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Preparation of Conducting Polymer/Metal Nanocomposites

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This study was primarily focused on the preparation and characterization of conducting polymer/metal nanocomposites. Poly(3,4-ethylenedithiathiophene) was prepared onto ITO electrodes as thin film shapes by electrochemical polymerization and reduced with constant potential. When the polymer films were doped with K_2PtCl_6 solution, they were easily get oxidized due to the concurrent reduction of Pt(IV) to Pt(0). This procedure ended up with the formation of polymer/metal composites. ***In-situ*** *spectroelectrochemistry was used to investigate the composite formation processes. The final composites were indentified with SEM and EDAX. Catalytic decomposition of methanol on these composite electrodes was observed by using cyclic voltammetry.*

Keywords: electrocatalytic; methanol oxidation; nanocomposite; PEDiTT; platinum

INTRODUCTION

Polymers had been mainly used as an electrical insulator for long time, but their conventional role was gradually changed to an electrical conductor with a wide range of novel applications. Owing to many

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researchers' effort, a new class of polymers known as conducting polymers has emerged [1–6]. Conducting polymers have conjugated π-bond on their backbone that is responsible for having novel electrical and optical properties. The conjugation system is consisted of alternating double and single bonds along the chain. Therefore, the easiness of oxidation of the π-electrons can induce the interesting characteristics such as electrical (semi)conductivity and variety of optical properties. Many research groups have investigated the functionalities of these materials and made numerous applications [7,8]. In spite of many potential applications in optoelectronics area, not many examples have been found in electrochemical, catalysis and sensor areas. The main reasons for this are based on poor solubility, weak mechanical strength, and environmental instability.

In this work, we have concentrated our effort into improving electrochemical catalytic property of this class of polymers by adopting poly(3,4-ethylenedithiathiophene) (PEDiTT), because this is completely soluble in 1-methyl-2-pyrrolidinone (NMP) and partly soluble in tetrahydrofuran (THF) and chloroform [9]. And it also has relatively good stability and high electrical conductivity due to regular backbone structure.

Among the novel metals, platinum fine particles show the highest catalytic activity, but supporting materials (or matrixes) are needed for practical applications. Introducing platinum nanoparticles into this polymer matrix only by doping reaction, the organic/inorganic nanocomposites were able to be formed. Electrochemical catalytic character for methanol oxidation was investigated by adopting various electrochemical methods because it is very important reaction for use of a direct methanol fuel cell (DMFC) and methanol is one of the most promising fuels for the future [10,11].

EXPERIMENTAL

The monomer, 3,4-ethylenedithiathiophene (EDiTT) was synthesized according to method published elsewhere [12]. Polymer, PEDiTT was synthesized as thin film shape on indium tin oxide (ITO) electrodes by applying cycling potential. The electrochemical polymerization was completed with 1 mM EDiTT in 0.1 M $LiClO_4/CH_3CN$ and three-electrode potentiostat (BAS 100B, Bioanalytical Systems Inc., USA) adopting ITO working, Pt plate counter, and Ag/AgCl (sat'd KCl) reference electrodes. Pieces of ITO glass (7 S/cm, Samsung Corning, Korea) were used as substrate electrodes. Thin films of PEDiTT were deposited on the substrates. *In-situ* UV/Vis spectra were measured by using UV/Vis spectrophotometer (HP 8453, HP, USA).

The synthesized PEDiTT was fully reduced in 0.1 M $LiClO_4/CH_3CN$ solution with constant potential method. To prepare the composites, the reduced PEDiTT was dipped in 0.01 M K_2PtCl_6/H_2O solution for 10, 20 and 60 min respectively. PEDiTT/Pt nanocomposites were identified with SEM (JSM 6700F, JEOL, Japan) and EDAX (JEM 2100F (JEOL, Japan) with EDS unit (Oxford INCA Energy)). All electrochemical experiments were performed after N_2 purging for 10 min. All potentials in this paper refer to the Ag/AgCl (sat'd KCl) electrode.

RESULTS AND DISCUSSION

PEDiTT films were prepared by electrochemical polymerization of monomer in electrolyte solution with potential window of $-0.10 \sim 1.30$ V. As shown in Figure 1(a), the monomer oxidation current in the first anodic scan rapidly increased at 1.10 V. This rapid increase mainly due to the pseudo catalytic oxidative polymerization of monomer occurred at this high potential and the polymerized product began to be deposited on the substrate as a film shape at this stage. After the first anodic scan, the potential scan is changed to cathodic direction. This continuing cathode scan makes the reduction peak (at 0.55 V) of PEDiTT film produced during the first oxidation process. By the successive cycles, the oxidation peak of PEDiTT appears at 0.95 V. As we repeat the potential scans, the heights of oxidation and reduction peaks were increased regularly. This implied that the polymer was being well deposited onto ITO glass electrode and the thickness of deposited film was increased gradually. This interpretation was also consistent with *in-situ* UV/Vis spectral change of PEDiTT appeared in Figure 1(b).

