Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Fabrication of Carboxylated Conducting Polymer/CNTs Composites Thin Films for Immunosensor Application

P. Netsuwan [a], S. Sriwichai [b], S. Phanichphant [b], A. Baba [c], K. Shinbo [c], K. Kato [c] & F. Kaneko [c]

[a] Nanoscience and Nanotechnology Program, The Graduate School, Chiang Mai University, Chiang Mai, Thailand

[b] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

[c] Center for Transdisciplinary Research and Graduate School of Science and Technology, Niigata University, Niigata, Japan

Published online: 11 Sep 2013.

To cite this article: P. Netsuwan, S. Sriwichai, S. Phanichphant, A. Baba, K. Shinbo, K. Kato & F. Kaneko (2013) Fabrication of Carboxylated Conducting Polymer/CNTs Composites Thin Films for Immunosensor Application, Molecular Crystals and Liquid Crystals, 580:1, 7-14, DOI: 10.1080/15421406.2013.803890

To link to this article: http://dx.doi.org/10.1080/15421406.2013.803890

Mol. Cryst. Liq. Cryst., Vol. 580: pp. 7–14, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.803890

Taylor & Francis
Taylor & Francis Group

Fabrication of Carboxylated Conducting Polymer/CNTs Composites Thin Films for Immunosensor Application

P. NETSUWAN,[1] S. SRIWICHAI,[2,*] S. PHANICHPHANT,[2]
A. BABA,[3] K. SHINBO, K. KATO,[3] AND F. KANEKO[3]

[1]Nanoscience and Nanotechnology Program, The Graduate School, Chiang Mai University, Chiang Mai, Thailand
[2]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand
[3]Center for Transdisciplinary Research and Graduate School of Science and Technology, Niigata University, Niigata, Japan

Electropolymerization of carboxylated conducting polymer/carbon nanotubes (CNTs) composites thin films has been studied by in situ electrochemical-surface plasmon resonance (EC-SPR) spectroscopy. Two derivatives of benzothiophene, thianaphthene-2-carboxylic acid and benzothiophene-2-propionic acid, composited with CNTs were electropolymerized in an acetonitrile with the potential range between 0 and 1.2 V at scan rate of 20 mV/s. The obtained films were characterized by in situ EC-SPR spectroscopy, UV-vis absorption spectroscopy, and atomic force microscopy. It was found that CNTs can improve properties of polymer/CNT composites films. Moreover, the obtained thianaphthene-2-carboxylic acid film can be further used for construction of immunosensor for detection of human IgG.

Keywords Benzothiophene-2-propionic acid; carbon nanotubes; composite; electrochemical-surface plasmon resonance; electropolymerization; thianaphthene-2-carboxylic acid

1. Introduction

Conducting polymers consist of π-bond in polymer backbone which led them to have unusual electrochemical, electrical and optical properties [1–2]. There have been many studies about the improvement of response property and sensitivity of conducting polymer based biosensors which conducting polymers were employed to transfer electrons between biomolecules and electrode [3–5]. Carbon nanotubes (CNTs) have the unique behavior in electrical, chemical, mechanical and structural properties [6]. CNTs can enhance the electrochemical reactivity of biomolecules and can promote the electron transfer of oxidation-reduction in electropolymerization and increased the amount of polymer loading on the large effective surface area of CNTs [7–9]. The well-known technique, in situ

*Address correspondence to Saengrawee Sriwichai, Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: +66 85 106 2185; Fax: +6653 892277. E-mail: saengrawee.s@cmu.ac.th

electrochemical-surface plasmon resonance (EC-SPR) spectroscopy, has been used for investigation the optical and electrical properties of conducting polymer films at solid/liquid interfaces. The technique was also employed to monitor the kinetic of electropolymerization and immobilization biomolecules on the conducting thin films [10–13].

In this work, the composites of two derivatives of benzothiophene, thianaphthene-2-carboxylic acid and benzothiophene-2-propionic acid, with CNTs were prepared. The kinetic during electropolymerization of these composites on gold-coated high refractive index glass substrate, which used as working electrode, was studied by in situ EC-SPR spectroscopy. The UV-vis absorption spectra were recorded before (composite solution) and after electropolymerization (composite thin films). The surface morphology of the films was obtained from AFM. Moreover, the thianaphthene-2-carboxylic acid film was examined for label-free detection of human immunoglobulin G (IgG).

