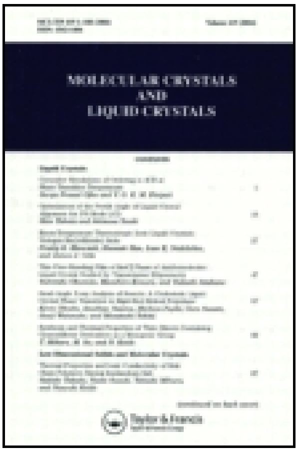

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of Silica Nanoparticle Content on the Structure and Electrostatic Bonding of PEDOT:PSS

Seok-Joo Wang [a] , Yong-June Choi [a] , Su Cheol Gong [a] , Yong-Hoon Kim [b] & Hyung-Ho Park [a]

[a] Department of Materials Science and Engineering, Yonsei University, Seoul, Korea

[b] Flexible Display Research Center, Korea Electronics Technology Institute, Seongnam, Korea

Version of record first published: 27 Sep 2012.

To cite this article: Seok-Joo Wang , Yong-June Choi , Su Cheol Gong , Yong-Hoon Kim & Hyung-Ho Park (2012): Effect of Silica Nanoparticle Content on the Structure and Electrostatic Bonding of PEDOT:PSS, Molecular Crystals and Liquid Crystals, 568:1, 179-185

To link to this article: http://dx.doi.org/10.1080/15421406.2012.708845

Mol. Cryst. Liq. Cryst., Vol. 568: pp. 179–185, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.708845

Effect of Silica Nanoparticle Content on the Structure and Electrostatic Bonding of PEDOT:PSS

SEOK-JOO WANG,[1] YONG-JUNE CHOI,[1] SU CHEOL GONG,[1]
YONG-HOON KIM,[2] AND HYUNG-HO PARK[1,*]

[1]Department of Materials Science and Engineering, Yonsei University, Seoul, Korea
[2]Flexible Display Research Center, Korea Electronics Technology Institute, Seongnam, Korea

Conducting poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate) (PEDOT:PSS) containing hydroxyl surface rich SiO_2 nanoparticles were investigated. Rearrangement and bonding of PEDOT:PSS were affected by the content of SiO_2 nanoparticles, which resulted in the modification of an electronic band structure and electrical characteristics. A slight decrease in work function and a shift of the highly occupied molecular orbital edge to the Fermi level were induced by SiO_2 nanoparticle addition. The current path was also tuned by SiO_2 nanoparticles and resistance of the composite film was diminished. SiO_2 nanoparticles affect electrostatic bonding between PEDOT:PSS and doping of PEDOT as well as increase the packing density of PEDOT:PSS.

Keywords PEDOT:PSS; SiO_2 nanoparticle; hydroxyl; electrostatic bond; packing density

I. Introduction

Nanocomposites of conjugated polymers and inorganic particles have received much attention. Conjugated polymers have great advantages due to their high electrical conductivity and redox properties, and extensive applications ranging from batteries to light emitting devices have been realized [1–4]. Many inorganic particles have been encapsulated in conjugated polymers. Such nanocomposites show various interesting characteristics, particularly in the study of dielectric properties, energy storage, catalytic activity, and magnetic susceptibility [5–7]. Composites of metal nanoparticles and conjugated polymers are useful for several applications, and incorporation of metal nanoparticles enhances the conductivity of polymers. The electronic structure of the polymer chain strongly influences the characteristics of embedded metal nanoparticles. Nanoscale metal particles have been studied for use as advanced materials with improved electronic, magnetic, optic, and thermal properties as well as catalytic properties [8–10]. These potentialities are due to a high specific surface area and the quantum size effect, which is derived from the dramatic reduction of

---

[*] Address correspondence to Prof. Hyung-Ho Park, Department of Materials Engineering, Yonsei University, Seoul 120-749, Korea (ROK).Tel: (+82)2123-2853; Fax: (+82)312-5375. E-mail: hhpark@yonsei.ac.kr

the number of free electrons in particles in the range of 1–10 nm [11]. Needless to say, an accurate control of the particle size is the vital to the investigation of those novel physical and chemical properties.