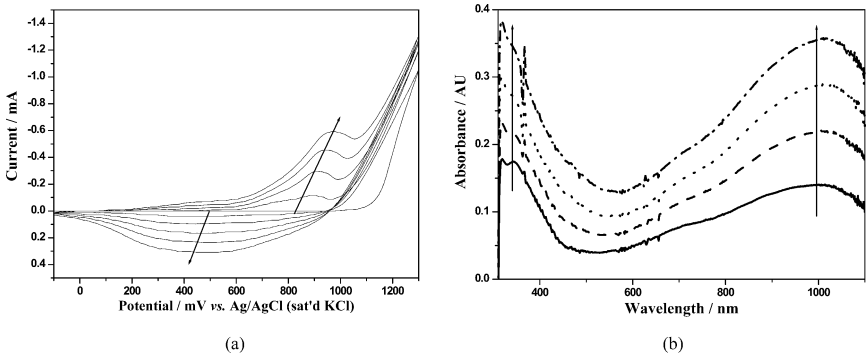

FIGURE 1 CV of EDiTT polymerization (a) and *in-situ* UV/Vis spectra taken at 1.30 V (b). Scan rate were 50 mV/s.

As the thickness of the PEDiTT film was increased, the absorbance of the film was also increased.

This polymer was characterized by cyclic voltammetry and *in-situ* UV/Vis spectrophotometry. As appeared in Figure 2(a), the cyclic voltammogram shows a sharp oxidation peaks at 0.95 V with a tiny pre-peak at 0.45 V and a broad reduction peak at 0.55 V. The whole shape and peak positions are well matched with reported results of polythiophene derivatives [13,14]. UV/Vis spectra in Figure 2(b) shows well developed absorption peaks at 330 and 430 nm for the reduced (or neutral) form of the polymer. The peak having higher energy was caused by the π–π^* transition (the excitation of nonbonding electrons in S atoms being in outside of heterocyclic rings to π^* orbitals of heterocyclic rings), while the peak at lower energy was attributed to the π-π^* transition [9]. As polymer was oxidized, the intensities of these two peaks were gradually decreased, on the other hand, new two peaks showed up at 710 and 1000 nm. The absorbance at 710 nm was steeply rising at first, but increasing rate was slow down later. And at this very moment, absorption increase at 1000 nm was remarkable. When it was reduced again, inverse process happened. Judging from by such a phenomenon, we could conclude that there were three species related by a serial electrochemical redox-reaction with two quasi-isosbestic points (at 480 and 750 nm).

The synthesized PEDiTT was reduced to prepare the matrix, which can hold metal particles by doping reaction. The reduction was done by applying constant potential. Results were illustrated in Figure 3. There is no current change after 300 sec with the application of −0.20 V.

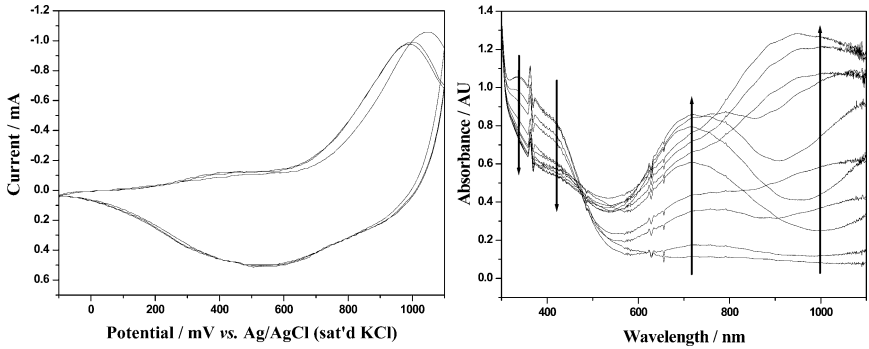

FIGURE 2 CV of electrochemically synthesized PEDiTT (a) and *in-situ* UV/Vis spectra during oxidation process (b).