2. Experimental Details

2.1 Materials

All chemicals were purchased from Sigma-Aldrich and used as received. A single-walled carbon nanotubes (SWNTs) was obtained from Microphase Co. The composite solution of monomer/SWNTs was solubilized by the following method. The mixture of 10 mM of thianaphthene-2-carboxylic acid or benzothiophene-2-propionic acid and 0.25 mg/mL SWNTs was obtained by mixing with 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in anhydrous acetonitrile and then sonicated for 24 h. The aggregated SWNTs was removed by centrifugation at 5000 rpm for 30 min. The supernatant was finally collected and characterized by UV-vis absorption spectroscopy (JASCO V-650 Spectrophotometer) before use in electropolymerization experiment.

2.2 Methods

All electropolymerization experiment was performed using 3 electrode setup potentiostat (HZ5000 model, Hokuto Denko Ltd., Japan) with Pt wire as counter electrode, Ag/Ag^+ non-aqueous electrode as reference electrode, and Au (thickness of 47 nm) coated on high refractive index glass substrate as working electrode, respectively. The kinetic during electropolymerization was monitored by EC-SPR spectroscopy. The potential range was ranging from 0 V to 1.2 V at scan rate of 20 mV/s for 5 cycles. The thickness of the films was calculated by fitting the obtained SPR angular scan reflectivity curve by Fresnel equation algorithm using Winspall version 2.2. Atomic force microscopy (SHIMUDZU, SPM9600) was employed to study morphology of the obtained thin films.

3. Results and Discussion

The UV-vis absorption spectra of the obtained composite solutions and films are shown in Fig. 1. The absorption peak of monomer and composite solutions and films appeared at around 500 nm. This indicated that CNTs did not exhibit the UV-vis absorption peak of the composite films.

Cyclic voltammogram (CV) traces for all electropolymerization experiments are shown in Fig. 2. As seen in Fig. 2(a) comparing with Fig. 2(b) and Fig. 2(c) comparing with Fig. 2(d), the oxidation onset peak of polymer/CNTs composites were occurred at lower potential than pure polymer. The reason of lower potential of oxidation might be from the

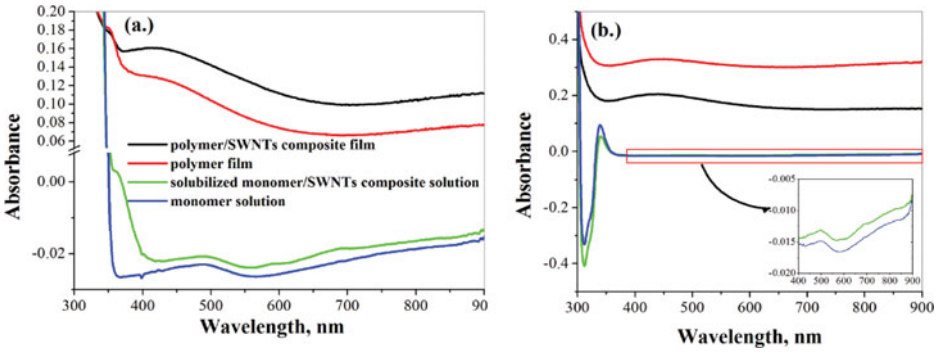

Figure 1. UV-vis spectra of (a) carboxylated thianaphthene-2-carboxylic acid and its composite and (b) carboxylated benzothiophene-2-propionic acid solution and its composite.

presence of CNTs promoted the electron transfer of oxidation-reduction. The oxidation onset peak at about 0.8 V corresponds to the deposition of polymer on the gold working electrode. Considering in term of the peak current, polythianaphthene-2-carboxylic acid/CNTs composite film showed higher peak current than the pure polymer film. The

