

Theoretical Investigation of the Electronic Properties of PEDOT: PSS Conducting Polymer on Indium Tin Dioxide (ITO) Surface: an Accelerated Quantum Chemical Molecular Dynamics Method

Chen Lv¹, Xiaojing Wang¹, Agalya Govindasamy¹, Hideyuki Tsuboi²,
Michihisa Koyama¹, Momoji Kubo^{1,3} and Akira Miyamoto^{1,2}

¹Department of Applied Chemistry, Graduate School of Engineering, Tohoku University,
Aoba-yama 07, Sendai 980-8579, Japan.

Fax: +81-22-217-7235, Phone: +81-22-217-7236, e-mail: lv@aki.che.tohoku.ac.jp

²New Industry Creation Hatchery Center, Tohoku University, Aoba-yama 10, Sendai 980-8579, Japan

³PRESTO, Japan Science and Technology, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

1. Introduction

Optical probes of conjugated polymer structures are particularly appealing to the investigation of polymer light-emitting diodes (LEDs). Following the discovery of polymer LEDs [1], much research has concentrated on identifying the major, which control their performance, and on developing ever more efficient structures.. Carrier injection into the polymer is found to be of paramount importance [2, 3] and since injection is regulated by the barrier height at the electrode-polymer interface, a careful choice of electrode materials is critical. Sn-doped In_2O_3 (ITO) is generally used as the anode because it is an n-type transparent conducting oxide (TCO) with extensive commercial applications, including flat-panel electro luminescent displays, solar cells, and energy efficient windows [4]. For devices in which the electroluminescent polymer is deposited on an ITO anode, oxidation of the polymer by oxygen diffusing out of the ITO limits the device lifetime [5]. A possible way to get around this problem is the introduction of an organic hole-injecting film, poly-(3,4-ethylene-dioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), between the ITO and the emissive polymer. This has indeed led to a dramatic improvement of the lifetime and also the luminous efficiency [6, 7]. However, until now electronic properties of the interface between ITO and PEDOT:PSS is not well understood or well controlled.

In this study, the effect of the Sn dopant in ITO has investigated by using our accelerated quantum chemical molecular dynamics program "Colors" and density functional theory. A comprehensive study of the electronic properties of ITO has also been carried out. Furthermore, the energy band level for PEDOT:PSS and ITO was derived. Moreover, the stable geometry structures of PEDOT and PSS were calculated by "Colors" and density functional theory, respectively.

2. Computational methods

The accelerated quantum chemical molecular dynamics program "Colors", which is based on our original tight-binding approximation, was used for the simulation. It realized 5000 times accelerations compared to the

traditional first-principles molecular dynamics method. First -principles density functional calculations were performed using the Amsterdam density functional (ADF) program [8] as well as periodic methodology of Dmol³ program [9]. In the former, the triple zeta plus polarization functions (TZpp) basis sets were used, while energies were calculated using the generalized gradient approximation (GGA) with Becke's exchange and Perdew correlation functions. In the case of the latter, double numerical atomic basis sets with polarization functions (DNP) were used, while the energies were calculated, as before, using GGA with Becke's exchange and Perdew correlation functions. ADF program is employed to determine the parameters for "Colors".

3. Results and discussions

Fig. 1 depicts the structures of the $\text{In}_{24}\text{O}_{36}$ and $\text{In}_{21}\text{Sn}_3\text{O}_{36}$ (In_2O_3 with 10% SnO_2 dopant), which were calculated by our accelerated quantum chemical molecular dynamics program, "Colors" program and density functional theory under the periodic boundary conditions. Calculated band gap energy of In_2O_3 , by "Colors" program as shown in Table 1, are well consistent with density functional theory calculations using Dmol³ program [9] and the experimental data [10]. For ITO, it is difficult to determine of the highest occupied molecular orbital (HOMO) and the lowest molecular orbital (LUMO) by experimental approach. Therefore, only theoretical calculation results of HOMO, LUMO and band gap energy

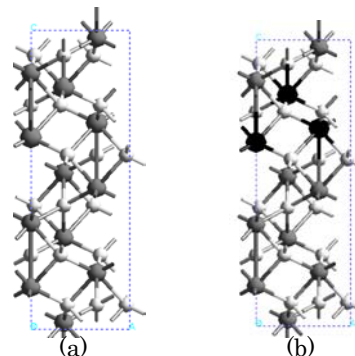


Fig. 1 The structure of (a) $\text{In}_{24}\text{O}_{36}$ (b) $\text{In}_{21}\text{Sn}_3\text{O}_{36}$ (In_2O_3 with 10% SnO_2 dopant). The white one is oxygen, the dark gray one is indium and the black one is tin atom.

of these models were shown in Table 1.

Moreover, the fully optimized structures of PEDOT and PSS were obtained by minimizing the total energy and atomic force by “Colors” and Dmol³ programs. The band gap energy of the PEDOT is calculated to be 1.39eV and 1.63eV by “Colors” program and Dmol³ program, respectively, while 1.5-1.6eV was reported experimentally. While the band gap energy of PSS molecule was 3.32 eV and 3.22 eV by “Colors” and Dmol³ programs, respectively. These results show that “Colors” program can reproduce the density functional theory calculation results and experimental value well.

