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Surface modification of ITO with polythiophene derivative, poly(3-TUTS), was done for molecular electronic device application purpose. In order to prepare a derivative of polythiophene having n-alkyltrichlorosilane at 3-position of the thiophene ring, the monomer of thienyl-functionalized n-alkyltrichlorosilane, 11-(3-thienyl)undecyltrichlorosilane (3TUTS), was synthesized. The monomer was identified by using NMR, UV/VIS spectroscopic methods. Surfaces of ITO substrates were modified with the synthesized 3TUTS to get SAM on them. Polymerization of the SAM was done by dipping this SAM into FeCl₃ solution. The polymer have been identified by using Cyclic Voltammetry, UV/VIS spectroscopy, scanning electron microscopy (SEM), DFM (Dynamic Force Microscopy) image analysis.

Keywords: DFM; ITO; Polythiophene; SAM; surface modification; 3-TUTS

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INTRODUCTION

Conductive polymers are renowned for having novel electrical and optical functionalities. Especially interests in film form of the material have driven the applications of thin polymer batteries [1], electrochromic displays [2], antistatic coatings [3], organic electronic circuits and devices [4], and various sensors [5]. Recent developments in fabrication allowed these materials got involved in the manufacturing process of micro or nano devices [6–8].

Since self-assembled monolayer (SAM) process have been accepted as one of the best ways to acquire regularly structure a substrate, many of SAM applications have been introduced such as, *n*-alkyltrichlorosilane on hydroxylated surfaces [9,10] and *n*-alkanethiols on gold, silver and copper [11]. Organosilicon compounds have been used to improve hydrophobic property and thermal stability of various surfaces by forming of siloxane films. For example, Octadecyltrichlorosilane (OTS) forms highly ordered SAMs on numerous substrates [12,13]. There has been widespread interest in using ω -substituted monolayer to create surface layers with tunable properties. Some of applications include promoting or preventing the adherence of materials to the substrate [14], changing the wetting behavior [15], or altering the frictional properties of the surface [16], and also the electrochemical properties of surface-bound layers have been reported on by Collard [17], Kim [18], and McCarley [19].

In this work, we tried to elucidate the polymerization process of monomer SAM layer of 3TUTS formed on ITO substrates by adopting chemical polymerization method. Because the final product of poly (3TUTS) could be used as a base material of molecular field effect transistor. The polymer SAM so obtained was identified by using Cyclic Voltammetry, UV/VIS spectroscopy, and SEM and DFM image analysis.

EXPERIMENTAL

Chemicals used in this work were of ACS grade and purchased from Sigma-Aldrich Korea Ltd. and used without further purification otherwise described. Platinum plate was used as a counter electrode and a Ag/AgCl (sat'd KCl) was used as counter and reference electrode, respectively. ITO glass (Samsung Corning, Korea) was used as a substrate and the SAM covered ITO was served as a working electrode. Electrochemical experiments were carried out with BAS 100B electrochemical work station (BAS Inc., USA). Scanning electron microscope (SEM) images were obtained by using JSM 6700F

(Jeol, Japan). SPA-400 (Seiko, Japan) AFM system was utilized to get DFM images.

The synthesis of 3TUTS was accomplished by following the procedure in the literature [20]. As a first step, 3-(10-undecenyl)thiophene was synthesized and identified with NMR spectroscopy. Later 3TUTS was prepared and purified by distillation using Kugelrohr apparatus under the pressure of ca. 10^{-3} torr. The final product was also analyzed with NMR spectroscopy.

3TUTS SAM structures were prepared under ambient laboratory conditions. Several pieces of the well cleaned ITO glass were immersed into a SAM solution for various periods. The concentration of the SAM solution was 10 mM 3TUTS in methylene chloride. The time periods are 24, 48, 72, 96, 144 hours. SAM deposition was carried out in a well cleaned glass vial with an air tight stopper which was preheated under vacuum before use. After deposition, the samples were thoroughly cleaned with sonication in methylene chloride followed by rinsing with ethanol and distilled water. They were then dried with argon blowing and kept under atmospheric condition. Before each analysis, the samples were rinsed with ethanol and distilled water and dried with nitrogen or argon blowing.

