

금 처리를 통한 PEDOT 마이크로튜브 전극의 과산화수소 검출 특성 향상

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Enhanced Sensitivity of PEDOT Microtubule Electrode to Hydrogen Peroxide by Treatment with Gold

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초록: 전류 감응형 바이오센서에 응용하기 위해 전도성 고분자 마이크로튜브 어레이를 제작하였다. Poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonic acid)(PEDOT/PSS) composite을 전도성 접착제로 하여 템플릿을 전극에 고정된 후 EDOT을 전기화학적으로 중합하였다. 마이크로튜브 어레이는 자체의 넓은 표면적으로 인해 감도 높은 바이오센서로 응용될 수 있으나, 주요 표적물질 중의 하나인 과산화수소에 대한 전기화학적 반응이 느렸다. 과산화수소 산화에 대한 감도를 향상시키기 위해 어레이 전극에 금을 도포하였다. 증착법과 전기화학적 석출법 두 가지 방법을 시도하여 금을 처리하였는데, 이렇게 처리한 전극은 모두 과산화수소에 대한 반응이 크게 향상되었다. 따라서 전도성 고분자 마이크로튜브 어레이에 금을 도포함으로써 과산화수소를 표적물질로 하는 감도 높은 바이오센서 제작이 가능할 것으로 기대된다.

Abstract: An array structure of conducting polymer microtubule was fabricated for an amperometric biosensor. 3,4-Ethylenedioxythiophene (EDOT) was electropolymerized in the microporous template membrane with poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonic acid) (PEDOT/PSS) composite as a binder. The array structure can provide enhanced current collecting capability due to large active surface area compared to the macroscopic area of the electrode itself. For a biosensor application, the array electrode was tested for H₂O₂ detection and showed very sluggish electrochemical response to H₂O₂. To enhance the detection efficiency to the oxidation of H₂O₂, gold was treated on the electrode by two different approaches: sputtering and electrochemical deposition. Gold treatment with either method greatly enhanced the sensitivity of the electrode to H₂O₂. So, conducting polymer microtubule array with gold treatment was expected to be a sensitive amperometric biosensor system based on the detection of H₂O₂.

Keywords: conducting polymer, EDOT, microtubule, gold treatment, hydrogen peroxide.

Introduction

Since Martin *et al.* proposed the scheme of preparing conducting polymer microtubule by template synthesis method,¹ it was widely applied to such areas as microfiltration, sensor array, delivery system, and so on.²⁻⁶ Among these applications, the sensor application was noticeable because of the advantages from its excellent collective properties and signal trans-

ducing capabilities. Some researchers made use of conducting polymer microtubule for preparing enzyme containing biosensor. Martin *et al.* constructed spectrophotometric glucose biosensor and electrochemical nitrate sensor by immobilizing corresponding enzyme in the conducting polymer microtubule.^{7,8} Nolte *et al.* used these microtubules to immobilize glucose oxidase and to probe the enzyme directly.⁹

Hydrogen peroxide is a molecule of interest to many fields such as clinical, food, pharmaceutical, and environmental analysis, and therefore numerous reports have appeared on analytical methods for its determination.¹⁰ Among them,

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electrochemical methods based on the measurement of current derived from H_2O_2 oxidation or reduction play a predominant role, especially in the topic of biosensors, because H_2O_2 is produced by the action of enzymes upon reaction with biosubstrates.¹¹ However, the oxidation of hydrogen peroxide at carbon electrodes requires large overpotential to take place at a rate sufficient for analytical applications. Therefore, most of the enzyme electrodes employ metal surfaces, which can decrease the overpotential significantly, for the electrochemical oxidation of hydrogen peroxide.^{12,13} By immobilizing glucose oxidase in polymers deposited on platinum or other catalytic electrode we can develop a glucose sensor with high sensitivity according to the catalytic effect of metals on the oxidation of H_2O_2 , the product of the action of the glucose oxidase. Nevertheless, in most of these electrode materials, the electrochemical oxidation of hydrogen peroxide is limited to the catalytic surfaces. In recent years, the metallic microparticles dispersed in conducting polymer films have been recognized to have potential applications in electrocatalytic fields, and in such a way the real catalytic surface area has been increased.¹⁴⁻¹⁶