In order to stabilize the anode interface and prevent indium and oxygen diffusion into the emissive polymer, the PEDOT: PSS were introduced to spin onto ITO. Table 2 shows the band gap energy, HOMO, LUMO and the Fermi level of PEDOT, PEDOT⁺, ITO/PEDOT and ITO/PEDOT⁺, which were calculated by “Colors” program. PEDOT⁺ indicates that the PEDOT has been doped with PSS in order to enhance the conductivity of film, while ITO/PEDOT and ITO/PEDOT⁺ indicates that PEDOT spun onto ITO and PSS-doped PEDOT spun onto ITO, respectively. An energy level diagram summarizing the band structure of the interface in ITO/PEDOT:PSS is depicted in Fig. 2. By studying how the energy level of the polymer line up at the ITO/conducting-polymer and conducting polymer/emissive polymer interfaces, however, it was found that conducting polymer layer determines the barrier for the hole injection. The barrier to hole injection is the difference between the Fermi level and the polymer valence band edge (ΔE in Fig. 2). The E_F -HOMO shown in Fig. 2 is equal to the energy barrier of hole injection. Comparison of the energy level, it shows that the doping level is going away from ITO surface. From Fig. 2 (b), it is clear that there is a 2.14eV ($\Delta E - \Delta E_1$) reduction of the barrier height at the anode/polymer interface. Thus, the beneficial effects of the PEDOT:PSS between the ITO and the emissive polymer are likely to ensue from a reduction of hole-injection barrier at the

Table. 1 HOMO, LOMO and Eg (band gap energy) of In₂O₃ and ITO bulk (In₂O₃ with 10% Sn dopant).

	Dmol	Colors	Exp. [10]
In ₂ O ₃			
HOMO (eV)	-7.82	-11.76	
LUMO (eV)	-5.76	-9.64	
Eg (eV)	2.06	2.12	2.60
ITO			
HOMO (eV)	-4.04	-7.76	
LUMO (eV)	-2.71	-6.58	
Eg (eV)	1.33	1.18	

Table 2 HOMO, LUMO band gap energy and Fermi level of PEDOT, PEDOT⁺, ITO/2PEDOT and ITO/(2PEDOT)⁺.

	PEDOT	PEDOT ⁺	ITO/PEDOT	ITO/PEDOT ⁺
HOMO(eV)	-10.50	-11.52	-9.13	-9.31
LUMO(eV)	-8.87	-9.99	-8.05	-8.20
Eg (eV)	1.63	1.54	1.07	1.11
E _F (eV)	-9.69	-10.52	-8.59	-7.94

anode interface, as a result of improving hole injection. Our results support experimental finding that by introducing conducting polymer to improve the device performance. It proves that our “Colors” program is a very effective tool.

4. Conclusions

In this study, we have studied the electronic properties of In₂O₃ and ITO, as well as PEDOT and PSS by “Colors” program and Dmol³ Program. Our “Colors” program can reproduce density functional calculation well. We also reported the interface formation between bulk ITO and PEDOT:PSS calculated by “Colors” program. It propose that such an improvement is mainly due to the hole inject layer effect of PEDOT:PSS.

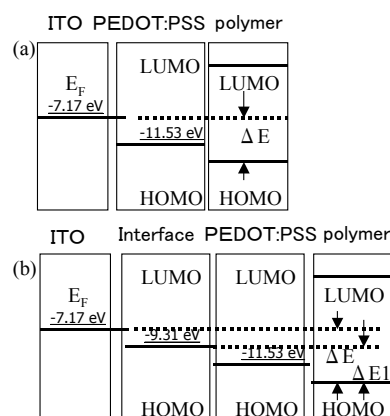


Fig. 2 Energy level diagram, an emissive polymer spun onto a doped conducting polymer (PEDOT-PSS) spun onto ITO. (a) No energy level of interface between PEDOT:PSS and ITO (b) energy level of interface between PEDOT:PSS and ITO was added. The Fermi level of ITO was depicted. Position of HOMO and LUMO of PEDOT:PSS and polymer was shown.

References

- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, Nature (London) **347** (1990) 539.
- [2] R. N. Marks, D. D. C. Bradley, R. W. Jackson, P. L. Burn and A. B. Holmes, Synth. Met. **55-57** (1993) 4128.
- [3] I. D. Parker, J. Appl. Phys. **75** (1994) 1656.
- [4] J. C. C. Fan and F. J. Bachner, J. Electrochem. Soc. **122** (1975) 1719.
- [5] J. C. Scott, J. H. Kaufman, P. J. Brock, R. DiPietro, J. Salem and J. A. Goitia, J. Appl. Phys. **79** (1996) 2745.
- [6] A. Berntsen, Y. Croonen, C. Liedenbaum, H. Schoo, R. J. Visser, J. Vleggaar and P. van de Weijer, Opt. Mater. **9** (1998) 125.
- [7] S. Karg, J. C. Scott, J. R. Salem, and M. Angelopoulos, Synth. Met. **80** (1996) 111.
- [8] F. C. Guerra, J. G. Snijders, B. Velde, and, E. J. Baerends, Theor. Chem. Acc., **99** (1998)391.
- [9] B. Delley, J. Chem. Phys., **92** (1990) 508.
- [10] R. L. Weiher, R. P. Ley, J. Appl. Pys. **37** (1966) 299.