

Fabrication and electrochemical properties of layer-by-layer deposited films containing phthalocyanine dyes

Kazunari Shinbo^{a,*}, Ken Onishi^b, Shunsuke Miyabayashi^a, Kazuki Takahashi^a, Shigenobu Katagiri^a, Keizo Kato^a, Futao Kaneko^a, Rigoberto C. Advincula^b

^aDepartment of Electrical and Electronic Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

^bDepartment of Chemistry, University of Houston, 136 Fleming Building, Houston, TX 77204-5003, USA

Abstract

Ultrathin films containing water-soluble copper (II) phthalocyanine-3,4',4'',4'''- tetrasulfonic acid (CuPcTs) and poly(diallyldimethylammonium chloride) (PDADMAC) were fabricated using the electrostatic layer-by-layer deposition technique. UV–vis absorption spectra and ellipsometry measurements suggested successive linear depositions of the bilayers of CuPcTs and PDADMAC. The thickness of the CuPcTs monolayer obtained from the ellipsometry was smaller than the plain size of CuPcTs and the molecule planes were considered and tilted in the film. The surface morphology was also observed using atomic force microscopy. The cyclic voltammogram (C–V) of the fabricated films in 0.1 M KCl aqueous solution suggested the oxidation and reduction of the CuPcTs at approximately +0.9 and +0.05 V vs. Ag/AgCl, respectively. UV–vis absorption spectra were observed for the films at applied voltages of +0.9 and 0.0 V in the KCl aqueous solution and electrochromisms were repeatedly observed.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Phthalocyanine; Poly(diallyldimethylammonium chloride); Layer-by-layer deposition; Cyclic voltammetry; Electrochromism

1. Introduction

Phthalocyanine derivatives have been attracting much interest for many optical and electronic applications [1]. For example, phthalocyanines are promising for non-linear optics [2] and optical memory [3]. In organic light-emitting diodes, phthalocyanines are useful for anode buffer layers [4,5] and can be used for emitting layers [6]. Moreover, sensors against toxic gases can be developed using the conductivity changes of phthalocyanines [6,7]. Efficient organic solar cells [8] and field effect transistors [9] also have been fabricated using various phthalocyanines. For secondary batteries, phthalocyanines are quite useful for developing electrodes [10,11]. Furthermore, electrochromism of phthalocyanines are very interesting for developing new type displays and have been investigated for many years [12,13].

The electrostatic layer-by-layer (LbL) self-assembly deposition technique [14] is quite useful for fabricating ultrathin films with nano-meter thickness. In this tech-

nique, several kinds of positively and negatively charged materials such as polyelectrolytes, clay [15], nanoparticles [16] and so on, can be alternately deposited due to coulombic interaction. Phthalocyanine derivatives with proper ionic groups can be fabricated using the technique [17]. However, only a few studies of electrochemical properties of phthalocyanine LbL deposited films have been reported until now [17,18]. In this study, ultrathin films of negatively charged copper phthalocyanines and positively charged polyelectrolytes were fabricated using the LbL deposition technique and the structure, the fundamental cyclic voltammogram and electrochromic properties of the films were observed in 0.1 M potassium chloride aqueous solution.

2. Experimental details

Fig. 1 shows the chemical structures of the molecules mainly used in this work. Copper (II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid, tetrasodium salt (CuPcTs) and poly (diallyldimethylammonium chloride) (PDADMAC), $M_w < 20\,000$, were purchased from Aldrich Chemical Co. The CuPcTs molecule has sulfonic acid groups and can be deposited using LbL deposition

*Corresponding author. Tel./fax: +81-25-262-67543.

E-mail address: kshinbo@eng.niigata-u.ac.jp (K. Shinbo).

