

## Fabrication and Electrochemical Properties of Water-soluble Phthalocyanine Layer-by-layer Deposited Films

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Ultrathin films containing anionic copper phthalocyanine dye (CuPcTs) and cationic polymer (PDADMAC) were fabricated using the electrostatic layer-by-layer deposition technique. Successive linear depositions of the alternate films of CuPcTs and PDADMAC were suggested from UV-vis absorption spectra and ellipsometry measurements. The thickness of the CuPcTs monolayer obtained from the ellipsometry is smaller than the plain size of CuPcTs and the molecules are considered to be tilted in the film. The surface morphologies of the films were also observed using atomic force microscopy and the mean roughnesses were 0.65 and 1.91 nm for the film with 5 and 20 bilayers. 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 around + 0.9 and + 0.05 V vs. Ag/AgCl, respectively. UV-vis absorption spectra were observed for the films at applied voltages of + 0.8 V and 0 V in the KCl aqueous solution and electrochromisms were reversibly observed.

Key words: phthalocyanine, poly(diallyldimethylammonium chloride), layer-by-layer self-assembly deposition, cyclic voltammetry, electrochromism

### 1. INTRODUCTION

Many studies have been reported using phthalocyanine derivatives for various optical and electronic applications [1]. For example, phthalocyanines are promising for non-linear optics [2] and optical memory [3]. In developing organic light-emitting diodes, phthalocyanines are useful for anode buffer layers [4,5] and can be used for emissive material [6]. Moreover, toxic gases can be detected using conductivity changes of phthalocyanines [6, 7]. Efficient organic solar cells [8] and field effect transistors [9] have been also 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 controlled thickness. Various kinds of charged materials such as polyelectrolytes, clay [15], nano-particles [16] are adapted to this method. Ultrathin films of phthalocyanine derivatives with proper ionic groups can be also 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

Figure 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), Mw<20,000, were purchased from Aldrich Chemical Co. The CuPcTs molecule has sulfonic acid groups and can be deposited using LbL deposition 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. 3-aminopropyltriethoxysilane (APS) [19] and polystyrenesulfonic acid (PSS, Aldrich Chemical Co.) were also used for fabricating the precursor film which contributes to excellent depositions of bilayer films of CuPcTs and PDADMAC. Aqueous solution of the CuPcTs with the concentration of 1mM and those of PDADMAC and PSS with the concentration of 1

mg/ml were prepared for the deposition. 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. The LbL deposited films of CuPcTs and PDADMAC were fabricated on ITO electrode or Si wafer covered with APS monolayer and 2 bilayers of PSS and PDADMAC. All the films were deposited by immersion to the aqueous solution of CuPcTs, PDADMAC or PSS for 30 min.

The UV-vis absorption spectra of the aqueous solutions of CuPcTs and the fabricated films were observed using a spectrophotometer (S-2000, Ocean Optics). Thicknesses of the deposited films on Si wafer were obtained using ellipsometry (Multiskop, Optrel GbR). 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  $0.1 \text{ M KCl}$  aqueous solution. The scan rate for the measurement was  $20 \text{ mVs}^{-1}$ .

The electrochromic measurements were carried out using a multichannel photodetector system (IMUC-7000, Otsuka Electronics) 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 of the LbL deposited film in the quartz cuvette.

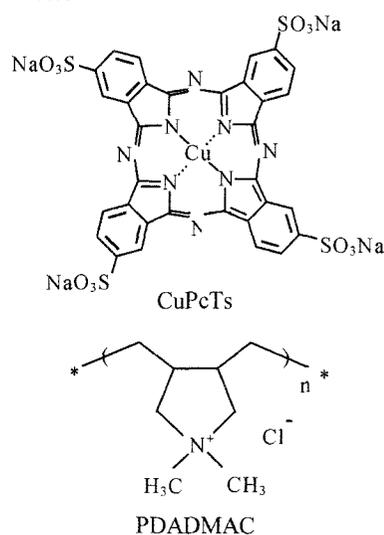


Figure 1. Structures of the used molecules.

### 3. RESULTS AND DISCUSSION

Figure 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 [20]. The absorptions

of Q-band have two peaks at around 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 peaks at 665 and 628 nm are considered to be due to monomer and aggregate of CuPcTs, respectively [17, 20].

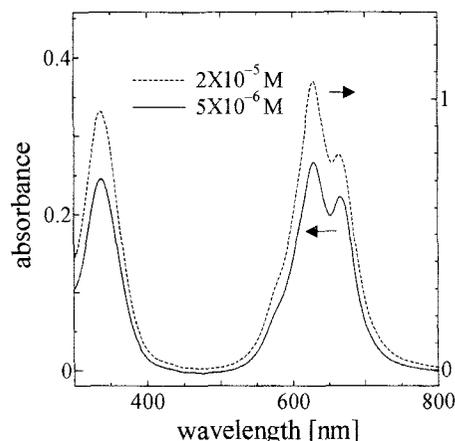


Figure 2. UV-vis spectra of CuPcTs aqueous solutions.

