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Electrochemical Polymerization of Ruthenium(II) Complex and Application to Acetaminophen Analysis

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A novel ruthenium(II) complex, $[RuCl_2(DMSO)_2(PhenTPy)]$ has been synthesized by the condensation of $RuCl_2(DMSO)_4$ with (1-(1,10-phenanthrolinyl)-2,5-di(2-thienyl)-1*H*-pyrrole)[PhenTPy] in $CHCl_3$ solution. The $[RuCl_2(DMSO)_2(PhenTPy)]$ complex modified electrode was fabricated through the electropolymerization of the monomer in a 0.1 M tetrabutylammonium perchlorate (TBAP)/CH_2Cl_2 solution, to take advantage of the electronic communication between metal ion center by the conjugated backbone. The UV-visible spectroscopy (UV), mass spectrometry (MS), and cyclic voltammetry (CV) were employed to characterize the $[RuCl_2(DMSO)_2(PhenTPy)]$ complex and its polymer (poly-Ru(II)Phen complex). The poly-Ru(II)Phen complex modified electrode exhibited an electrocatalytic activity to the oxidation of acetaminophen and the catalytic property was used for the analysis of acetaminophen at the concentration range between 0.09 and 0.01 mM in a phosphate buffer solution (pH 7.0).

Key Words : Ruthenium (II) complex, Voltammetric, Electrocatalysis, Acetaminophen, Modified electrode, Conducting polymer complex

Introduction

Conjugated-metallopolymers, which metal sites are involved in the direct electronic communication with a conjugated organic backbone, have recently attracted significant attention.[1-3] A study for the electron transfer of these materials provide an insight into the long range electron-transfer mechanism and is likely to be important in the development of viable molecular electronic devices and electrocatalytic polymers.[4] Generally, redox sites of conjugated conductive polymers[5] are delocalized over a conjugated 'π' system. On the other hands, the redox polymers that are composed of metal ion in their structure are different from the conductive polymers. Although the redox polymers based on transition-metal complexes have potential advantages in applications such as electrocatalysis and electronic devices, the investigation for applications using conducting polymers with coordinating metal ions, however, has been an area of interest.[2,6,7] There could, therefore, be opportunities for the exploitation of transition-metal center in conducting polymers. The few examples which involve the direct electronic interaction between the conductive polymer and the metal ions have been demonstrated as novel electronics and chemical sensors,[8] outer-sphere electron-transfer agents,[9] and catalysts.[10]

Electrochemical polymerization, one of the methods to obtain conducting polymer surface, involves either reducing or oxidizing a monomer at a potential that gives an activated species, generally a radical anion or cation. These species undergo coupling to give dimers first, and subsequently longer oligomers and polymers.[11] It allows the formation of stable, ordered, and highly covered surfaces.[12] There are a few papers for the metal ion containing conducting polymers,[6,13,14] while diverse organic conductive polymers have been reported.[1-3] For examples, the transition metal complexes using 1,10-phenanthroline or its derivative as ligands are capable of selective binding DNA through intercalation. The oxidative electropolymerization of the transition metal complexes of 5-amino-1,10-phenanthroline (Aphen) was reported.[16] They were effectively used for catalyst or mediate for the electronanlysis of specific chemicals with enhanced sensitivity or selectivity.

Of the chemical analysis, the drug analysis plays important roles in drug quality control that impact on public health greatly. Therefore, a simple, sensitive, and accurate method to analyze active ingredients is essential. Acetaminophen is one of drugs called analgesics (pain relievers) and antipyretics (fever reducers). Several clinically important and electrochemically active species, such as ascorbic acid, acetaminophen, and dopamine are oxidized at the similar potential.[17] There are many reports for the voltammetric characteristics for acetaminophen and representatives of its known metabolites.[18,19] Many electrochemical method use chemically modified electrodes including C-60-modified electrode,[20] boron-doped diamond thin film electrode,[21] nanogold-modified indium tin oxide electrode.[22] To date, no comprehensive study of the electrochemically grown film containing ruthenium or other transition metal ions has been reported for the chemical analysis for acetaminophen.