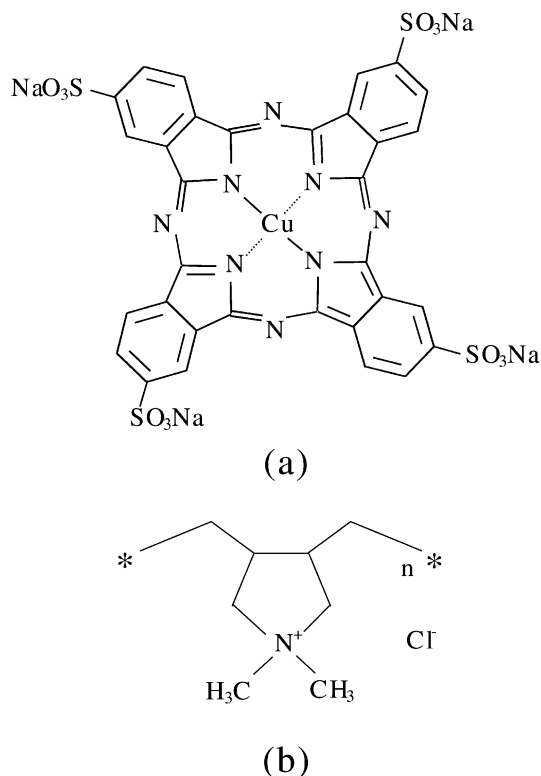


Fig. 1. Chemical structures of the molecules used in this work: CuPcTs (a) and PDADMAC (b).

technique [17]. PDADMAC is transparent in the visible light region and is useful to fabricate ultrathin films with well-ordered structure using LbL deposition technique [19]. 3-aminopropyltriethoxysilane (APS) [16] and polystyrenesulfonic acid (PSS, Aldrich Chemical Co.) have positively and negatively charged groups, respectively, and were also used for fabricating precursor films which contribute to excellent depositions of bilayer films of CuPcTs and PDADMAC. Aqueous solution of the CuPcTs with the concentration of 1 mM and those of PDADMAC and PSS with the concentration of 1 mg/ml were prepared for the deposition [17]. Water with resistivity higher than $18.2 \text{ M}\Omega$ was purified using a Milli-Q purification system (Milli-Q Academic, Millipore Co.). Freshly cleaned glass substrates with ITO electrode or Si wafer were used for the deposition. As the precursor films, APS monolayers were firstly deposited on the substrates by immersion to toluene containing 0.1% APS [16] and then 2 bilayers of PSS and PDADMAC were deposited. The surface of the precursor film is positively charged due to the top PDADMAC layer, which enhances the CuPcTs molecule deposition. The ultrathin films of bilayers of CuPcTs and PDADMAC were fabricated on the precursor films. All the films of CuPcTs, PDADMAC or PSS were deposited by immersion to the aqueous solution for 30 min [20,21].

The UV–vis absorption spectra of the aqueous solutions of CuPcTs and the fabricated films were observed using a spectrophotometer (USB2000, Ocean Optics). Thicknesses of the deposited films on Si wafer were obtained using ellipsometry (Multiskop, Optrel GbR). He–Ne laser beam with wavelength of 632.8 nm was used for the ellipsometry measurement. Atomic force microscopy (AFM) imaging was performed in air using a Nanoscope IIIa system (Digital Instruments).

The cyclic voltammetry (C–V) experiments were carried out using an Amel 2049 potentiostat/galvanostat and Power lab system with ITO plate working electrodes coupled with a Pt Plate counter and an Ag/AgCl reference electrode in 0.1 M KCl aqueous solution. The scan rate for the measurement was 20 mV s^{-1} .

The electrochromic measurements were carried out using the spectrophotometer system combined with the electrochemical cell of quartz cuvette ($l = 1 \text{ cm}$) and the potentiostat/galvanostat set-up for electrochemistry above. The absorption spectra were measured in situ while electrochemically color changing on the LbL deposited film on ITO plate in the quartz cuvette.