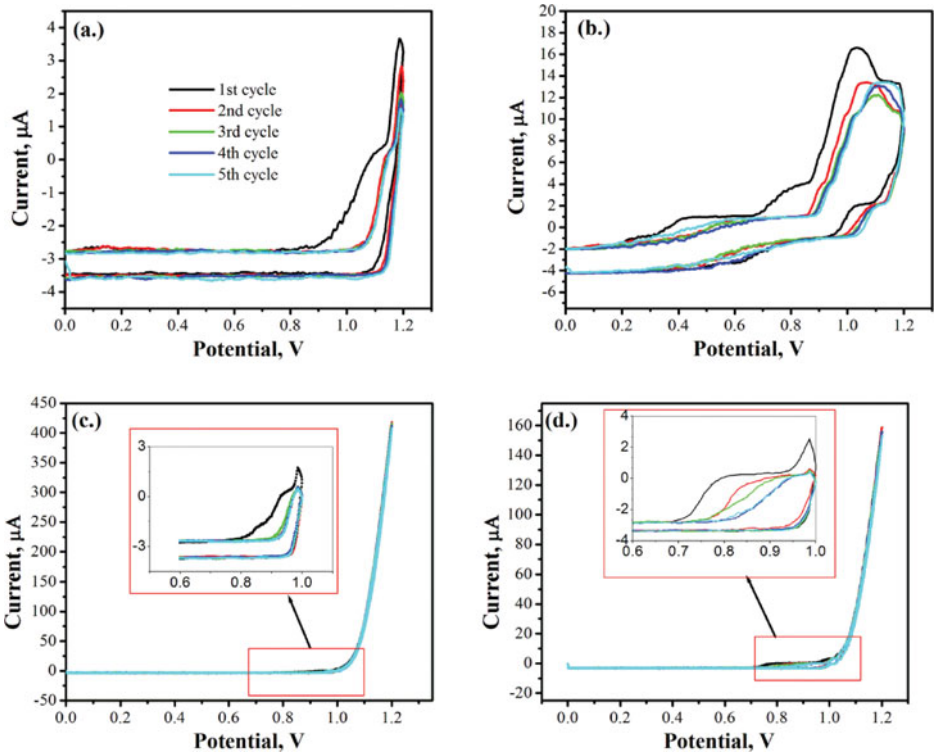

Figure 2. CV traces during electropolymerization for 5 cycles at scan rate of 20 mV/s (a) polythianaphthene-2-carboxylic acid (b) polythianaphthene-2-carboxylic acid/CNTs composite (c) polybenzothiophene-2-propionic acid and (d) polybenzothiophene-2-propionic acid/CNTs composite.

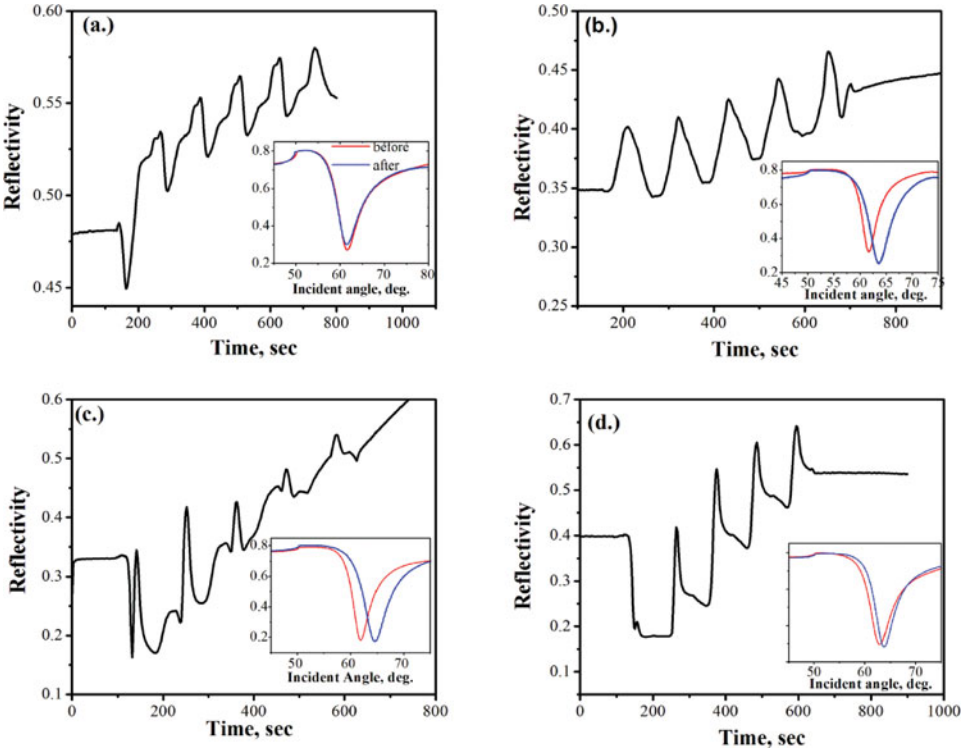

Figure 3. SPR reflectivity change during electropolymerization of (a) polythianaphthene-2-carboxylic acid (b) polythianaphthene-2-carboxylic acid/SWNTs composite (c) polybenzothiophene-2-propionic acid and (d) polybenzothiophene-2-propionic acid/SWNTs composite. The insets show the angular scan measurement before and after electropolymerization.