Several works on SiO_2/conjugated polymers have been reported indicating that the conjugation length of the polymer increases with increased nanoparticles concentration. Several factors can influence the charge injection into the polymer and polymer movement inside the composites: the morphology of the contact between the film and the electrode, the dielectric and chemical properties of the particles, and the rupture of the polymer chain. In this work, we report the role of SiO_2 nanoparticles on the properties of poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate) (PEDOT:PSS) considering their electrically insulating nature and the effect of surface hydroxyl groups.

II. Experimental Procedures

SiO_2 nanoparticles were purchased from Degussa and dispersed in isopropyl alcohol (IPA) for blending with an aqueous solution of PEDOT:PSS (Baytron AI 4083 from HC Stark). The dispersed SiO_2 nanoparticles in IPA were added in an aqueous solution of PEDOT:PSS and then the blending solution was agitated by ultrasonication during 5 min and vigorous stirring was conducted for 24 hrs in order to distribute SiO_2 nanoparticles uniformly in PEDOT:PSS matrix in nitrogen atmosphere at room temperature. SiO_2/PEDOT:PSS nanocomposite films were prepared by spin casting at 500 revolution per minute in nitrogen atmosphere. The films were annealed for 15 min stepwise at each temperature of 80, 100, and 230°C under nitrogen atmosphere. The final thickness of the nanocomposite films was measured to be around 100 nm by using a stylus profilometer.

Atomic force microscopy (AFM) images were obtained using a NanoScope IIIa Dimension 3100 with tapping mode. To examine the chemical bonding states and electronic structure of SiO_2/PEDOT:PSS nanocomposite films, synchrotron radiation photoemission spectroscopy (SRPES), C 1s and O 1s K-edge near edge X-ray absorption fine structure

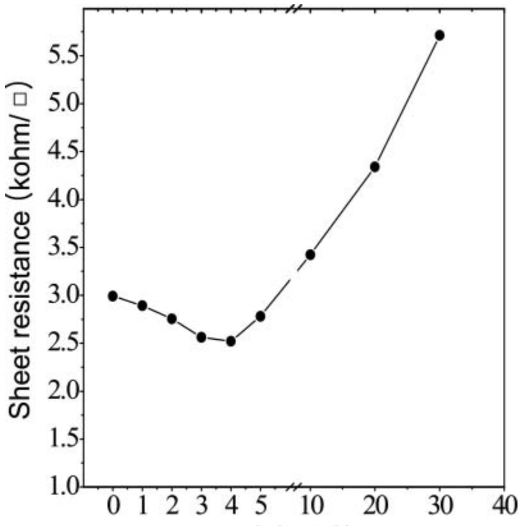

Figure 1. Sheet resistance of PEDOT:PSS films with various contents of SiO_2 NPs.