Existence of SAM on the substrate was examined with cyclic voltammetry which can monitor the redox of a solution probe species of $\text{Fe}(\text{CN})_6^{3-}$. To do this, the SAM coated ITO was dipped in a investigating solution of $\text{Fe}(\text{CN})_6^{3-}$. The applied potential cycles were in a range of $-0.2 \sim 0.6$ V vs. $\text{Ag}/\text{AgCl}(\text{sat'd KCl})$. UV/VIS absorption spectra of the SAM before and after polymerization were taken with ITO blanks. SEM and DFM images were also taken before and after polymerization of the SAM and analyzed.

RESULTS AND DISCUSSION

For our purpose 3-(10-Undecenyl)thiophene and 11-(3-thienyl)undecyltrichlorosilane has to be synthesized. Figure 1 shows the synthetic scheme. The synthetic products were verified by ^1H NMR, their coupling constants were consistent with literature results [21]. The data is given below. Analytical data of 3-(10-Undecenyl)thiophene: δ_{H} 7.25–7.22 (dd, 1H, $J = 2.9, J = 4.8$), 6.95–6.92 (m, 2H), 5.98–5.77 (m, 1H), 5.05–4.94 (m, 2H), 2.64 (t, 2H, $J = 7.7$), 2.10–2.03 (q, 2H, $J = 6.9$), 1.61–1.53 (m, 2H), 1.37–1.24 (m, 12H). Analytical data of 11-(3-thienyl)undecyltrichlorosilane: ^1H -NMR (300 MHz, CDCl_3) δ_{H} 7.26–7.23 (dd, 1H, $J = 2.9, J = 4.9$), 6.95–6.92 (m, 2H), 2.63 (t, 2H, $J = 7.7$), 1.65–1.55 (m, 2H), 1.43–1.23 (m, 18H).

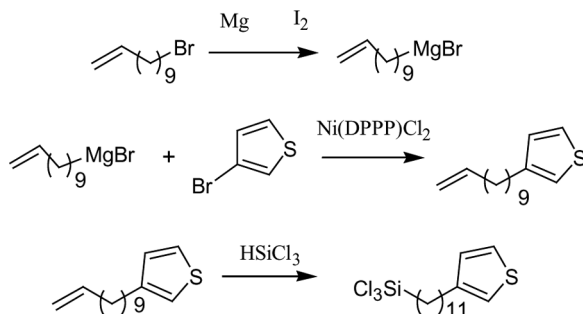


FIGURE 1 Synthetic scheme for 3TUTS. The alkyl chain is joined to the thiophene ring by a metal-mediated cross coupling, and then the trichlorosilane functionality is added.

SAM electrodes of 24, 48, 72, 96, 120 hour deposition were tested by using electrochemical cyclic voltammetry method using an electrolyte of 0.2 mM K₃Fe(CN)₆ in 0.1 M KCl/H₂O solution with the application of potential cycling between -0.20 and 0.60 V on the scan rate of 50 mV/s. The resulting cyclic voltammograms (CV) are appeared in Figure 2. The shape of CV changes as a function of deposition period. The CV obtained from bare ITO electrode shows a nice looking symmetric CV constructed with redox peak pair at 180 mV and 280 mV. This indicates that there exists a reversible redox reaction of the probe species Fe(CN)₆³⁻ in electrolyte. What we expected was that the deposition time increases the redox peak heights are decreasing and the peak position are shifting to higher potentials. After long enough period, the whole active ITO surface could be covered with inert SAM during this period, the redox peaks would be disappeared completely; completely irreversible redox process. But the results in Figure 2 are a little different from what we expected. The decreases in peak height and shifts in peak position to higher potential region are recognizable as in the figure, but the redox peaks are not disappeared completely even for the one of 120 hour modification. If the SAM between ITO and Fe(CN)₆³⁻ solution species behaves as a complete passive layer, the redox peak would be disappearing as a function of modification time. In spite of long time ITO exposure to the 3TUTS solution to form a complete SAM, the redox pick pair is not disappeared completely. This may be attributed to sluggish electron transfer capability of the long alkyl chain on 3TUTS under electrochemical circumstances [22]. As appeared in inset of the figure, 30 hour is enough to deposit the 3TUTS SAM.