In this study, conducting polymer microtubule electrode was fabricated by electrochemical template synthesis of poly(1,4-ethylenedioxythiophene) (PEDOT). This acted as a possible housing cabinet for the enzyme and also increased the active surface of the electrode. To improve the detection sensitivity of the conducting polymer electrode to H_2O_2 , the enzymatic product of glucose, gold was treated as an electrocatalytic agent on the conducting polymer microtubule. Two strategies for gold treatment were tried: sputtering of gold onto a template before making polymeric microtubules and electrochemical gold deposition after making polymeric microtubules in a template. Characterization of electrode was performed with electron microscope and the electrochemical responses to H_2O_2 before and after gold treatment were compared.

Experimental

Materials & Equipments. EDOT was obtained from Aldrich and used as received. Aqueous dispersion of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonic acid) (PEDOT/PSS) was purchased from Bayer(Baytron P 4083). Poly(vinyl alcohol) (PVA) was gratefully donated by OCI(Korea). LiClO_4 from Aldrich were used as received. Inner diameters of 1.2 μm polycarbonate membranes were purchased from Millipore (Isopore). 30%(w/w) hydrogen peroxide solution was purchased from Junsei Chemical Co., Ltd.. Phosphate buffered

saline (PBS) solution consisted of 0.1 M Na_2HPO_4 , 0.1 M NaH_2PO_4 and 0.15 M NaCl and was adjusted to pH 7.4 with 3 M NaOH. The conducting ITO glass (Samsung Corning, Korea) was immersed in acetone for one day and then rinsed with UP grade water immediately before use.

Spin coating was performed with an EC101DT photo resist spinner (Headway Research, Inc., USA) equipped with a rotary vacuum pump. Gold sputtering on a 1.2 μm membrane was performed with Emitech ion sputter (model K550). The electrochemical measurements were performed using a BAS 100B (BAS, USA) driven with a BAS 100W software. All electrochemical potentials in this study were referred to a Ag/AgCl(Sat'd KCl) reference electrode. Morphologies of the structures were examined using a Jeol field emission scanning electron microscope (JSM 6700F).

Preparation of Conducting Polymer Microtubule. The preparing procedure for the microstructure was previously described.¹⁷ A brief review is described as follows. As a substrate electrode, a piece of ITO electrode was chosen. A homemade conducting polymer paste was spin coated onto an ITO glass sample. PVA and PEDOT/PSS were used to prepare the conducting paste composite. A piece of membrane having 1.2 μm pores was fixed on the ITO glass before the composite dried out. Then, the electrochemical polymerization of EDOT was carried out by applying an electrochemical potential directly to the ITO electrode which is immersed in the monomer solution. The monomer solution contained 0.1 M EDOT in acetonitrile with 0.1 M LiClO_4 as a supporting electrolyte. The polymerization was performed by cycling the applied potential ranging from 0.3 to 1.2 V. The scanning electron microscope (SEM) images of polymer microstructure were obtained after tubule formation procedure. The polycarbonate (PC) membrane was removed by dipping it in methylene chloride solution for 10 min. Then, the polymer structure was sputtered with a thin film of platinum prior to imaging.

Gold Treatment. Gold was treated on the membrane or microtubule to improve the sensitivity by adopting one of the following two methods. (1) Pre-treatment: Gold was sputtered on PC membrane having 1.2 μm pores before attaching it onto ITO electrode by ion sputter (Emitech, K550) with the current of 10 mA for 1.5 min. (2) Post-treatment: Gold was electrochemically deposited on tubules formed in 1.2 μm membrane. The electroplating solution was 1 mM HAuCl_4 in 0.5 M H_2SO_4 aqueous solution and depositing condition was varied. After depositing it, SEM and EDAX were used to confirm the deposition.

