between the additives and the PEDOT:PSS chains sensitively depend on the driving force due to the conformational change.

Keywords: NIR shielding, Transmittance, PEDOT:PSS, SWCNT, PEG

1. Introduction

Transparent and electrically conductive coating films have a variety of fast-growing applications ranging from window glass to flat-panel displays. These mainly include semiconductive metal oxides such as indium tin oxide (ITO), antimony tin oxide (ATO) and polymers such as poly(3,4-ethylenedioxythiophene) doped and stabilized with poly(styrene sulfonate) (PEDOT/PSS). Furthermore, conductive polymer of PEDOT:PSS is one of the candidates for IR shielding materials. It has many merits compared to other conducting polymers such as a high transparency in the visible range, outstanding thermal stability and it was possible to process in aqueous solution.

In the other hand, many attempts have been done to increase the conductivity of PEDOT:PSS films by mixture with organic solvents or the addition of small amount of different additives. Especially, there has been an increasing interest in the conducting polymers using single-wall carbon nanotubes (SWNT) and poly(ethylene glycol)(PEG) as alternatives to ITO and ATO in recent years. Carbon nanotube (CNT) are a good conductive dopant for conducting polymer and these CNT-based technologies offer conducting substrates having a broad range of conductivity, excellent transparency, neutral color tone, good adhesion, abrasion resistance, and flexibility as well as the reliability of processing and patterning. PEG was reported that the conductivity of PEDOT:PSS film can be enhanced by more than an order of magnitude by the addition of PEG (OH group on each molecule of PEG may form hydrogen bond with sulfonic group of

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PSSH, and hence weaken the electrostatic interaction between PEDOT cationic chains and PSS anionic chains).

In this paper, we will be investigated the NIR shielding properties on alternative material to ITO and conducting polymers, PEDOT:PSS composites thin films with the SWCNTs and the PEG as additives and the mechanism of conductivity enhancement in the composite films will also be studied. Finally, our study suggests that transparent and electrically conductive coating films were expected the many commercial application fields because of the photovoltaics, smart windows, flat-panel displays, light-emitting diodes, touch screens, electromagnetic shielding, et.

2. Experimental Procedure

2.1. Materials

The SWCNTs were sonicated for 6 h, 24 h in a (3:1) mixture of concentrated nitric acid and sulfuric acid at a frequency of 40 kHz. The acid-treated SWNTs were rinsed with DI water repeatedly and filtered through a cellouse membrane filter with a pore size 0.2 ㎛. These procedures were repeated until PH 7~8. The surface of purified SWNT was modified by carboxylation of SWNT walls. PEDOT:PSS aqueous solution(Clevios PH 500) was purchased from Bayer AG. The ratio of PEDOT to PSS was approximately 1-2.5. Poly Ethylene glycol(PEG) was purchased from Aldrich and used as received.

2.2. Sample Preparation

The constant amounts of PEDOT:PSS were dispersed in various additives. 2.5 wt% of PEG(Mn=12,000) was mixed in constant PEDOT:PSS solution with a mechanical stirrer for 1 days [4],[5]. And the SWCNT was dispersed in a fixed PEDOT:PSS solution with a various weight ratio 0.1, 0.3, 0.5 wt%. We prepared acid-treated SWCNT(t-SWCNT) was fixed 0.3 wt%. Thin composites films were cast on glass substrate by spin-coating method. The slide glasses were cleaned with organic solvents(acetone, methanol) to remove impurities, then rinsed in ultrasonic bath with DI water, dried in a vacuum oven.

The spin-coating method was performed on slide glass with a spin coater for 60 s, spin speeds 1500 rpm, to fabricate composite films with different thickness by coating number to control the film thickness. When the spin speed was below 1000 rpm, the uniformity of the composite film became error range [3]. So, we fixed the spin speed 1500 rpm. The number of coating to fabricate composites films with different thickness.

3. Result and Discussion

Fig.1 shows the relation between coating number and transmittance in the visible/near-infrared range. As mentioned in experimental section, the pure PEDOT:PSS film on slide glass was coated 1-10 times in increment 2 times. The pure PEDOT:PSS film was examined a good optical transmittance in wavelength range in 550 nm.(average 95 %) As the coating were increased, transmittance tendency of the pure PEDOT:PSS thin films were uniform shape. And near-infrared curve of the pure PEDOT:PSS thin films were observed a gentle slope on the wavelength range from 800 to 1000 nm, which gradually declined

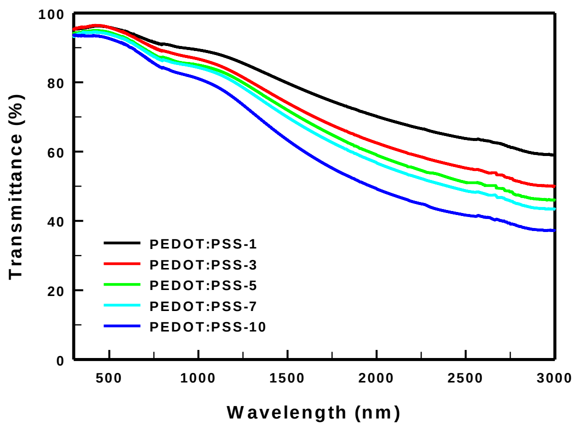

Fig. 1: The Infrared properties of PEDOT:PSS coating number.