In the present study, we have synthesized a novel complex $[RuCl_2(DMSO)_2(PhenTPy)]$ and its conjugated-metallopolymers, poly-Ru(II)Phen complex, and they were characterized using UV-Visible spectroscopy and voltammetric methods. The electrochemical behavior of the monomer and the poly-Ru(II)Phen complex modified electrodes were studied using cyclic voltammetry (CV). Applicability of

conjugated-metallopolymers modified on the electrode was examined for the determination of acetaminophen in a phosphate buffer solution (pH 7.0) with CV and chronoamperometry. The detection limit and hydrodynamic range was determined at the optimized analysis condition.

Experimental

Materials and Methods. $RuCl_3 \cdot 3H_2O$ and acetaminophen were purchased from Sigma-Aldrich Co (USA). Ttetrabutylammonium perchlorate (TBAP) was received from Fluka (USA), which purified and dried under vacuum at 10^{-5} Torr. Other chemicals were of extra-pure quality. Dimethyl sulphoxide (DMSO), methanol, dichloromethane, and chloroform were purchased from Sigma-Aldrich Co (USA) and used as received without further purification. All aqueous solutions were prepared in doubly distilled water, which was obtained from a Milli-Q water-purifying system (18 MΩ cm). An analytically pure sample of $[RuCl_2(DMSO)_4]$ was prepared by the previous method.[23]

Measurements. The NMR (^1H and ^{13}C) spectra were recorded in DMSO-d_6 and/or $CDCl_3$ solvents with a Bruker 300 MHz spectrometer using tetramethylsilane (TMS). UV-visible spectra were obtained using a Shimadzu PC-2401 double beam spectrophotometer. Emission spectra were recorded by a PerkinElmer LS50B spectrofluorometer at room temperature. Cyclic voltammograms (CVs) and chronoamperograms (CAs) were recorded using Potentiostat/Galvanostat, Kosentech model KST-P2 (S. Korea). Poly-$[RuC1_2(DMSO)_2(PhenTPy)]$ modified GCE with an electrode area of 0.07 cm^2, an Ag/AgCl (sat'd KCl), and a Pt wire were used as working, reference, and counter electrodes, respectively.

Synthesis of Materials.

Synthesis of 1-(1,10-Phenanthrolinyl)-2,5-di(2-thienyl)-1H-pyrrole, [PhenTPy]: A round-bottom flask equipped with a nitrogen inlet and a magnetic stirrer was charged with 1,4-di(2-thienyl)-1,4-butanedione (5 mM, 1.25 g), 5-amino-1,10-phenanthroline (2 mM, 0.40 g), *p*-toluenesulfonic acid (PTSA) (5.4 mM, 1.03 g) and toluene (15 mL). The result mixture was stirred and refluxed for 32 h under nitrogen. Evaporation of the toluene, followed by flash column chromatography (SiO_2, dichloromethane), afforded the desired compound as a brown solid (85%). mp 130 °C, ^1H-NMR (300 MHz; $CDCl_3$) 6.51 (m, 2H), 6.65 (m, 2H), 6.72 (s, 2H), 6.88 (dd, J = 5.1 Hz, 2H), 7.52 (m, 1H), 7.69 (m, 2H), 8.00 (s, 1H), 8.27 (d, J = 1.72 Hz, 1H), 9.17 (dd, J = 4.3 Hz, 1H), 9.28 (dd, J = 4.3 Hz, 1H); ^{13}C-NMR (300 MHz; $CDCl_3$) 102.87, 112.90, 116.88, 118.95, 121.52, 122.24, 127.60, 128.00, 128.58, 130.41, 132.28, 133.59, 136.43, 139.90, 149.86, 154.69. MS 409 (M^+, 100%), Exact MS Caled for $C_{24}H_{15}N_3S_2$: 409.0707. Found: 409.0620.