Electrochemical Measurements. Preparation of the Microtubule: Electrochemical polymerization was performed by using a one-compartment, three-electrode electrochemical cell. The cell consisted of a Teflon tube with an O-ring joint on one end. The working electrode was a membrane-attached ITO glass electrode and was confined with the O-ring (4 mm diameter). The auxiliary electrode was a Pt plate and the reference electrode was a Ag/AgCl (Sat'd KCl) electrode.

Electrochemical Behavior of Hydrogen Peroxide: Measurements were carried out in a PBS solution (pH 7.4). Steady-state current measurements at fixed potentials (+0.70 V) were made in a 10 mL electrochemical cell equipped with a Pt plate counter electrode and a Ag/AgCl reference electrode in PBS solution. The modified electrodes were polarized 30 min to attain a stationary background current. The H_2O_2 concentration increased by 0.1 mM step. Amperometric experiments were performed at room temperature ($20 \pm 2^\circ\text{C}$) under forced-convection (stirring) condition.

Results and Discussion

Preparation of Microtubule. Figure 1 is a cyclic voltammogram for the polymerization of EDOT in acetonitrile.¹⁷ A potential > 0.3 V was applied to keep the composite glue in the conducting state. At 1.05 V the initiation of monomer oxidation was found and a large current loop was clearly seen in the first scan. This polymerization potential, however, dropped slightly and the loop reduced in size with each successive scan. It can be explained with the greater ease of EDOT oxidation on the deposited polymer than on the conducting composite.

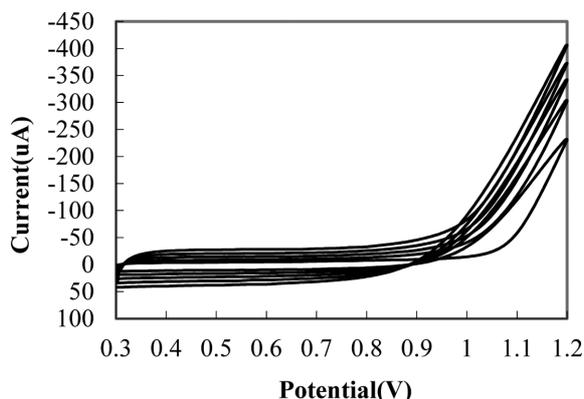


Figure 1. Cyclic voltammogram of EDOT for the electrochemical polymerization in the $1.2 \mu\text{m}$ pores of the template membrane. The solution is 0.1 M EDOT in acetonitrile containing 0.1 M LiClO_4 . Potential scan from 0.3 to 1.2 V was performed 5 cycles vs. Ag/AgCl (Sat'd KCl). Scan rate is 50 mV/s.

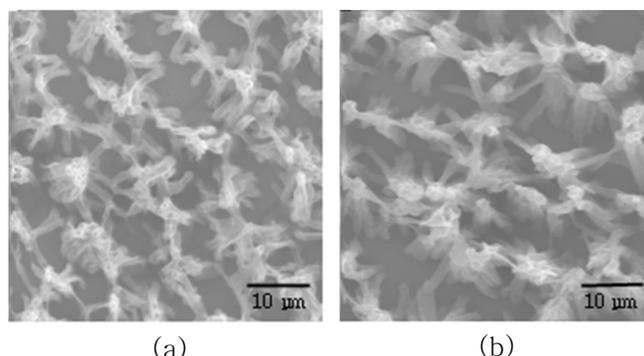


Figure 2. SEM images of tubules prepared with different numbers of potential cycling. (a) 5 cycles; (b) 15 cycles. The template membrane was removed.

The current curve was crossed on the reverse scan in each step, which is typical for the deposition of conducting polymer films with nucleation. The increase of capacitive response below the polymerization potential indicates that an ACN-insoluble polymer film was formed on the electrode as a result of electrochemical polymerization and the surface area was getting larger.