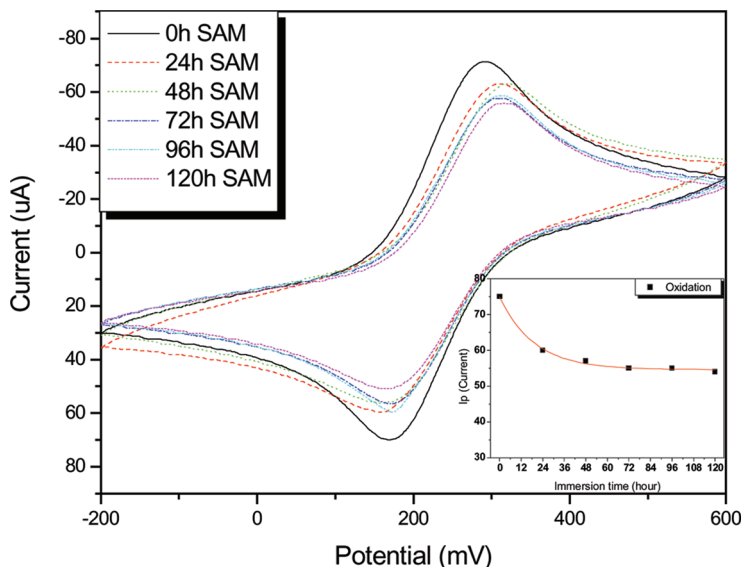


FIGURE 2 CV of $K_3Fe(CN)_6$ in 0.2-mM $K_3Fe(CN)_6/0.1M$ KCl/ H_2O solution obtained by using different SAM electrodes. (See COLOR PLATE I)

Polymerization of the 3TUTS SAM was carried out by dipping the SAM into 0.08 M solution of $FeCl_3$ in chloroform for 24 hours. Figure 3 (a), (b), (c), (d) show UV/VIS absorption spectra of the SAM before and after polymerization. Spectrum of 3TUTS SAM formed during 48 hours shows absorption peaks at ca. 300 and 400 nm with a weak broad band at long wavelength region. After the polymerization, the measured spectrum shows peak shifts to new positions ca. 380 and 630 nm. Modified polythiophenes have been responsible to show this type of absorption [23]. As the modification time increases, the relative absorbance of each polymerized film compared the one for its SAM is increases. We also examined the polymerization of the SAM with the image analysis obtained from SEM and DFM methods. Figure 4 shows SEM images of 3TUTS modified ITO samples before and after polymerization. The 24 hour 3TUTS modification allowed SAM shows surface image without special structures and looks not much different from the one ITO glass produced in Figure 4(a). Polymerization of the 24 hour SAM induced small structures in (b) of the same figure. This is indicating the possibility of occurrence of the over layered 3TUTS on the adsorbed species. Figure 4(c) clarifies this assumption; the longer time of modification generates the more complex three dimensional structures on the surface. The only possibility of forming