Decrement rate of transmittance is from 90 % to 80 %. Accordingly, our results demonstrated that the Vis transmittance is high proportion. But IR shielding effectiveness is not good. PEDOT:PSS dispersion, as a conducting polymer, PEDOT is the charge transporting spices. PSS only acts as a charge-compensating counter-ion to stabilize the p-doped conducting polymer, and forms a water-borne dispersion of negatively charged swollen colloidal particles consisting of PEDOT and excess PSS. Since PSS chains typically consist of a few hundred monomer units, the polymer grains are probably defined by the PSS random coil with PEDOT chains ionically attached along them. And we were studied Infrared shielding effectiveness and transmission spectra of pure PEDOT:PSS film and PEDOT:PSS nanocomposites film using various additives such as PEG, SWCNT, t-SWCNT.

Fig. 2 showed the relation between NIR shielding effect and SWCNT concentrations. As the SWCNT concentration increased from 0.1 wt%, 0.3 wt% and 0.5 wt%, transmittance value were declined from 85 to 40 % at 550 nm and the decrement gap is constant about 20 %. Especially, this figure clearly indicated that the distinic absorption valley around 1000 nm. Generally, in order for a conductor to be transparent to visible light, but absorb or reflect near-infrared range, its plasma frequency must be 800~1,000 nm. The Near Infrared shielding effect increased from 20 to 60 % at 1000 nm. The SEM micrographs of the fractured surface of PEDOT:PSS/SWCNT composite films are shown in Fig. 3(b). As can be seen, SWCNTs are pulled-out from the fractured surface and the number of pulled-out SWCNTs increases with the increased loading density. The SEM images support our discussion on the dispersion states of SWCNTs in PEDOT:PSS matrix. Although 0.5 wt% SWCNTs bundles were observed aggregation on the fractured surface, NIR shielding effectiveness steadily increased. SWCNTs are of a typical conjugated polyenes structure, where each sp2 hybridized carbon bonded together in a hexagonal network, electrons can move freely from an unhybrized p orbital to another, forming an endless delocalized π bond network. When SWCNT are doped with π-electron conjugated PEDOT:PSS film , there will be some possible physico-chemical interactions between SWCNTs and PEDOT:PSS solution, which will give rise to important effects. The PEDOT:PSS/SWCNT network is considerably low absorption more than pure PEDOT:PSS film in the near infrared range due to density of electronic state(DOS) in a SWCNT. The energy levels for the particle and polymer should be chosen so that they promote charge separation and transfer optimum values could be determined.

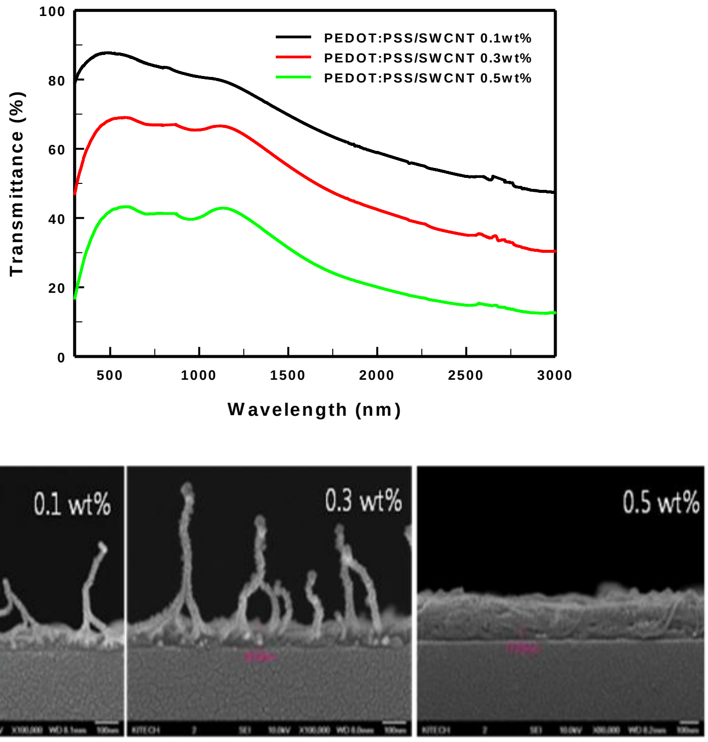

Fig. 2: The Infrared properties of PEDOT:PSS / SWCNT.