Figure 2 shows scanning electron micrograph of a part of the polymeric PEDOT tubules formed in the membrane cavity. The SEM image was taken after removing the PC template membrane by dipping the whole electrode in methylene chloride for the observation of the tubule structure only. The tubule formation was monitored by varying the number of polymerization cycle. When 5 cycles were done, the tubules were very weak and leaned upon each other near the surface of ITO after template membrane was removed. As the cycle number increases to 15, they became stiff to stand alone firmly on the surface of ITO electrode. This is because the thickness of the tubule wall increases as the polymerization proceeded with the potential cycling.

The underlying conducting composite layer acted as a glue to stick the membrane firmly onto the ITO electrode. It also offered the electrical contact between the monomer solution and the ITO electrode, making the tubule formation and growth possible. The length and diameter of the tubule were approximately equal to the thickness (ca. $15 \mu\text{m}$) and pore diameter of the membrane and the top of the tubule was open and circular.¹⁷

Preparation of Gold-deposited Electrode. To enhance the sensitivity of the electrode to H_2O_2 , gold was applied. For the pre-treatment, gold was sputtered onto the rough side of PC membrane before electrochemical formation of the tubules

with an emission current of 10 mA for 1.5 min. Figure 3(a) is SEM images of rough side surface of gold sputtered membrane with 1.2 μm pores. A fairly clear image was taken even without additional metal treatment for getting it, which represents the existence of considerable amount of conductivity at the surface. Elemental analysis data in Figure 3(c) says gold actually exists on the surface. It was also found from the SEM image and elemental analysis obtained in the opposite side that the sputtered gold didn't get there (Figure 3(b)).

As a post-treatment, deposition of gold particles onto the surface of microtubules from aqueous gold chloride solution was performed after making polymeric PEDOT microtubules from naive PC membrane. Figure 4 is the cyclic voltam-

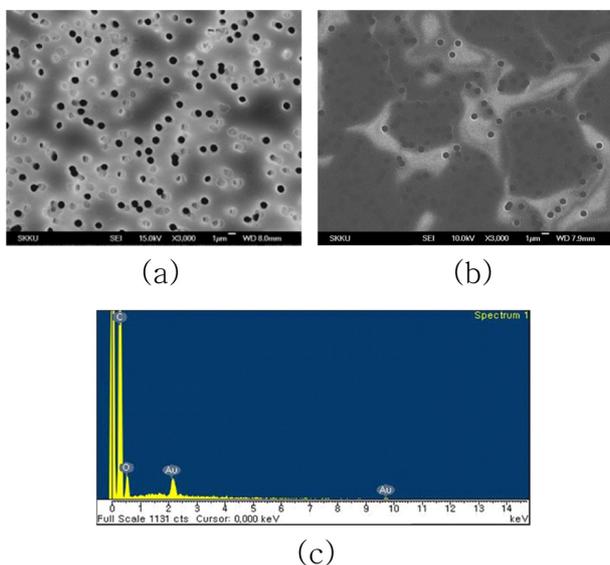


Figure 3. SEM images (a, b); EDAX data (c) of PC membrane (1.2 μm pore size) sputtered with gold. (a), (c) from gold-sputtered surface and (b) from the opposite side.

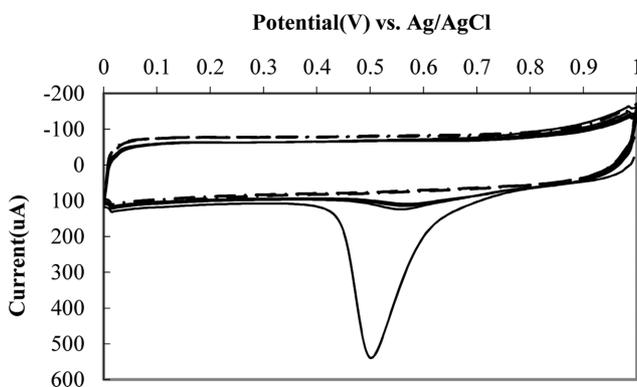


Figure 4. Cyclic voltammograms of microtubule array electrode in 0.5 M H_2SO_4 with (line) and without (dashed) 1 mM HAuCl_4 . Scan rate = 50 mVs^{-1} .

mogram of depositing gold from 1 mM HAuCl_4 aqueous solution in 0.5 M sulfuric acid.