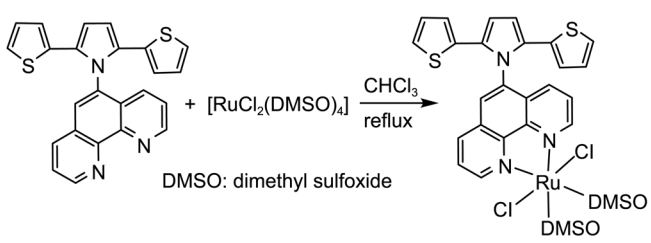
Synthesis of Ruthenium(II) Complex, $[RuC1_2(DMSO)_2(PhenTPy)]$: As shown in Scheme 1, a 84 mg, 0.206 mM reddish orange PhenTPy in a 5 mL $CHC1_3$ solution was added to 100 mg, 0.206 mM yellow $[RuC1_2(DMSO)_4]$ in a 10 mL $CHC1_3$ solution. The mixing solution was refluxed for 8 h under nitrogen atmosphere until it changed a dark brown color solution. After the solvent was removed, the precipitate was washed two times with diethyl ether. Then, the precipitate was recrystallized from DMSO. After filtration and drying a red precipitate (30%) was obtained; HRMS(FAB) *m/z* calc for ($C_{28}H_{27}C_{l2}N_3O_2RuS_4$) 736.9407; found 736.9390.

Electrode Modification. The GCE was polished with alumina slurry of 0.5 μm diameter on an emery paper to a mirror finish, and then rinsed with doubly distilled water. The solution was deoxygenated by purging N_2 for 15 min through the solution before the electropolymerization steps, and it was maintained oxygen-free by passing a stream of N_2 over the solution during the experiments. $[RuC1_2(DMSO)_2(PhenTPy)]$(Ru(II)PhenTPy) was separately polymerized onto the GCE in a 0.1 M TBAP/CH_2Cl_2 solution containing 1.0 mM monomer by the potential cycling five times method from +0.45 to +1.2V *vs*. Ag/AgCl) at a scan rate of 100 mV/s. Before the subsequent experiment, the poly-$[RuC1_2(DMSO)_2(PhenTPy)]$ (poly-Ru(II)PhenTPy) modified electrode was washed with CH_2Cl_2 to remove the excess monomer from the electrode surface, and stored until use.

Results and Discussion

Voltammetric Behavior of the $[RuC1_2(DMSO)_2(PhenTPy)]$ Complex Monomer. First, $RuC1_2(DMSO)_2$ complex was synthesized according to the previous method,[19] and recrystallized from a hot (DMSO)/acetone (1:6) solution. The $RuC1_2(DMSO)_2(PhenTPy)$ (Ru(II)PhenTPy) was prepared from $RuC1_2(DMSO)_2$ and PhenTPy by one step procedure, illustrated in Scheme 1. The poly-Ru(II)PhenTPy was characterized using UV-visible, and MS spectrometry. Figure 1 shows the UV-visible spectra of the complex in a CH_2Cl_2 solution. The absorption band was observed at about 330 nm (Figure 1, solid line), due to the metal-ligand charge transfer (MLCT) process occurring in the complex.[23] After the complex monomer was excited at this particular wavelength, an emission band was observed at about 400 nm.

The voltammetric behavior of the complex monomer was studied in a 0.1 M TBAP/CH_2Cl_2 solution (Figure 2, solid line). As shown, a well defined redox couple of (II/II') is observed at +0.13/+0.22 V, corresponding to the Ru^{III}/Ru^{II} reaction. Since DMSO is an ambidentate ligand known for linkage isomerization depending upon the O-bound or S-bound DMSO moieties, the ruthenium complex exhibits the oxidation peaks. The redox couple appeared at the lower potential indicates that the ruthenium ion has interacted to



Scheme 1. Synthesis of ruthenium (II) complex monomer.

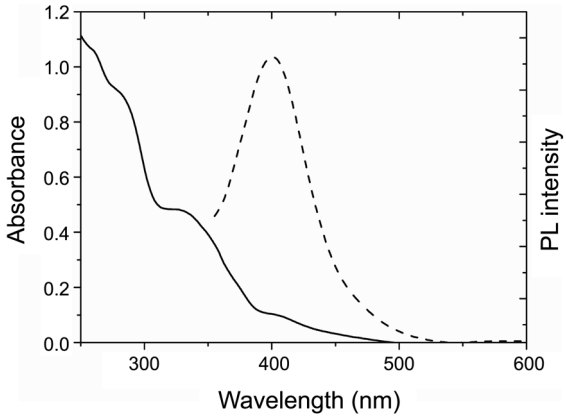


Figure 1. UV-visible spectra (solid line) and photoluminescence (dashed line) for $[RuCl_2(DMSO)_2(PhenTPy)]$ in CH_2Cl_2.