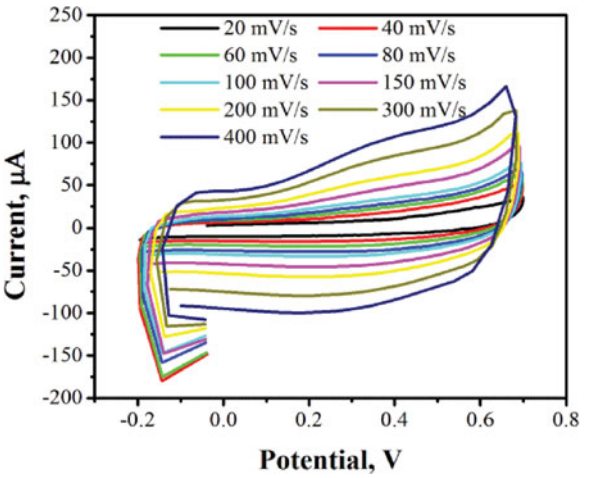

Figure 4. CV traces of poly(thianaphthene-2-carboxylic acid) film at different scan rates in PBS solution.

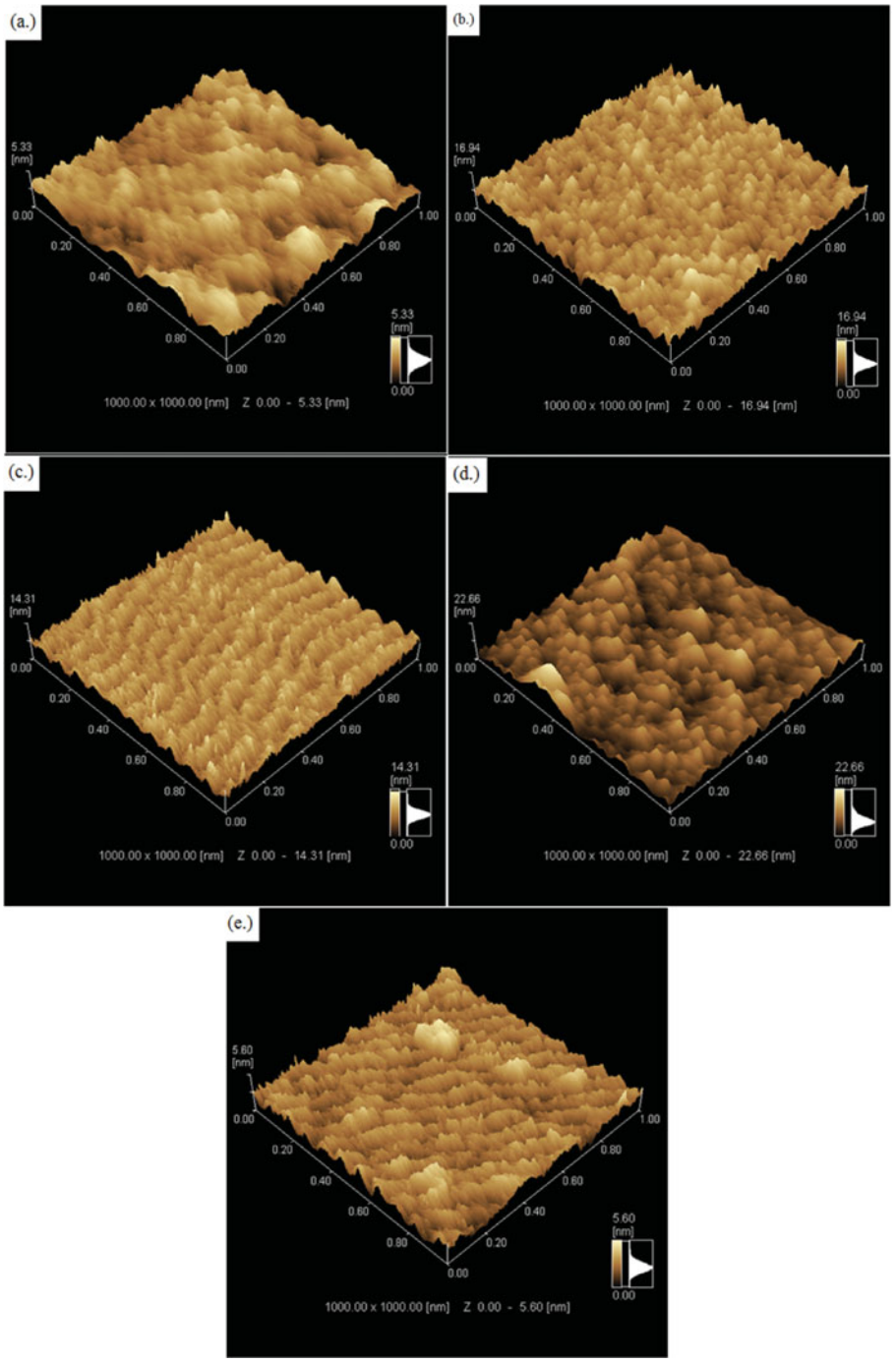

Figure 5. AFM images of the prepared films (a) bare gold (b) polythianphthene-2-carboxylic acid (c) polythianaphthene-2-carboxylic acid/CNTs composite (d) polybenzothiophene-2-propionic acid (e) polybenzothiophene-2-propionic acid/CNTs composite.

reason for higher peak current of the composite film than the pure polymer film is that CNTs had large specific surface area which can enhance the amount of polymer loading. However, the peak current of polybenzothiophene-2-propionic acid film in Fig. 2(c) is higher than its composite film (Fig. 2(d)). It indicated that the less amount of polybenzothiophene-2-propionic acid loaded on the CNTs surface which showed the lower peak current in the composite film.

The kinetic during electropolymerization was monitored at a fixed incident angle as shown in Fig. 3. The reflectivity increased with number of cycle increased. As shown in the insets, the dip angle of angular scan reflectivity curve after electropolymerization was shifted to higher angle comparing with the dip angle of the curve before electropolymerization. These results indicated that the polymers were deposited on the gold substrates. The thickness of the polymer films was calculated by fitting this curve using Fresnel equation algorithm (Winspall