3. Results and discussion

Fig. 2 shows the UV–vis absorption spectra of the aqueous solutions of CuPcTs. Absorption peaks at UV and visible light regions are due to B and Q bands, respectively [17]. The absorptions of Q-band have two peaks at approximately 628 and 665 nm and the relative intensity of absorption at 628 nm becomes larger than that at 665 nm with the solution concentration. The

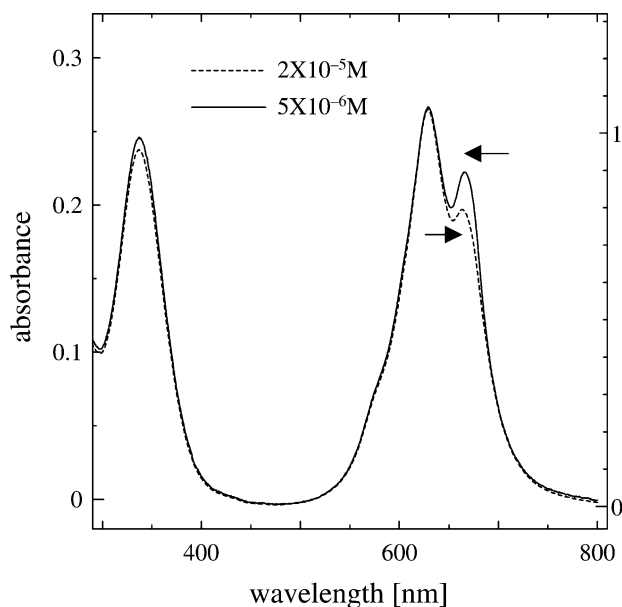


Fig. 2. UV–vis spectra of CuPcTs aqueous solutions with concentrations of $5 \times 10^{-4} \text{ M}$ and $5 \times 10^{-6} \text{ M}$.

peaks at 665 and 628 nm are due to monomer and aggregate of CuPcTs, respectively [17,22].

The absorption spectra of the 6, 12, 18, 24 bilayers of CuPcTs/PDADMAC films on glass substrates with ITO are shown in Fig. 3a. The absorption peaks of B and Q bands were observed at approximately 332 and 612 nm. The relationship between the absorption peak at 612 nm and the number of the bilayers are shown in Fig. 3b. Although the plots are almost linear beyond 6th bilayer, the slope of the curve is small until 6th bilayer, which suggests poor deposition.

The thicknesses of the CuPcTs/PDADMAC films deposited on Si wafer were obtained using the ellipsometry as shown in Fig. 4. The refractive index of CuPcTs/PDADMAC film was assumed to be $1.80 + i \cdot 0.3$. A linear relationship was also obtained beyond the 12th bilayer. The poor depositions on glass substrates with ITO until 6th bilayer and those on Si wafer until 12th bilayer were probably due to the initial inhomogeneity in the substrate surfaces, i.e. surface charges, which eventually became homogenous with deposition. Both the thicknesses of CuPcTs and PDADMAC monolayer beyond 12th bilayer were approximately 1.2 nm [17]. The thickness of CuPcTs monolayer was smaller than the size of the molecular plane of the CuPcTs molecule [23]. The CuPcTs molecule plane was considered and tilted in the film.

AFM images were observed for the films with various numbers of bilayers. Top view and cross-section images of a CuPcTs/PDADMAC film (20 bilayers) are shown in Fig. 5a and b, respectively. The roughness tends to become larger with the number of bilayers and the mean roughnesses are 0.65 and 1.91 nm for the films of 5 and 20 bilayers.