The sweep was cycled 5 times from 1.0 to 0.0 V vs. Ag/AgCl electrode. At 0.8 V the reduction was initiated and at 0.5 V the bell shaped peak appeared. Because the diameter of the microtubule is less than 1.2 μm , the electrochemical reaction in this tubule is analogous to that of the thin layer for irreversible reactions, resulting in a skewed bell-shaped peak.¹⁸ The peak current decreased sharply in the 2nd cycle. This indicates that HAuCl_4 solution in microtubule was fully reduced to gold particles and supplies from the bulk solution was too sluggish to recover the magnitude of the first peak in this time scale. The peak, however, is still symmetrical to its axis, indicating the reduction takes place mainly inside the tubule instead of membrane surface. This implies the tubule structure was formed only inside of the membrane pores. Figure 5 is the SEM images of as-prepared microtubule electrode in the PC membrane. We can see that gold particle was deposited inside the pore and also at its mouth in some cases. It is likely that this difference in deposition area came from the different tubule length; that is, gold particles were deposited in the mouth of the pores in which the tubules grew to that height. The elemental analysis data showed that the small particles in the pores are gold.

Based on the above cyclic voltammetric experiments, chronoamperometry was also tried to deposit gold inside the micro-

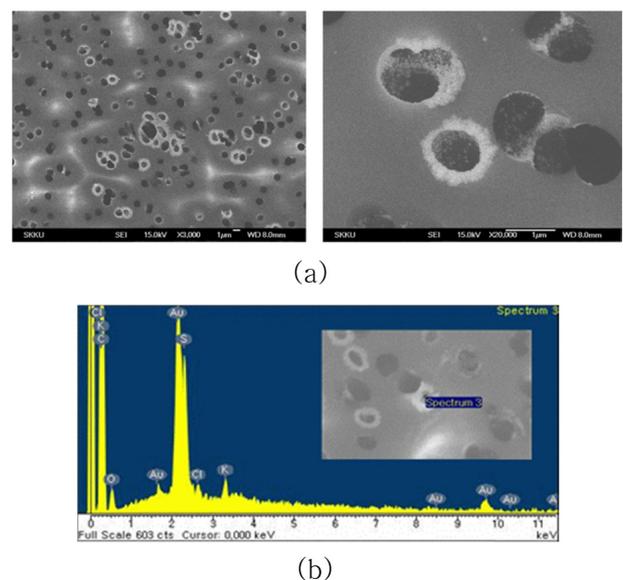


Figure 5. SEM images (a; $\times 3000$, $\times 20000$); EDAX data (b) of the microtubule electrode array after electrochemical deposition of HAuCl_4 solution by CV (scan rate = 50 mVs^{-1}).

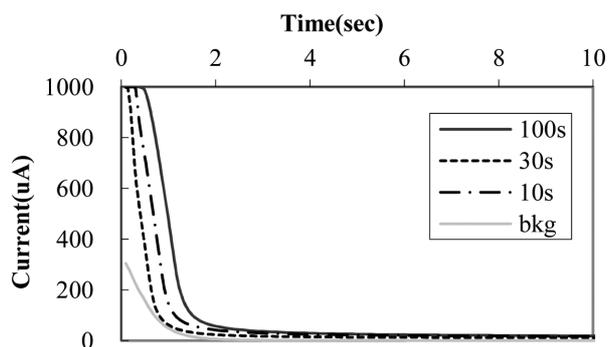


Figure 6. Chronoamperograms of microtubule array electrode for gold deposition. Duration time = 10, 30, 100 sec in 1 mM $\text{HAuCl}_4/0.5 \text{ M H}_2\text{SO}_4$ and 100 sec in 0.5 M H_2SO_4 (background). Potential step = 0.9 V to 0.2 V vs. Ag/AgCl, counter = Pt plate.