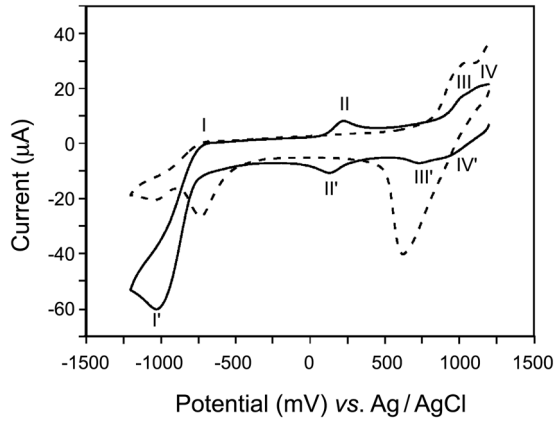


Figure 2. Cyclic voltammograms of a 1.0 mM $[RuCl_2(DMSO)_2$-(PhenTPy)] (solid line) and 1.0 mM ligand PhenTPy (dashed line) in 0.1 M TBAP/CH_2Cl_2 solution, scan rate of 100 mV/s.

the O-bound DMSO ligand.[24] For comparison, the CV of PhenTPy ligand was recorded as shown in Figure 2 (dotted line), where the redox peak is not observed at the position of (II/II') that is corresponded to the reaction of Ru^{III}/Ru^{II}. The redox peaks of ligand, however, clearly appeared at (I/I') and (III/III') that are related to the redox of phenanthroline moiety of PhenTPy ligand itself[25] and the oxidation of thiophen backbone to be polymerized.[26] In this case, reversibility of the redox peaks of Ru(II) complex was better than that of the mere ligand and we also observed "prewave" at the positive foot of the PhenTPy ligand-based reduction.[25] Additionally, the redox peak of (IV/IV') observed at +0.94/+1.12 V corresponded to the Ru^{III}/Ru^{IV} reaction.[27]

Electropolymerization of the $[RuC1_2(DMSO)_2(PhenTPy)]$ Complex. Figure 3(a) shows the consecutively scanned CVs recorded for 1.0 mM Ru(II)PhenTPy in a 0.1 M TBAP/CH_2Cl_2 solution. An anodic peak was observed at +0.72 V due to the monomer oxidation. As the number of potential scan increased, the oxidation peak current increased and new redox peaks were observed at +0.72/+0.80 V by the polymerization. Both cathodic and anodic peak currents were increased as the cycle number increased, indicating the formation and growth of the compelx polymer (poly-Ru(II)Phen) film.