Fig. 6 shows the C–V curve of the CuPcTs/PDADMAC LbL film (12 bilayers) on ITO electrode in 0.1

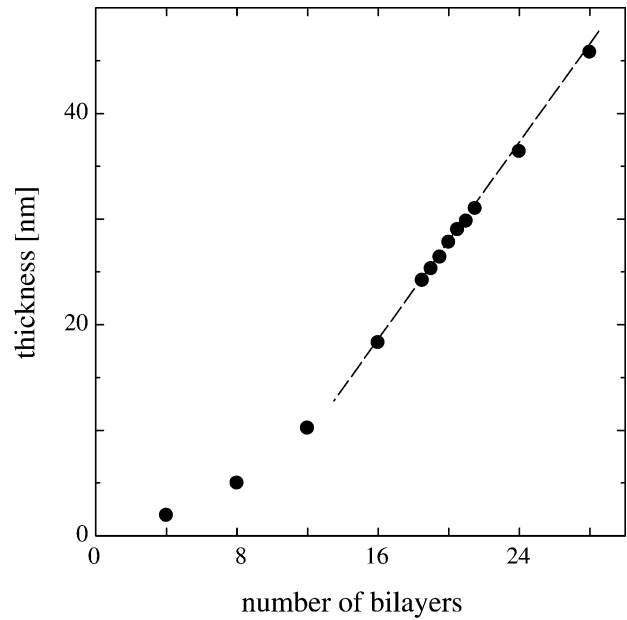


Fig. 4. Thickness vs. the number of the bilayer relationship of CuPcTs/PDADMAC LbL deposited ultrathin films obtained using ellipsometry.

M KCl aqueous solution. A pair of peaks was observed at approximately +0.9 and +0.05 V vs. Ag/AgCl and was considered to be due to oxidation and reduction of CuPcTs. The electrochromic properties of the film in the solutions were also observed for the voltage application of +0.9 and 0.0 V vs. Ag/AgCl. The absorption spectra before and 10 s after the application of +0.9 V are shown in curves *a* and *b* in Fig. 7. The Q band at approximately 612 nm decreased and the absorption from approximately 380 to 550 nm slightly increased. The absorption almost recovered after the application of

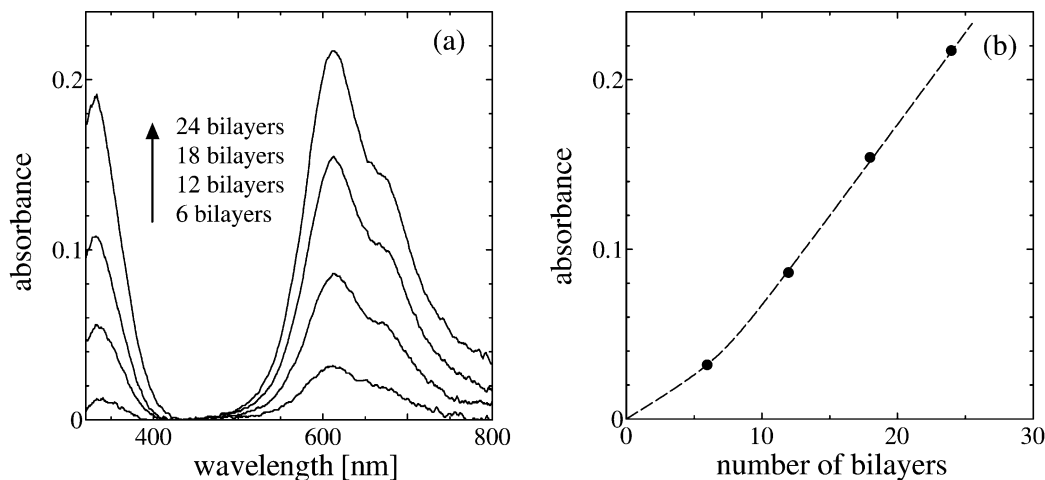


Fig. 3. Absorption spectra of CuPcTs/PDADMAC LbL deposited films (a) and relationship between absorbance at 612 nm and the number of bilayers (b).