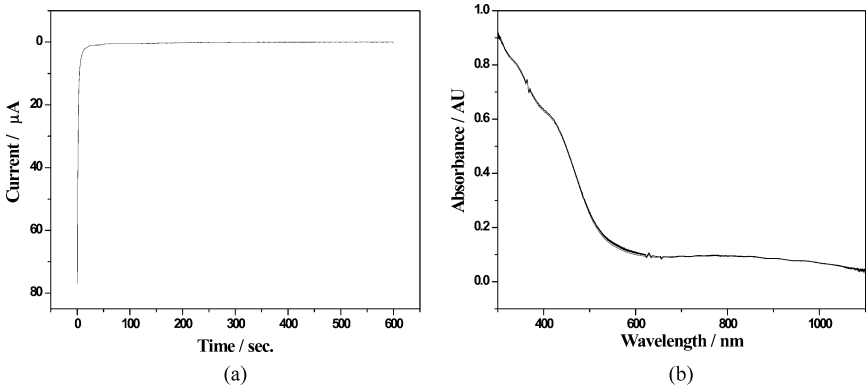

FIGURE 3 Chronoamperogram of PEDiTT with –0.2 V (a) and its *in-situ* UV/Vis spectra (b).

The absorption spectra show no definite change. After reducing, we dipped PEDiTT electrodes into 0.01 M K_2PtCl_6/H_2O solution to induce doping reaction. The spectral change due to the doping was monitored by measuring *in-situ* absorption changes. As shown in Figure 4, polymer films were oxidized by the dopant K_2PtCl_6. In this process, some part of Pt(IV) was simultaneously reduced to Pt(0) and

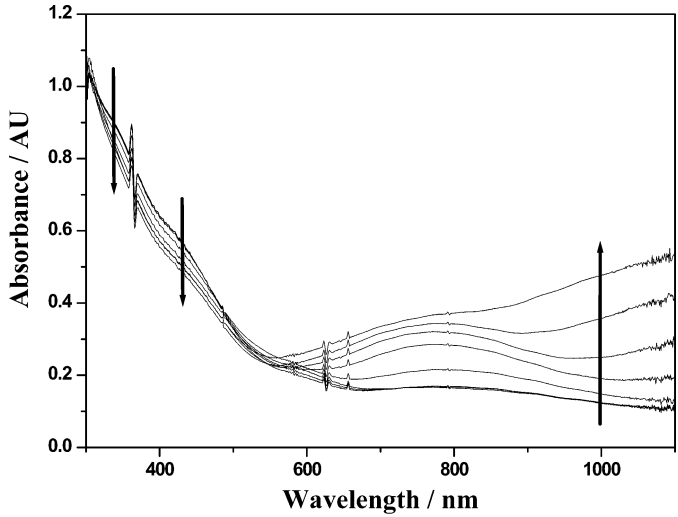

FIGURE 4 Spectral change during doping reaction in 0.01 M K_2PtCl_6 for 10 min.

the platinum crystals can grow inside the polymer. After finishing the doping, cyclic voltammetric tests were performed to the composite films. The results show that these composites provide similar spectroelectrochemical responses to those in Figure 2.

The composites were tested by identifying the existence of platinum particles inside the matrix. SEM images of the composite were carefully investigated and EDAX spectrum was also obtained. The Figure 5(a) shows that PEDiTT is in small size conglomerated and platinum particles are in square shape. As doping time was longer, platinum particles grew up and their distributions were becoming dominant. After even 60 min, polymers went out of sight and only platinum particles eventually came into sight (Fig. 5(c)). EDAX spectrum of the composite proved the presence and uniform distribution of platinum (Fig. 5(d)). Piecing these images and spectrum together, platinum particles were well formed and evenly distributed in PEDiTT

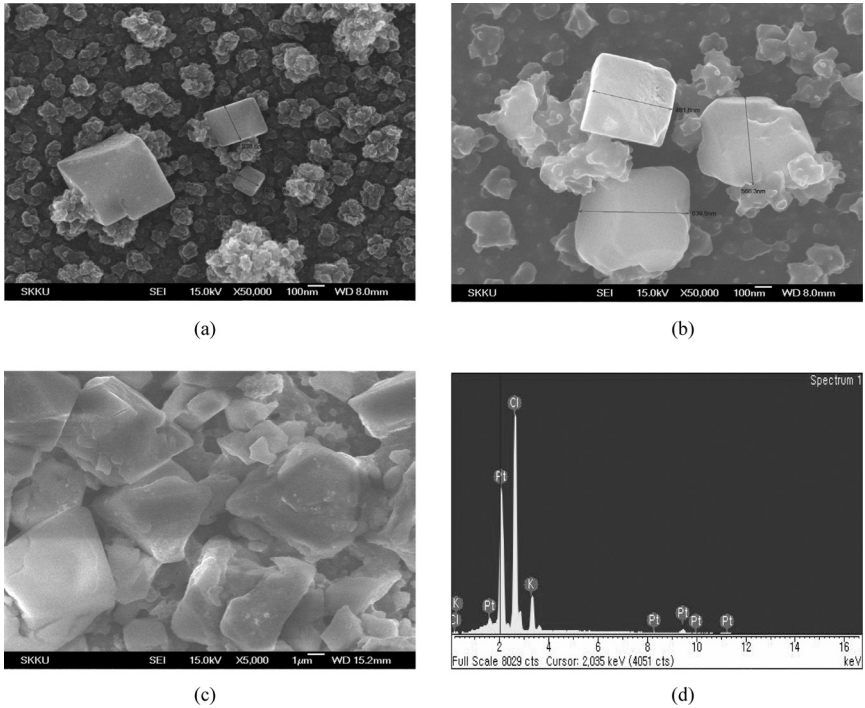

FIGURE 5 SEM images of PEDiTT/Pt nanocomposites. For 10 min (a), for 20 min (b), and for 60 min (c). EDAX spectrum taken from (c) composite (d).