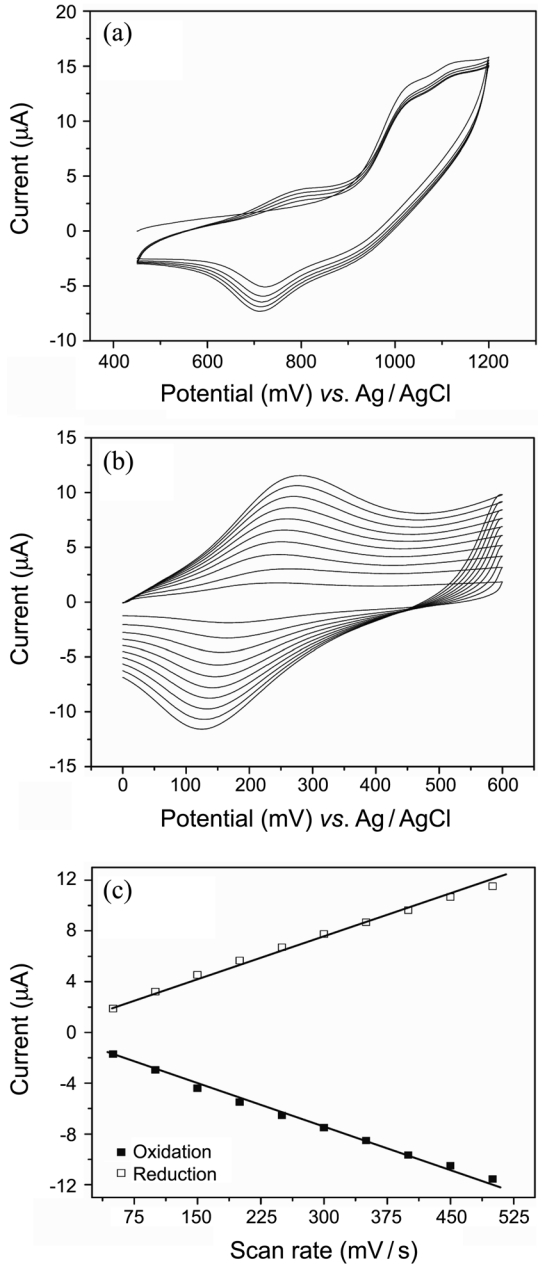


Figure 3. (a) Cyclic voltammograms of the electropolymerization of 1.0 mM $[RuCl_2(DMSO)_2(PhenTPy)]$ in 0.1 M TBAP/CH_2Cl_2 solution on GCE, scan rate of 100 mV/s. (b) CVs recorded of $[RuCl_2(DMSO)_2(PhenTPy)]$ modified electrode in 0.1 M TBAP/CH_2Cl_2 solution, at various scan rates: 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV/s. (c) Plots of the redox peak currents *vs.* scan rate.

Typical CVs of the poly-Ru(II)Phen modified electrode in a CH_2Cl_2 solution at the different scan rates are shown in Figure 3(b). It is clear that the potentials of the anodic and cathodic peaks hardly change with the scan rate, i.e., the peak potential is independent of the scan rate in the range between 50 and 500 mV/s. As shown in Figure 3(c), the peak current is directly proportional to the scan rate, indicating involvement of the surface adsorbed species. This suggests that the thickness of the film is smaller than the