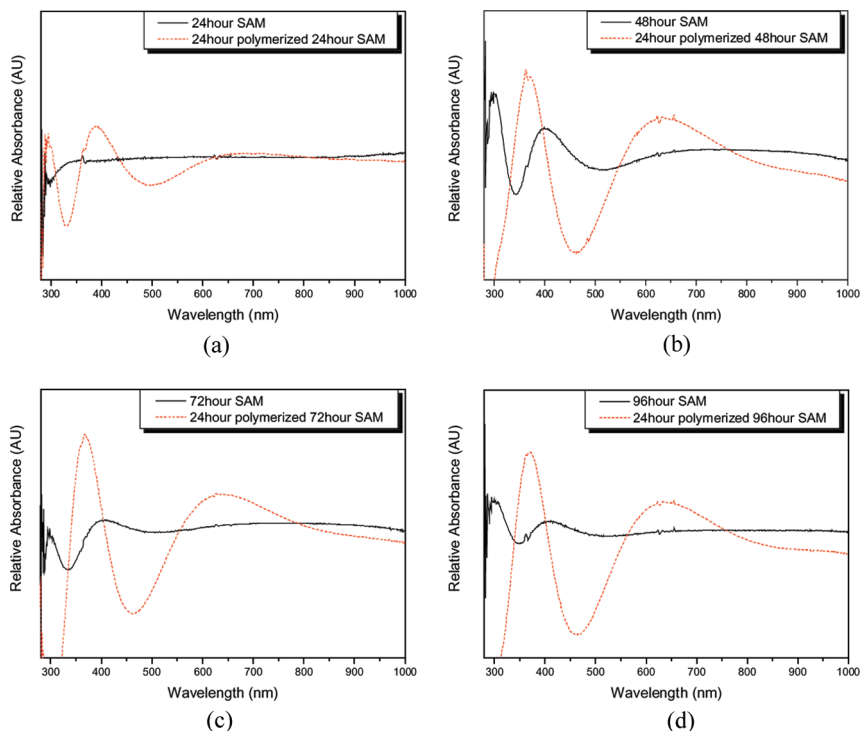


FIGURE 3 UV/VIS absorption spectra of 3TUTS SAM modified ITO glass before and after polymerization: (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h SAM. (See COLOR PLATE II)

three dimensional structures on SAM may be due to polymerization of the excess 3-TUTS aggregated on top of the SAM. DFM images obtained from the similar samples are shown in Figure 5. The results show fairly good matching up with those appeared in Figure 4. The DFM image of 24 hour 3TUTS modified ITO (a) shows relatively roughened surface structure of the ITO. There is no special structures are observed. This could be the anticipated results from the SEM image in Figure 4 (a). After polymerization, new smaller surface structures are covering the surface (b) and some parts gets larger structure. Most of the ITO structure is disappeared in this figure because the new polymerized structures can cover it. Finally in (c), most of the surface is covered with the regular dot like structures which is larger than the one in (b). These DFM images could provide information similar to those obtained from Figure 4. From this we can infer that the 3TUTS SAM could be polymerized and the polymerization can make