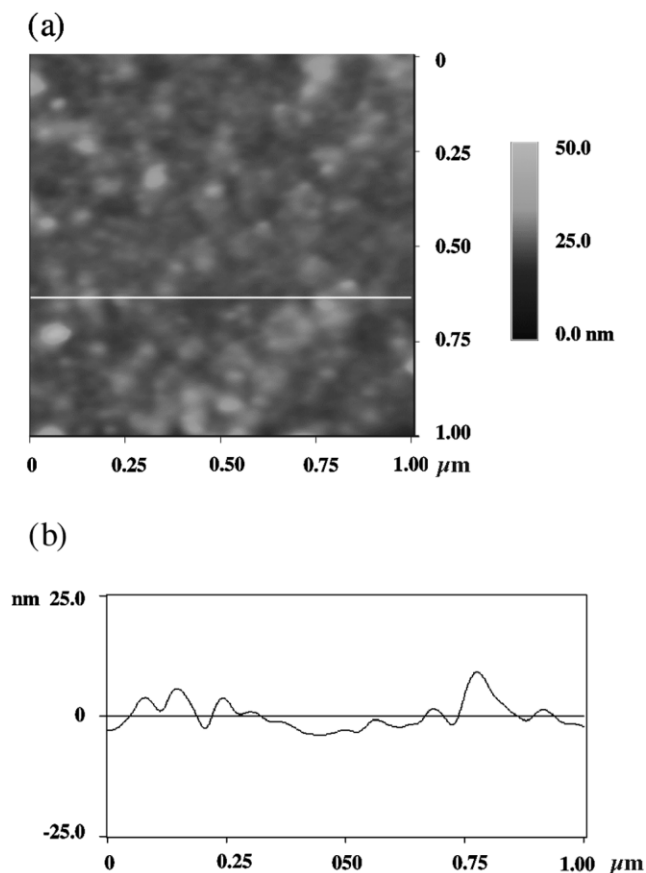


Fig. 5. AFM images of a CuPcTs/PDADMAC LbL deposited film (20 bilayers): (a) top view and (b) horizontal cross-section at the line in Fig. (a).

0.0 V (curve *c* in Fig. 7). The electrochemical color changes were repeatedly observed. These absorption changes are considered to be due to the oxidation and reduction of CuPcTs. In-situ measurements were also carried out for the absorption changes. Fig. 8a shows the absorption spectra during the application of +0.9 V. The main change of the spectra was observed in a few seconds after the voltage application. The absorption at 612 nm during applied voltage of +0.9 and 0.0 V is also shown in Fig. 8b. It also shows that the absorption mainly changes in a few seconds after the voltage switching [13].

The thickness and the structure of the films can be easily controlled using the LbL deposition technique and the results in this study are useful for developing phthalocyanine electrochemical devices.

4. Conclusion

LbL deposited ultrathin films of CuPcTs and PDADMAC were fabricated and the structure and fundamental electrochemical properties were investigated. Successive linear depositions were observed after several bilayers

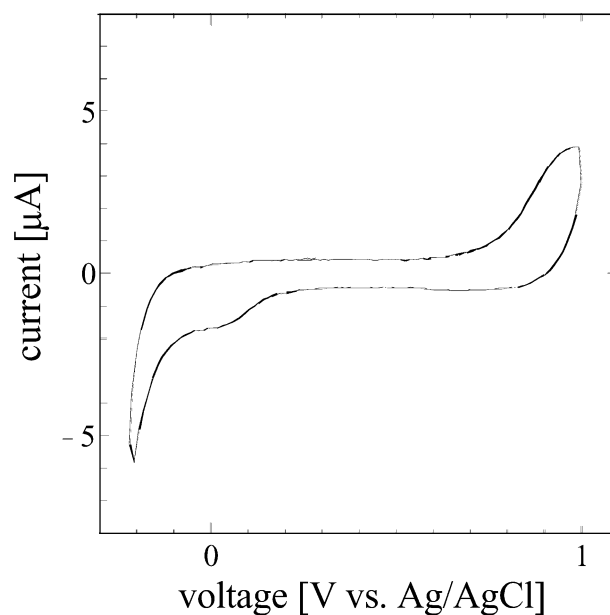


Fig. 6. Cyclic voltammogram of the CuPcTs/PDADMAC LbL deposited film (12 bilayers) in 0.1 M KCl aqueous solution at scan rate of 20 mV/s.