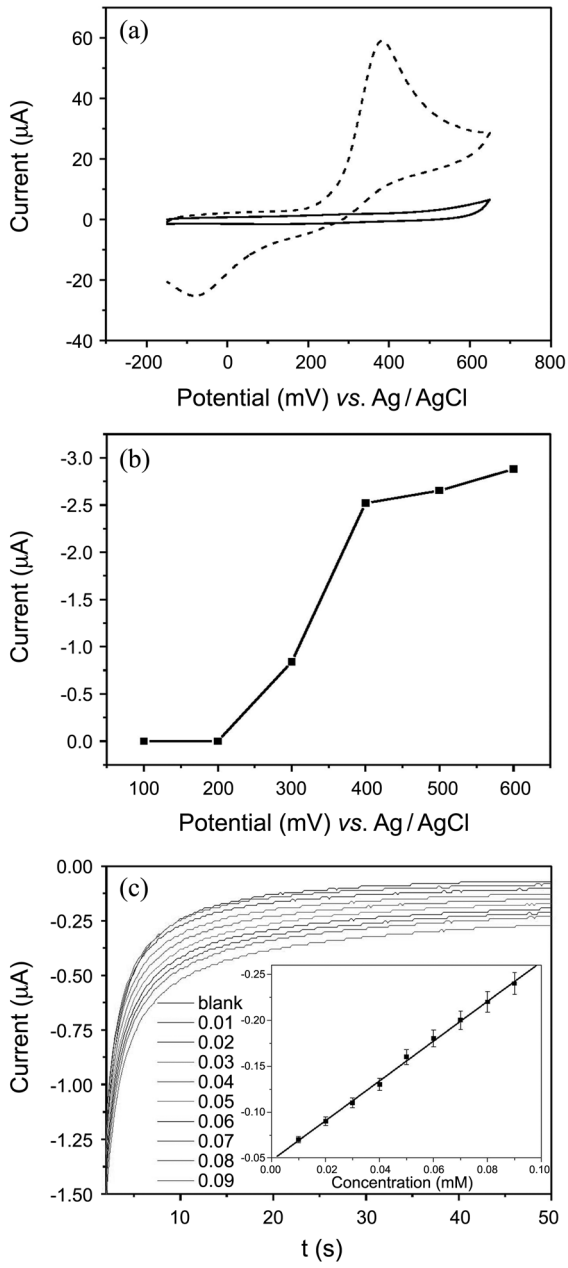


Figure 4. (a) CVs recorded for a bare poly-[$RuC1_2(DMSO)_2$-(PhenTPy)] modified electrode (solid line) and a poly-[$RuC1_2$-$(DMSO)_2$(PhenTPy)] modified in a PBS solution (pH 7.0) containing 1.0 mM acetaminophen (dashed line). (b) Effect of applied potential on the oxidation of acetaminophen at [$RuCl_2(DMSO)_2$-(PhenTPy)] modified electrode in a PBS solution containing 0.1 mM acetaminophen. (c) Chronoamperograms of various concentration of acetaminophen at poly-[$RuC1_2(DMSO)_2$(PhenTPy)] electrode in 0.1 M phosphate buffer solution (pH 7.0) at 0.4 V. Inset shows the corresponding calibration plot of acetaminophen.

diffusion layer thickness of counter anions on the CV time scale, through which the anions must diffuse in and out during the doping and de-doping processes. The oxidation peaks are shifted to the more positive potential at higher scan rates than 50 mV/s due to quasi- reversibility of the redox reaction. The cathodic and anodic peak currents of poly-Ru(II)Phen modified electrode were linear in the range 50 to 500 mV/s with a correlation coefficient of 0.9979 and 0.9983, respectively.

Electrocatalytic Oxidation of Acetaminophen on the Poly-[$RuC1_2(DMSO)_2$(PhenTPy)] Complex Modified Electrode. The analytical performance of the poly-Ru(II)-PhenTPy modified electrode was examined for acetaminophen detection with CV and CA. Figure 4(a) shows the CVs recorded for (a) a mere poly-PhenTpy modified electrode (solid line) and (b) a poly-Ru(II)PhenTPy modified electrode in a PBS solution (pH 7.0) containing 1.0 mM acetaminophen (dashed line). As shown in the figure, the anodic current of acetaminophen is significantly increased at the complex polymer modified electrode as compared to the mere polymer coated electrode. This is attributed to the catalytic oxidation of acetaminophen medicated by the Ru^{II}/Ru^{III} reaction of poly-Ru(II)PhenTPy. A tentative mechanism for this catalytic oxidation reaction is shown in Scheme 2. Figure 4(b) shows the effect of the applied potential on the amperometric response for acetaminophen with the poly-Ru(II)PhenTPy modified electrode in a PBS solution containing 0.1 mM acetaminophen. The current response increases as the applied potential increases from +100 mV to the more positive potential, and the maximum response is obtained at +400 mV. However, upon further increasing the applied potential over +600 mV, the current response do not show a significant increase. Thus, +400 mV was selected as the optimum applied potential for the acetaminophen analysis. At this oxidation potential, the oxidation of other compound such as dopamine, ascorbic acid, and uric acid did not interfere. Thus, the modified electrode was used for the selectivity determination of acetaminophen in the present of dopamine, ascorbic acid, and uric acid. The amperometric method with the complex modified electrode was exploited for simple determining of the concentration of acetaminophen. Figure 4(c) shows the CAs obtained for various concentrations of acetaminophen in a phosphate buffer solution (pH 7.0). The peak current for acetaminophen oxidation increases linearly with the increases in the concentration of acetaminophen. A linear calibration plot (inset Figure 4(c)) was obtained for the acetaminophen in the concentration range between 0.01 and 0.09 mM at 40 sec. The detection limit of acetaminophen was determined to be 7.9×10^{-6} M with a correlation coefficient $R^2 = 0.998$ (n = 9). The present work was compared to the results that were obtained from other group, where the detection limit was 3.1×10^{-6} M. The result obtained by our method is comparable with the one from the other group.[28]

Conclusions

The complex monomer, $RuC1_2(DMSO)_2$(PhenTPy), was successfully synthesized and characterized. When the complex monomer was excited at about 330 nm, an emission band at about 400 nm was observed due to the metal-ligand charge transfer (MLCT) process occurring in the complex. The polymer complex, Poly-[$RuC1_2(DMSO)_2$(PhenTPy)], has been prepared via electropolymerization of the complex

monomer in a 0.1 M TBAP/CH_2Cl_2 solution. The polymer modified electrode was showed to be electrochemically active which was due to the electron transfer of Ru^{II}/Ru^{III} reaction. In addition, the modified electrode exhibited electrocatlytic activity towards the oxidation of acetaminophen in a phosphate buffer solution (pH 7.0), which was examined for acetaminophen detection. Using amperometry showed the detection limit of 7.9×10^{-6} M (n = 9) for the acetaminophen determination.