Fig. 3 represented the relation between coating number and Infrared shielding effectiveness using PEG in the visible/near-infrared range. We found that enhancement of interaction between PEDOT:PSS chain and additive. As the coating number increased, transmittance value were declined from 95 % to 50 % at 550 nm and Near Infrared shielding effect rapidly increased from 10% to 80% at 1000 nm. Especially, when coating number is 3 times over, this figure clearly indicated that the absorption valley around 1000 nm. This may result from some absorptions of PEG in the above wavelength range. This fact demonstrated that PEG may form hydrogen bond with sulfonic groups of PSSH, and weaken the electrostatic interactions between PEDOT cationic chains and PSS anionic chains. The PEG seems to interact strongly with the PEDOT:PSS solution.

We could compared transmittance spectra of pure PEDOT:PSS and PEDOT:PSS/PEG, which shown curve patterns. The transmittance value were decreased more than pristine PEDOT:PSS film at 550 nm. However, NIR shielding effect rapidly increased to 60 % at 1000 nm and slope were almost reached to bottom at over 2000 nm. It clearly demonstrated that the PEG is improved heat shielding effect than SWCNTs. The thickness of the PEDO:PSS nanocomposites film increased with adding PEG in the PEDOT:PSS solution. The increase of the film thickness by the additive may be induced by PSS molecules washed away by the solvent from the surface region of the PEDOT;PSS film. It is considerable the PEDOT:PSS/PEG nanocomposites film may consist of the bigger aggregates of primary particles with decreased diameters by the wash-effect.

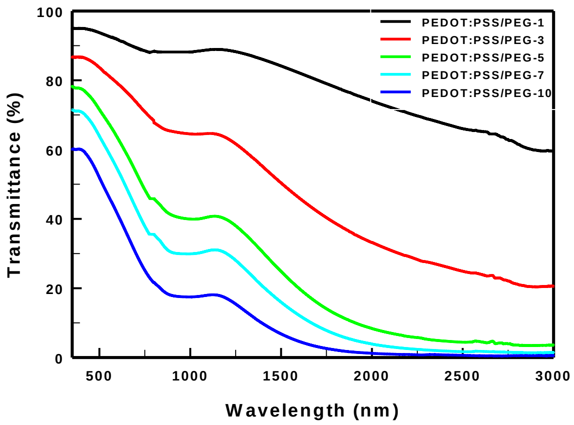

Fig. 3: The Infrared properties of PEDOT:PSS / PEG.

A comparison of the transmission spectra of PEDOT:PSS and various additive as SWCNT, t-SWCNT, PEG nanocomposites film in the near-infrared range is shown in Fig. 4. As the PEG added, NIR transmittance curve of the pure PEODT:PSS films were exhibited a broad slope whereas PEODT:PSS/ PEG films were a slight sharp slope in wavelength from 800 to 1000 nm. This result indicates that the addition PEG was assumed be the most effect at the NIR shielding.

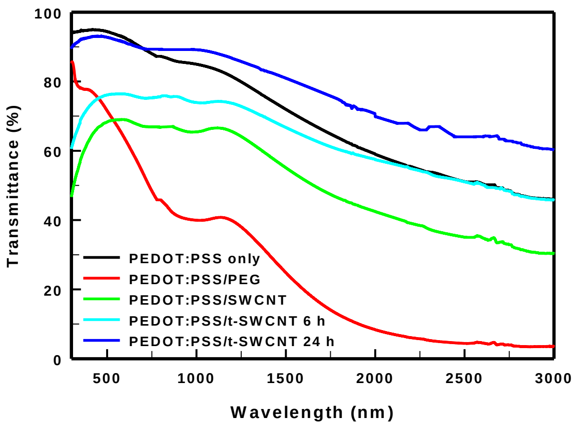

Fig. 4: Optical transmission spectra of pristine PEDOT:PSS, SWCNT, t-SWCNT, and PEG films.

4. Conclusions

In this work, we have studied the NIR cut-off properties of PEDOT:PSS/additives nanocomposites film using various kinds of additives such as PEG, SWCNT and t-SWCNTs by using the NIR spectrometer, XPS and Raman spectrometer. Our results clearly show that the NIR shielding effect and electrical conductivity increased with increasing the content of additives. The pristine PEDOT:PSS films were showed a high optical transmittance in the wavelength range of 550 nm(average 95 %) and the transmittance of its tend to be uniform shape. In case of PEDOT:PSS/PEG film, in order to enhancement of interaction between PEDOT:PSS chain and additive, the transmittance value were decreased more than pristine PEDOT:PSS film at 550 nm. However, NIR shielding effect rapidly increased to 60% at 1000 nm and slope were almost reached to bottom at over 2000 nm. This fact demonstrate that the interaction between the additive and the PEDOT:PSS chain be depend on hydrogen bond with sulfonic group of PSSH, and hence weaken the electrostatic interaction between PEDOT cationic chains and PSS anionic chains. In the other hand, the Infrared shielding effect of SWCNTs increased with increasing the concentrations as well as transmittance increased in visible range over 75 %, 90 %, respectively. This result indicated that the fractured surface of PEDOT:PSS/t-SWCNTs composite films by SWCNT cut were retained high dispersion with increasing acid treatment time(6, 24 h).

5. References

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