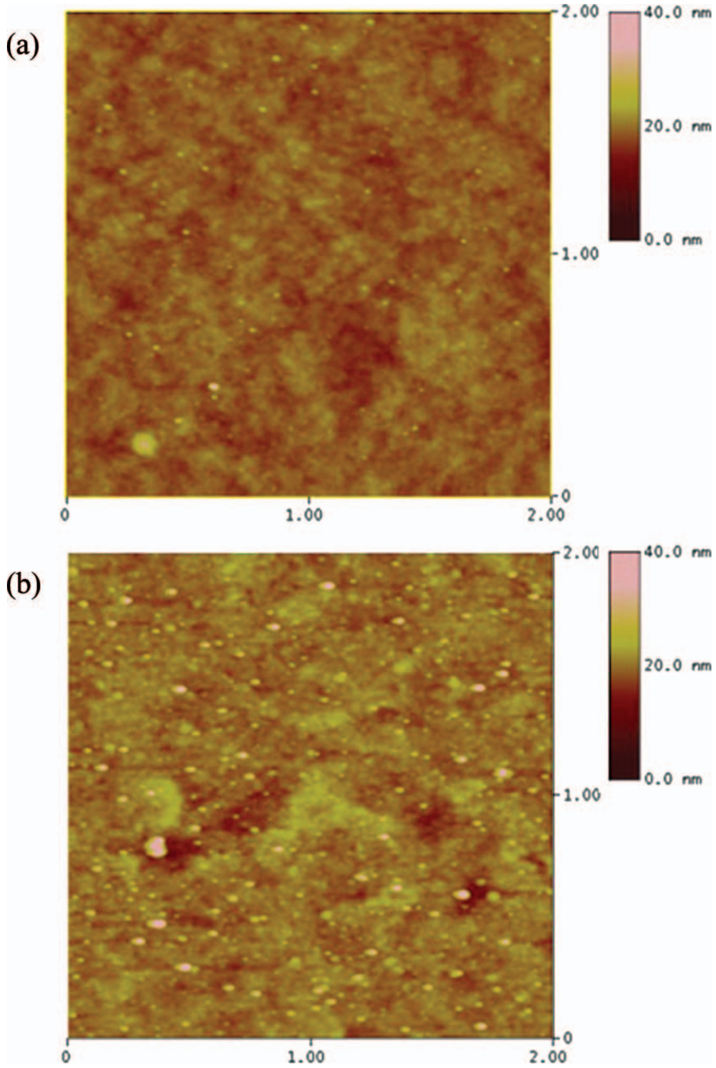

Figure 2. AFM height images of PEDOT:PSS composite films doped with SiO_2 NPs of (a) 1 wt% and (b) 5 wt%.

(NEXAFS), and ultra-violet photoelectron spectroscopy (UPS) measurements were carried out using the 4B1 beam line at the Pohang Accelerator Laboratory (PAL). An incident photon energy of 650 eV was used to obtain PES spectra and was calibrated with the core level spectrum of Au 4f. For the UPS, an energy of He I ($h\upsilon = 21.2$ eV) was used. Current-voltage curves were obtained using Agilent Technology E5270B without a visible ray.

III. Results And Discussion

Sheet resistance of PEDOT:PSS/SiO_2 nanocomposite films as a function of the content of SiO_2 nanoparticles is plotted in Fig. 1. We used 7–8 nm sized commercial SiO_2 nanoparticles. PEDOT:PSS/SiO_2 nanocomposites have a lower sheet resistance at 5 wt% addition than pristine PEDOT:PSS; further addition increased resistance. From these results, it

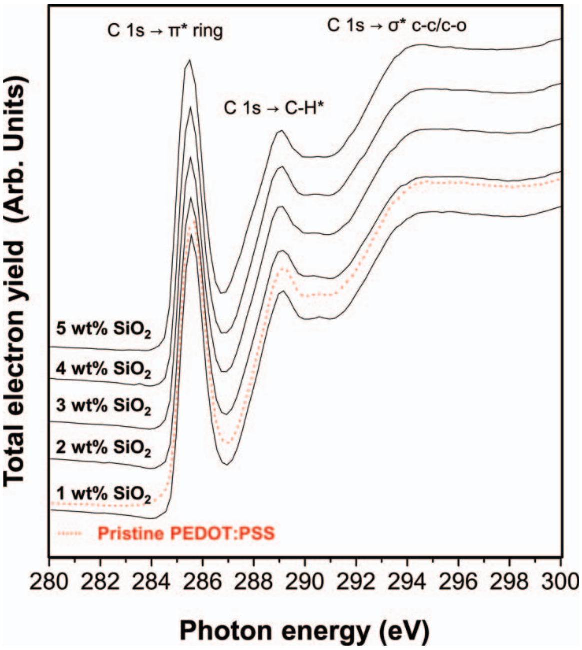

Figure 3. C 1s NEXAFS spectra of PEDOT:PSS films with various content of SiO_2 NPs.

can be inferred that insulating SiO_2 NPs decreases film resistance at moderate loadings by shortening the conductive charge path or by inducing other PEDOT:PSS structural changes.

Surface morphologies of SiO_2 NP doped PEDOT:PSS films were studied by AFM. A relatively rough surface is shown in the topographic images ($2\ \mu m \times 2\ \mu m$) of Fig. 2, with the rms roughness of (a) 1.081 nm and (b) 2.040 nm for 1 and 5 wt% SiO_2 nanoparticles content, respectively. From these observations, it is clear that SiO_2 NPs in the spun coated films were slightly agglomerated, but were otherwise well dispersed over a wide area. The presence of doped silver NPs could be easily identified as bright spots in the height images. In any case, surface roughness was increased and larger particles were observed in the AFM observations with increasing SiO_2 NPs content.