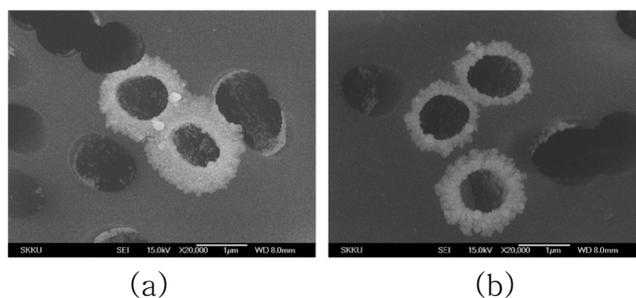


Figure 7. SEM images ($\times 20000$) of the microtubule electrode array after electrochemical deposition of HAuCl_4 solution by chronoamperometry (duration time = 10 sec (a); 100 sec (b)).

tubule. Figure 6 is the chronoamperograms of the microtubule electrode in HAuCl_4 solution. After applying potential step from 0.9 to 0.2 V, there showed large current both in background H_2SO_4 solution and in 1 mM $\text{HAuCl}_4/\text{H}_2\text{SO}_4$ solution within 2 sec. Whilst the current in H_2SO_4 solution was just about 300 μA , that in 1 mM HAuCl_4 solution was above 1000 μA in the initial step. This discrepancy in current would be attributed to the reduction of AuCl_4^- ion in solution. The gap was diminished after 2 sec but was maintained during the monitoring time.

The images of the surface were obtained and displayed in Figure 7. The images from different duration time gave similar images, which agrees with the chronoamperometric data where most part of the gold deposition took place within 2 sec after applying potential step. We can just see that the particles prepared for 100 sec are slightly thicker and larger than those prepared for 10 sec. Anyway, the overall images are not so different from those obtained by cyclic voltammetry.

Responses to Hydrogen Peroxide. The response characteristics of those electrodes to hydrogen peroxide was exam-

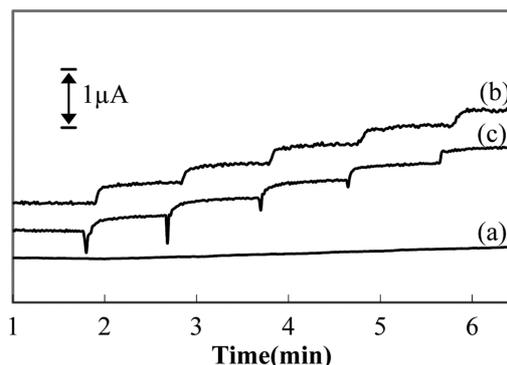


Figure 8. Comparison of responses to H_2O_2 between naive (a); gold-treated (b,c) tubule electrode. (b) is the electrode from gold-sputtered membrane; (c) is the electrochemically gold-deposited electrode. H_2O_2 was increased gradually from 0 to 0.5 mM by 0.1 mM step. ($E=0.7 \text{ V vs. Ag/AgCl}$, counter = Pt plate).

ined. After the background current was stabilized at 110 sec, the concentration of H_2O_2 was changed to 0.1 mM by adding 1 M H_2O_2 stock solution and increased gradually to 0.5 mM. Figure 8(a) is the chronoamperogram of the naive tubule electrode in the PBS solution. There showed nearly no change in current. A very slight change in current was observed even after 0.5 mM H_2O_2 was added, which is usually observed in the system adopting conducting polymer microtubule electrode. This is because the overvoltage necessary for the oxidation of H_2O_2 on the conducting polymer is rather high.¹⁹

Figure 8(b) is the chronoamperogram of the microtubule array electrode prepared from gold sputtered PC membrane. The electrode showed about 9 fold larger response compared with the one made from naive PC membrane when 0.5 mM H_2O_2 was added. This observation means that gold deposition catalyzes the oxidation of H_2O_2 and that the conducting polymer tubule is porous in its structure allowing the electro-active H_2O_2 molecule to permeate the polymer and to be oxidized at the underlying gold layer.