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References

1. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1998.
2. Park, S.-M. Electrochemistry of π-conjugated polymer, in: Nalwa, H. S., Ed.; *Handbook of Organic Conductive Molecules and Polymers*; 3, Wiley: Chichester, 1997; 429.
3. Pittman, C. U.; Carraher, C. E.; Reynolds, J. R. *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, **1987**, *10*, 541.
4. Cameron, C. G.; Pickup, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 7710.
5. Lyons, M. E. G. In *Electroactive Polymer Electrochemistry, Part 1:Fundamentals*; Lyons, M. E. G., Ed.; Plenum Press: New York, 1994; 1-235.
6. (a) Miller, J. S. *Adv. Mater.* **1993**, *5*, 587. (b) Miller, J. S. *Adv. Mater*. **1993**, *5*, 671.
7. Lee, J.-W.; Park, D.-S.; Park, S.-M.; Shim, Y.-B. *J. Electrochem. Soc*. **1992**, *139*, 3507.
8. Rahman, M. A.; Kumar, P.; Park, D.-S.; Shim, Y.-B. *Sensors* **2008**, 118.
9. Sahami, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 2511.
10. (a) Cameron, C. G.; Pickup, P. G. *Chem. Commun.* **1997**, 303. (b) Wolf, M. O.; Wrighton, M. S. *Chem. Mater.* **1994**, *6*, 1526. (c) Zhu, S. S.; Swager, T. M. *Adv. Mater.* **1996**, *8*, 497.
11. Wolf, M. O. *Adv. Mater*. **2001**, *13*, 545.
12. Garcia, C.; Villagra, D.; Caruso, F.; Rossi, M.; Matsuhiro, B.; Mendoza, L.; Aguirre, M. J.; Isaacs, M. *Inorg. Chem. Commun.* **2009**, *12*, 392.
13. Rahman, M. A.; Lee, K.-S.; Park, D.-S.; Won, M.-S.; Shim, Y.-B. *Biosens. Bioelectron*. **2008**, *23*, 857.
14. Koh, W. C. A.; Son, J. I.; Choe, E. S.; Shim, Y.-B. *Anal. Chem*. **2010**, *82*, 10075.
15. Wang, J.; Cai, X.; Rivas, G.; Shiraishi, H.; Farias, P. A. M.; Dontha, N. *Anal. Chem*. **1996**, *68*, 2629.
16. Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1283.
17. Eddy, S.; Warriner, K.; Christie, I.; Ashworth, D.; Purkiss, C.; Vadgama, P. *Biosens. Bioelectron*. **1995**, *10*, 831.
18. Miner, D. J.; Rice, J. R.; Riggin, R. M. *Anal. Chem.* **1981**, *53*, 2258.
19. Boopathi, M.; Won, M.-S.; Shim, Y.-B. *Anal. Chim. Acta*. **2004**, *512*, 191.
20. Goyal, R. N.; Singh, S. P. *Electrochim. Acta.* **2006**, *51*, 3008.
21. Wangfuengkanagul, N.; Chailapakul, O. *J. Pharm. Biomed. Anal.* **2002**, *28*, 841.
22. Rajendra, N. G.; Vinod, K. G.; Munetaka, O.; Neeta, B. *Electrochem. Commun.* **2005**, *7*, 803.
23. Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
24. Kojima, T.; Amano, T.; Ishii, Y.; Ohba, M.; Okaue, Y.; Matsuda, Y. *Inorg. Chem.* **1998**, *37*, 4076.
25. Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, R. J. *Inorg. Chem.* **1983**, *22*, 1283.
26. Hwang, J. Y.; Son, J. I.; Shim, Y.-B. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1286.
27. Eskelinen, E.; Costa, P. D.; Haukka, M. *J. Electroanal. Chem*. **2005**, *579*, 257.
28. González-Sánchez, M. I.; Rubio-Retama, J.; López-Cabarcos, E.; Valero, E. *Biosens. Bioelectron*. **2011**, *26*, 1883.