In Fig. 3, C 1s NEXAFS spectra showed a sharp C1s-π^* resonance at an absorption edge of 285.3 eV. The relative intensity change of π^* to σ^* resonance slightly increased through SiO_2 NPs addition. This corresponds to a slight increase in packing density of PEDOT from increased ordering and π-conjugation of PEDOT:PSS, which is induced from the hydrogen bonding between PEDOT chains and SiO_2 NPs, and a shortening of chain length by the steric effect.

The dependence of the work function and valence band spectra of PEDOT:PSS/SiO_2 with various SiO_2 NP contents are shown in Figs. 4 and 5. The work function decreased from an initial value of pristine PEDOT:PSS, 5.2 eV to about 5.1 eV with incorporation of 1 wt% SiO_2 NPs, and to 4.9 eV for 5 wt% addition. This lowering of the work function in the composite film was induced by an inhibition of electrostatic bonding between PEDOT and PSS from the presence of agglomerated SiO_2 NPs, which causes a weak doping state in PEDOT due to coulombic bond formation with SiO_2 NPs.

In the valence band spectra of Fig. 5, it is shown that there is little change in the valence band structure with SiO_2 NPs content. This can also be ascribed to the weak doping effect

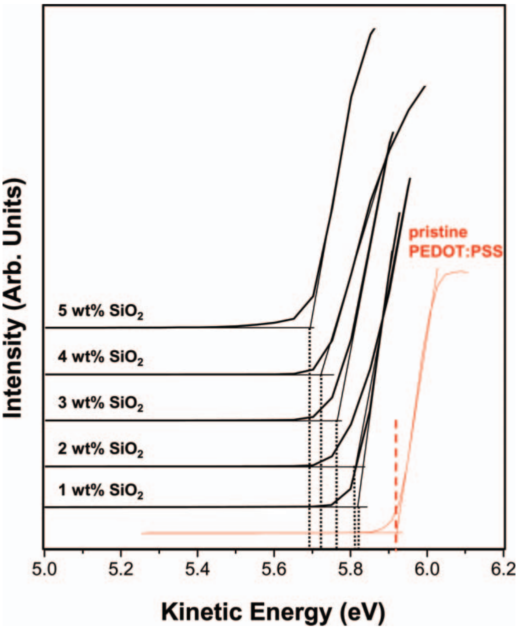

Figure 4. Secondary electron emission spectra of SiO_2 NPs incorporated PEDOT:PSS films.

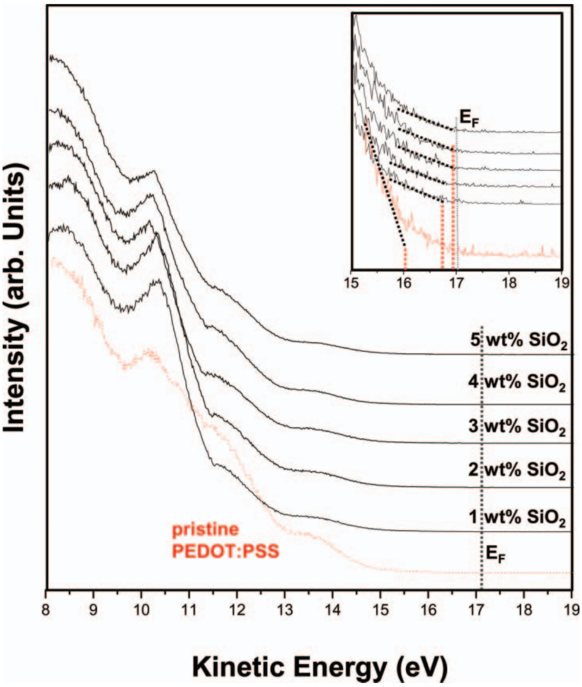

Figure 5. Valence band spectra of SiO_2 NPs incorporated PEDOT:PSS films.