software version 2.2) which were estimated to be 0.50, 7.24, 3.61, and 2.28 nm for polythianaphthene-2-carboxylic acid, polythianaphthene-2-carboxylic acid/SWNTs composite, polybenzothiophene-2-propionic acid, and polybenzothiophene-2-propionic acid/SWNTs composite, respectively.

For further construction of immunosensor, the electroactivity of the obtained poly(thianaphthene-2-carboxylic acid) film was studied in phosphate buffer saline (PBS) solution (pH 7.4). The potential range was from 0 V to 0.7 V with varying scan rates from 20 to 400 mV/s. The results as shown in Fig. 4 indicated that the poly(thianaphthene-2-carboxylic acid) film has electroactivity in this neutral solution.

Surface morphology of conducting polymer/CNTs composite films was further studied by AFM. The AFM images of the films are shown in Fig. 5. The roughness of the films was changed to higher values comparing with the bare Au substrates which indicating the deposition of the polymer and its composite films on the substrates after electropolymerization. The roughness of polythianaphthene-2-carboxylic acid, polythianaphthene-2-carboxylic acid/CNTs composite, polybenzothiophene-2-propionic acid and polybenzothiophene-2-propionic acid/CNTs thin films are 1.007, 1.300, 1.003 and 1.961, respectively.

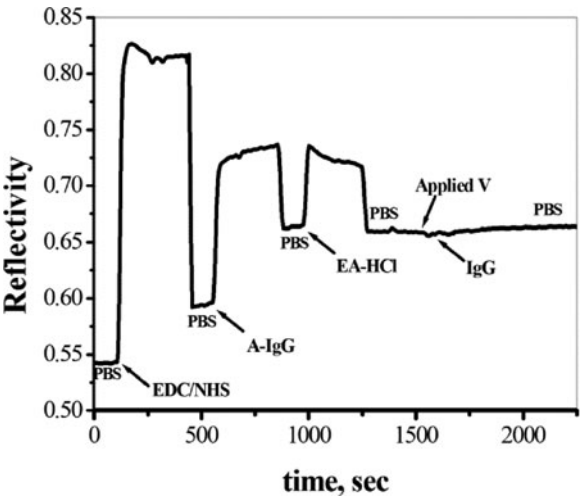

Figure 6. SPR response during the construction of poly(thianaphthene-2-carboxylic acid)-based sensor for detection of human IgG.