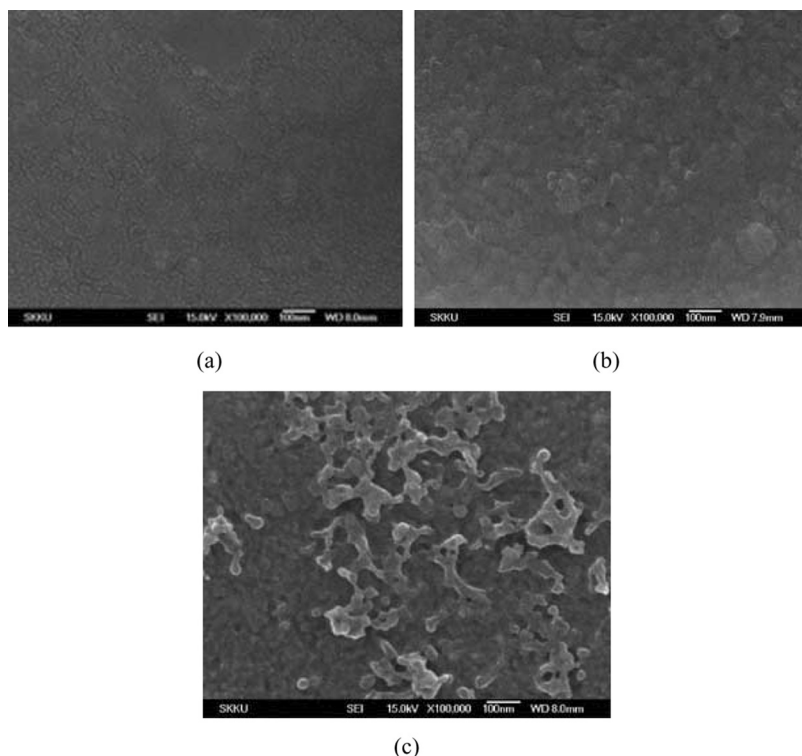


FIGURE 4 SEM images of 3TUTS modified ITO before and after polymerization: (a) 24 hour SAM only; (b) after polymerization, 24 hour SAM; (c) after polymerization, 144 hour SAM.

some three dimensional structure on top of the polymer SAM. The three dimensional structure could be controlled by varying the monomer modification period.

CONCLUDING REMARKS

We have synthesized 11-(3-thienyl)undecyltrichlorosilane and verified with ^1H NMR. 3TUTS SAM was formed by using normal solution technique on ITO glass slides. This SAM film allows slow electron transfer so that the film can not, in electrochemical view point, cover the surface. UV/VIS absorption spectroscopy allowed us to conclude that the SAM formation in this condition need more than 24 hours. Polymerization of the SAM could be possible with FeCl_3 solution. The polymerization of the SAM provided three dimensional structures

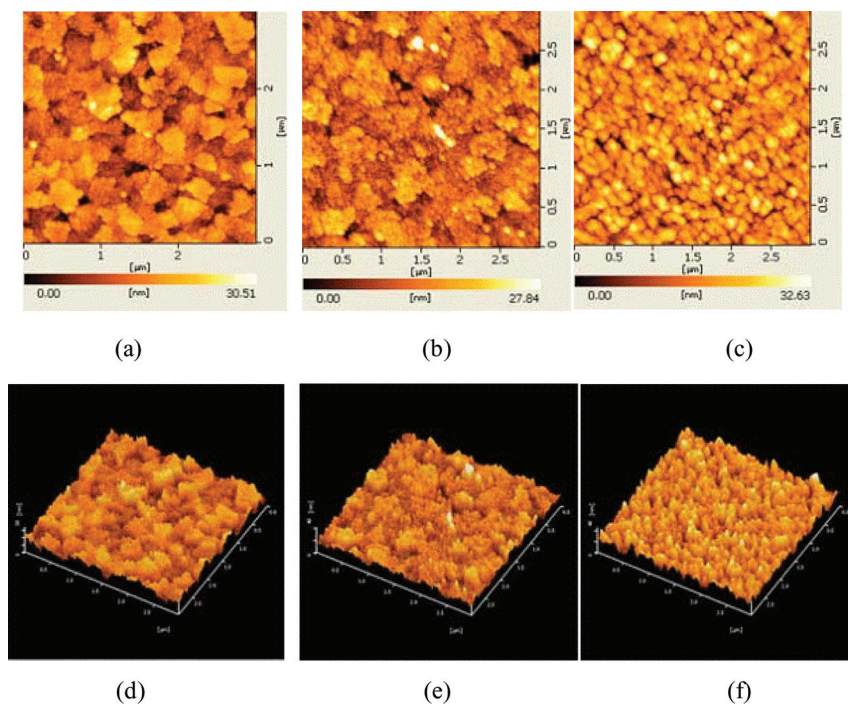


FIGURE 5 DFM images of 3TUTS modified ITO before and after polymerization: (a, d) 24 hour SAM only; (b, e) after polymerization, 24 h SAM; (c, f) after polymerization, 144 h SAM. (See COLOR PLATE III)

on top of the polymerized SAM. The three dimensional polymer structures may be due to the monomer 3-TUTS aggregated on top of the SAM during surface modification. Research for the application of this surface modification to devices is going on this laboratory.

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