matrix. We also verified that the more PEDiTT was doped with K_2PtCl_6, the bigger platinum particles were formed in the matrix.

We lastly checked the electrocatalytic characteristics of our composites for methanol oxidation using cyclic voltammetry. Figure 6(a) shows there was no significant response related to methanol oxidation when pure PEDiTT surface was used. When PEDiTT/Pt nanocomposites were used, however, cyclic voltammogram displayed two remarkable catalytic oxidation peaks as in Figure 6(b), (c) and (d) [10,11]. Some hysteresis in cyclic voltammogram was attributed to blocking of composites surface, especially platinum particles by chemisorbed CO species that are oxidized at more anodic potential [15]. Moreover, the longer the doping time in K_2PtCl_6 solution is, the bigger charge for methanol oxidation is. As platinum particles were formed much more, composites could provide the more active surface for

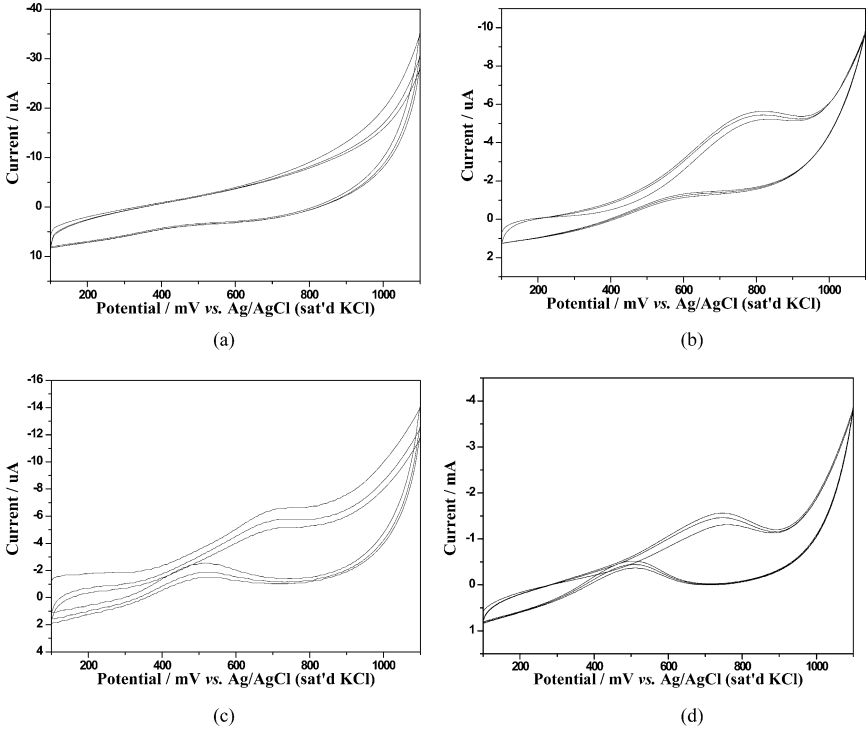

FIGURE 6 Electrocatalytic properties of PEDiTT/Pt nanocomposites. CV performed in 2 M CH_3OH/1M H_2SO_4. Doping time; 0 min (a), 10 min (b), 20 min (c), and 60 min, respectively.

methanol oxidation. This fact agrees with results of SEM images shown in Figure 5.

CONCLUDING REMARKS

Conducting polymers have potential applications such as secondary batteries, electrochromic devices, sensors and molecular electronic devices. However its actual applications are very limited because of poor solubility, processability and stability. To overcome these, we used PEDiTT that was soluble in some organic solvents and had relatively good stability and highly electrical conductivity. Introducing platinum particles into polymer matrix, PEDiTT/Pt nanocomposites were prepared to give them electrochemical catalytic character for methanol oxidation. K_2PtCl_6 was used as dopant to introduce platinum particles. PEDiTT/Pt nanocomposites were characterized by *in-situ* spectroelectrochemistry, SEM and EDAX. The electrochemical responses of composites mainly showed the matrix's characters. PEDiTT/Pt nanocomposites showed the catalytic behavior for methanol oxidation.

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