Figure 6 shows the example of the SPR kinetic curve during the construction of polymer-based immunosensor. The PBS solution was employed as the baseline before the activation of the carboxylic group of polymer, poly(thianaphthene-2-carboxylic acid), with a 1:1 ratio of 0.4 M 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride/0.1 M *N*-hydroxysuccinimide (EDC/NHS) solution as a coupling reagent. After rinsing with PBS solution, 100 μg/ml of anti-human IgG solution was then injected to immobilize on the polymer surface. An aqueous solution of 0.2 M ethanolamine hydrochloride (EA-HCl) was used for blocking the remaining free binding sites. After rinsing with PBS, a constant potential was applied to obtain the baseline before adding human IgG which is associated with the binding process of anti-human IgG and human IgG. This could be confirmed that the prepared film could be used for immunosensor application with further polymer/CNTs composite film for immunosensor experiment is undergoing.

4. Conclusion

Polythianaphthene-2-carboxylic acid/CNTs and polybenzothiophene-2-propionic acid/CNTs composite films were successfully prepared. The kinetic during electropolymerization process was in situ monitored by EC-SPR spectroscopy. The thickness of polymer films was calculated by fitting the obtained SPR angular curves by a Fresnel equation algorithm using Winspall software version 2.2. The polymer/CNTs films showed electroactivity in neutral PBS solution which can be used as immunosensor in the further work.

Acknowledgments

This work was partially supported by the NANOTEC, NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network. S. S. would like to acknowledge Chiang Mai University for young staff research funding and the Research Grant for New Scholar (MRG5580133) from the Thailand Research Fund (TRF), the Thailand's Office of the Higher Education Commission (CHE) and Chiang Mai University. P. N. would like to acknowledge the Thailand's Office of the Higher Education Commission, Rajamangala University of Technology Lanna, and the Graduate School, Chiang Mai University, Thailand and the "Global Circus" Program of Niigata University supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan for financial support.

References

[1] Tele, F. R. R., & Fonseca, L. P. (2008). *Mater. Sci. Eng., C*, *28*, 1530.
[2] Ramakrishnan, S. (1997). *Resonance*, 48.
[3] Luo, X., Killard, A. J., Morrin, A. M., & Smyth, R. (2006). *Anal. Chim. Acta*, *575*, 39.
[4] Ramanavičius, A., Kaušaitė, A., & Ramanavičienė, A. (2005). *Sens. Actuators, B*, *111*, 532.
[5] Wang, J., Yuan, R., Chai, Y., Cao, S., Guan, S., Fu, P., & Min, L. (2010). *Biochem. Eng. J.*, *51*, 95.
[6] Wang, J. (2005). *Electroanalysis*, *17*, 7.
[7] Hu, L., Hecht, D. S., & Gruner, G. (2010). *Chem. Rev.*, *110*, 5790.
[8] El-Maghraby, A. A., Abou-Elenien, G. M., & El-Abdallah, M. (2010). *Synth. Met.*, *160*, 1335.
[9] Xia, L., Wei, Z., & Wan, M. (2010). *J. Colloid Interface Sci.*, *341*, 1.
[10] Tanaka, K., & Yamabe, T. (1991). *J. Appl. Phys.*, *70*, 5653.

[11] Sriwichai, S., Baba, A., Phanichphant, S., Shinbo, K., Kato, K., & Kaneko, F. (2010). *Sens. Actuators B*, *147*, 322.
[12] Janmanee, R., Baba, A., Phanichphant, S., Sriwichai, S., Shinbo, K., Kato, K., & Kaneko, F. (2011). *Jpn. J. Appl. Phys.*, *50*, 01BK02−1.
[13] Dong, H., Cao, X., Li, C. M., & Hu, W. (2008). *Biosens. Bioelectron.*, *23*, 1055.
[14] Suzuki, M., Nakashima, Y., & Mori, Y. (1999). *Sens. Actuators, B*, *54*, 176.
[15] Baba, A., Taranekar, P., Ponnapati, R. R., Knoll, W., & Advincula, Rigoberto C. (2010). *Appl. Mater. Interfaces*, *2*, 2347.