Figure 8(c) is the amperometric response of the microtubule electrode paved with gold by electrochemical method as described above. There also showed a significant increase of current like Figure 8(b). Gold on the surface of microtubule played a role in this case. So, we can see that gold treatment without regard to the procedure changed a very sluggish response of conducting polymer microtubule electrode to a much faster and sensitive one.

Conclusions

Conducting polymer microtubule array electrode was pre-

pared by electrochemical polymerization of EDOT with template synthesis method. The home-made conducting composite (PVA and PEDOT/PSS) played roles in attaching the template membrane to the supporting ITO electrode and electrically connecting the monomer solution and the electrode. Gold was treated to enhance the response of this microtubule electrode to hydrogen peroxide. One approach was to sputter gold on the template membrane before tubule formation. The other approach was to electrochemically deposit gold after tubule formation. SEM and EDAX data demonstrated the deposition of gold on the membrane and the microtubule. The conducting polymer microtubule electrode introducing one of two approaches showed very sensitive response to hydrogen peroxide.

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References

1. Z. Cai and C. R. Martin, *J. Am. Chem. Soc.*, **111**, 4138 (1989).
2. K. Sukchol, S. Thongyai, P. Praserttham, and G. A. Sotzing, *Synth. Met.*, **179**, 10 (2013).
3. L. Xia, Z. Wei, and M. Wan, *J. Colloid Interf. Sci.*, **341**, 1 (2011).
4. Rajesh, T. Ahuja, and D. Kumar, *Sensor Actuat. B- Chem.*, **136**, 275 (2009).
5. M. Atobe, N. Yoshida, K. Sakamoto, K. Sugino, and T. Fuchigami, *Electrochim. Acta*, **87**, 409 (2013).
6. U. Lange, N. V. Roznyatovskaya, and V. M. Mirsky, *Anal. Chim. Acta*, **614**, 1 (2008).
7. R. V. Parthasarathy and C. R. Martin, *Nature*, **369**, 298 (1994).
8. L. M. Moretto, P. Ugo, M. Zanata, P. Guerriero, and C. R. Martin, *Anal. Chem.*, **70**, 2163 (1998).
9. A. Kros, S. W. F. M. Van Hövell, N. A. J. M. Sommerdijk, and R. J. M. Nolte, *Adv. Mater.*, **13**, 1555 (2001).
10. Y. Nakabayashi and H. Yoshikawa, *Anal. Sci.*, **16**, 609 (2000).
11. J. Wang, *J. Pharmaceut. Biomed. Anal.*, **19**, 47 (1999).
12. M. Mathew and N. Sandhyarani, *Biosens. Bioelectron.*, **28**, 210 (2011).
13. C. X. Guo and C. M. Li, *Phys. Chem. Chem. Phys.*, **12**, 12153 (2010).
14. H. Zhou, H. Chen, S. Luo, J. Chen, W. Wei, and Y. Kuang, *Biosens. Bioelectron.*, **20**, 1305 (2005).
15. B. Kim, M. S. Cho, Y. S. Kim, Y. Son, and Y. Lee, *Synth. Met.*, **153**, 149 (2005).
16. A. Balamurugan, K.-C. Ho, S.-M. Chen, and T.-Y. Huang, *Colloid Surface A*, **362**, 1 (2010).
17. J. Park, J. Kim, and Y. Son, *Synth. Met.*, **156**, 714 (2006).
18. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2000.
19. N. F. Atta, A. Galal, and F. Khalifa, *Appl. Surf. Sci.*, **253**, 4273 (2007).