and the planes of CuPcTs molecules were considered to tilt in the film. The redox responses of CuPcTs molecules were observed in C–V curve at approximately +0.9 and +0.05 V. Furthermore, changes of optical absorption were observed repeatedly with voltage applications of +0.9 V and 0.0 V. These results are considered to be useful for developing electrochemical devices using LbL films containing phthalocyanines.

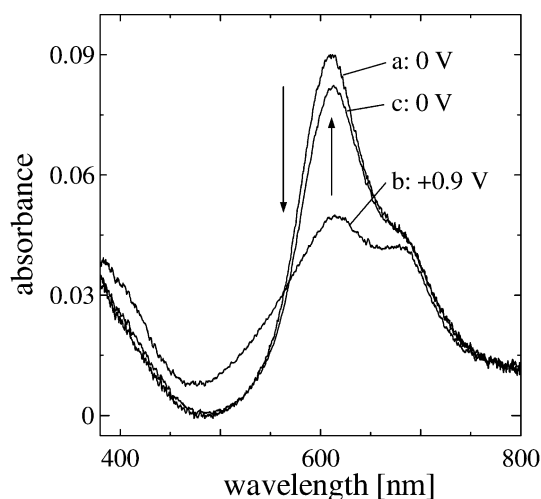


Fig. 7. UV–vis spectra of CuPcTs/PDADMAC LbL deposited film (12 bilayers) in 0.1 M KCl aqueous solution: before and 10 s after voltage application of +0.9 V (curves a, b) and 15 s after voltage application of 0.0 V (curve c).

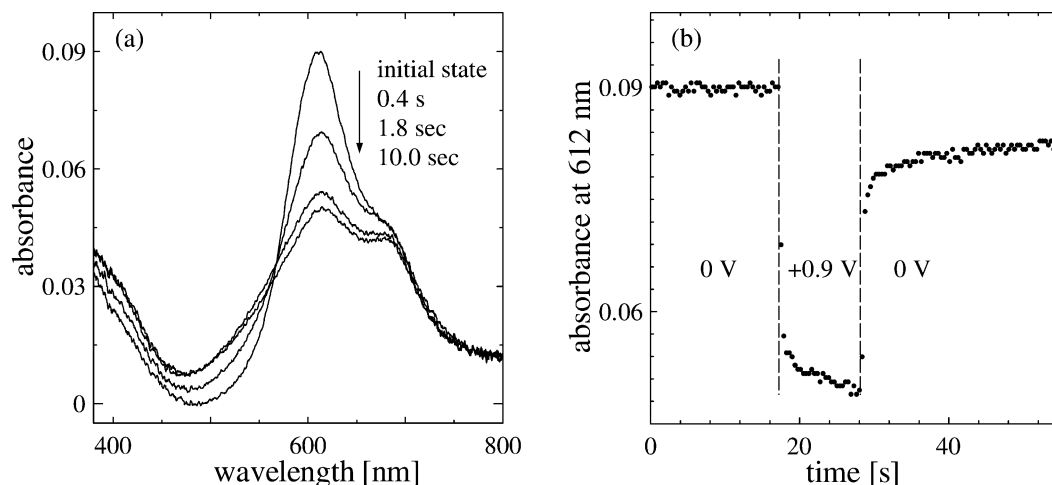


Fig. 8. Absorption changes of CuPcTs/PDADMAC LbL deposited film (12 bilayers): UV-vis spectra after the voltage application of +0.9 V (a) and absorbance change at 612 nm due to the switching of the applied voltage (b).