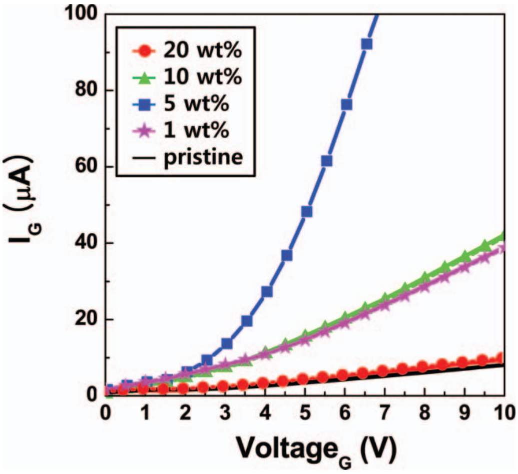

Figure 6. Current-voltage characteristic curves of the PEDOT:PSS film and nanocomposite films of PEDOT:PSS and SiO_2 NPs with structure of Au/PEDOT:PSS(SiO_2)/p-Si.

and coulombic force between SiO_2 NPs and PEDOT:PSS. A closer look near the region of 17 eV, as given in an inset, shows the highly occupied molecular orbital (HOMO) edge slightly shift to the Fermi energy level, which can be caused by electron localization on SiO_2 NPs from PEDOT by electrostatic bond formation.

Current-voltage curves in Fig. 6, showed an increase in film conductivity with SiO_2 NPs content. In the case of 5 wt% SiO_2 NPs in PEDOT:PSS, the lowest film resistance was observed and 1 and 10 wt% added films showed somewhat good conduction characteristic and similar conductivity behavior with applied voltage. However, in the 20% added sample, current flow was similar to the pristine PEDOT:PSS due to a scarce current path. So, SiO_2 NPs can enhance the conductivity of PEDOT:PSS when they are added below 10 wt%. This current-voltage result is well matched with the sheet resistance result, as given in Fig. 1.

IV. Conclusions

In this study, the role of SiO_2 NPs in PEDOT:PSS thin films were investigated and their steric effect and surface hydroxyl bonds were found to be important to the surface morphology, electron band structure, and electrical conductivity of PEDOT:PSS nanocomposite films. Relatively rough surface morphologies were observed by inclusion of SiO_2 NPs. An enhancement in the compact density and alignment of chain structure was induced by SiO_2 NPs addition and this was confirmed by C 1s NEXAFS measurements. A slight reduction in work function and a HOMO edge shift to the Fermi energy level were also induced from the steric effect of SiO_2 NPs and the weak doping of PEDOT by hydroxyl groups on the surface of SiO_2 NPs. Moreover, increased electrical conductivity was obtained with moderate SiO_2 NPs content, resulting from a reduced conducting path.

Acknowledgments

This study was supported by a grant (#10041220) from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

References

[1] Yang, S. H., Nguyen, T. P., Le Rendu, P., & Hsu, C. S. (2005). *Composites: Part A, 36*, 509.

[2] Yoon, S., Choi, H. J., Yang, J. K., & Park, H. H. (2004). *Appl. Surf. Sci.*, *237*, 450.

[3] Han, M. G., & Armes, S. P. (2003). *Langmuir*, *19*, 4523.

[4] Lu, G., Tang, H., Qu, Y., Li, L., & Yang, X. (2007). *Macromolecules*, *40*, 6579.

[5] Dutta, K., & De, S. K. (2007). *J. of Nanoparticle Research*, *9*, 631.

[6] Hao, L., Zhu, C., Chen, C., Kang, P., Hu, Y., Fan, W., & Chen, Z. (2003). *Synth. Met.*, *139*, 391.

[7] Jang, J. S., Ha, J. S., & Lim, B. K. (2006). *ChemComm*, *15*, 1622.

[8] Li, Z. F., Swihart, M. T., & Ruckenstein, E. (2004). *Langmuir*, *20*(5), 1963.

[9] Lei, X., & Su, Z. (2007). *Polym. Adv. Technol.*, *18*, 472.

[10] Koch, N., Ghijsen, J., Pireaux, J. J., Schwartz, J., Johnson, R. L., Elschaner, A., & Kahn, A. (2003). *Appl. Phys. Lett.*, *82*, 70.

[11] He, S. T., Yao, J. N., Jiang, P., Shi, D. X., Zhang, H. X., Xie, S. S., Pang, S. J., & Gao, H. J. (2001). *Langmuir*, *17*, 1571.