References

- [1] C.C. Lenzhoff, A.B.P. Lever, Phthalocyanines Properties and Applications, 1–3., VCH, Weinheim, 1989, See for example.
- [2] M. Hosoda, T. Wada, T. Yamamoto, A. Kaneko, A.F. Garito, H. Sasabe, *Jpn. J. Appl. Phys.* 31 (1992) 1071.
- [3] R. Ao, L. Kümmerl, D. Hoarer, *Adv. Mater.* 9 (1997) 42.
- [4] H. Riel, W. Brutting, T. Beierlein, E. Haskal, P. Muller, W. Rieß, *Synthetic Met.* 111–112 (2000) 303.
- [5] K. Shinbo, E. Sakai, F. Kaneko, K. Kato, T. Kawakami, T. Tadokoro, S. Ohta, R.C. Advincula, *IEICE Trans. Electron.* E85-C (2002) 1233.
- [6] K. Shinbo, M. Minagawa, H. Takasaka, K. Kato, F. Kaneko, T. Kawakami, *Colloids Surf. A* 198–200 (2002) 905.
- [7] M.I. Newton, T.K.H. Starke, M.R. Willis, G. McHale, *Sensors Actuators B: Chem.* 67 (2000) 307.
- [8] K. Petritsch, J.J. Dittmer, E.A. Marseglia, R.H. Friend, A. Lux, G.G. Rozenberg, S.C. Moratti, A.B. Holmes, *Sol. Energy Mater. Sol. Cells* 61 (2000) 63, for example.
- [9] J. Locklin, K. Shinbo, K. Onishi, F. Kaneko, R.C. Advincula, *Chem. Mat.* (to be published).
- [10] Y. Asai, K. Onishi, T. Arai, M. Matsumoto, S. Miyata, K. Shigehara, *Electrochimica Acta* 46 (2000) 77.
- [11] S.-J. Kim, K. Onishi, K. Shigehara, *J. Porphyrins Phthalocyanines* 5 (4) (2001) 397.
- [12] J.M. Green, L.R. Faulkner, *J. Am. Chem. Soc.* 105 (1983) 2950.
- [13] C.-L. Lin, C.-C. Lee, K.-C. Ho, *J. Electroanal. Chem.* 81 (2002) 524.
- [14] G. Decher, J.-D. Hong, J. Schmitt, *Thin Solid Films* 210–211 (1992) 831.
- [15] N.A. Kotov, T. Haraszti, L. Turi, G. Zavala, R.E. Geer, I. Deekayen, J.H. Fendler, *J. Am. Chem. Soc.* 119 (1997) 6821.
- [16] K.V. Sarathy, P.J. Thomas, G.U. Kulkarni, C.N.R. Rao, *J. Phys. Chem. B* 10 (1999) 399.
- [17] Y.M. Lvov, G.N. Kamau, D.-L. Zhou, J.F. Rusling, *J. Colloid Interface Sci.* 212 (1999) 570.
- [18] K. Shinbo, K. Onishi, S. Miyabayashi, K. Kato, F. Kaneko, R.C. Advincula, *Trans. MRS-J* 28 (2003) 63.
- [19] K. Shinbo, A. Baba, F. Kaneko, T. Kato, K. Kato, R.C. Advincula, W. Knoll, *Mater. Sci. Eng. C* 22 (2002) 319.
- [20] A. Baba, F. Kaneko, R.C. Advincula, *Coll. Surf. A* 173 (2000) 39.
- [21] Y. Lvov, S. Yamada, T. Kunitake, *Thin Solid Films* 300 (1997) 107.
- [22] K. Saito, *Jpn. J. Appl. Phys.* 34 (1995) 3832.
- [23] J.E.S. Kim, E. Lim, K. Lee, D. Cha, B. Friedman, *Appl. Surf. Sci.* 205 (2003) 274.