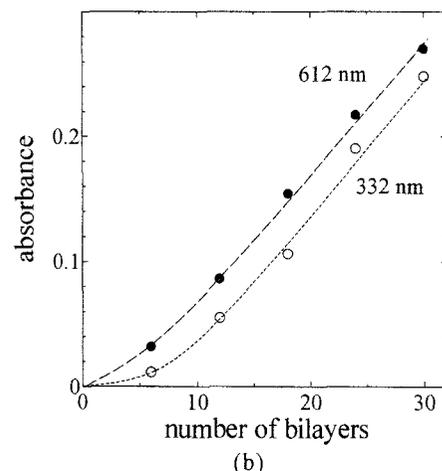
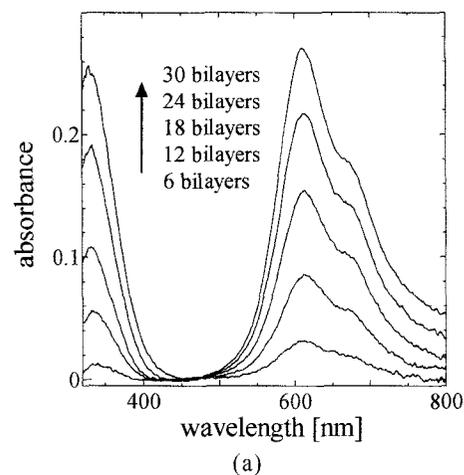


Figure 3. Absorption spectra (a) and absorbance vs. number of bilayer characteristic of the CuPcTs/PDADMAC LbL deposited films.

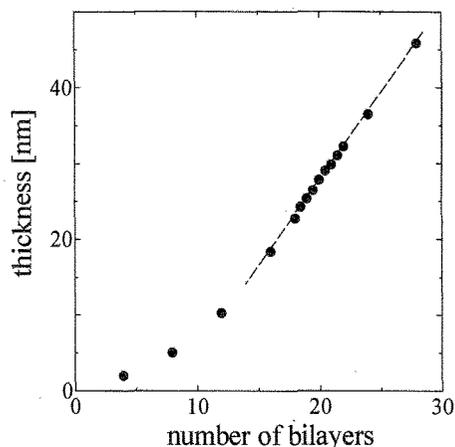


Figure 4. Thickness vs. the number of the bilayer property.

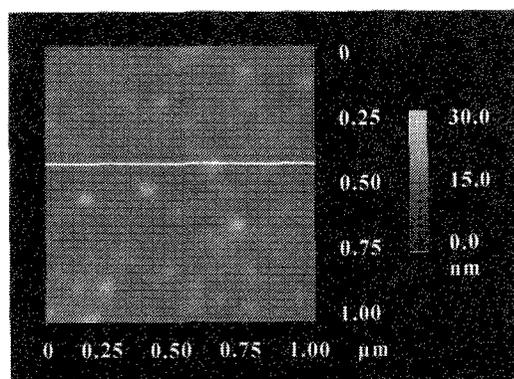
The absorption spectra of the 6, 12, 18, 24, 30 bilayers of CuPcTs/PDADMAC films on glass with ITO are shown in Fig.3 (a). The absorption peaks of B and Q bands were observed at around 332 and 612 nm. The relationship between the absorption peak at 612 and 332 nm and the number of the bilayers are shown in Fig.3 (b). Although the plots are almost linear beyond 6<sup>th</sup> bilayers, the slope of the curve was small until 6<sup>th</sup> bilayers suggesting poor deposition.

The thicknesses of the CuPcTs/PDADMAC films deposited on Si wafer were obtained using the ellipsometry. Thickness vs. the number of layer characteristic is 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 12<sup>th</sup> bilayer. The thickness of one CuPcTs monolayer beyond 12<sup>th</sup> bilayer was about 1.2 nm and is smaller than the plane size of CuPcTs molecules [21]. The molecules are considered to be tilted in the film. The poor depositions on glass with ITO until 6<sup>th</sup> bilayers and those on Si wafer until 12<sup>th</sup> bilayers were probably due to the initial inhomogeneity in the substrate surfaces, i.e., surface charges, which eventually became homogenous with deposition.

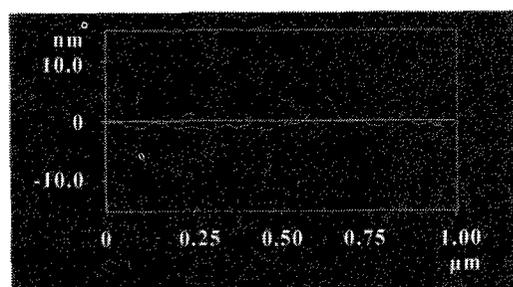
AFM images were observed for the films with various numbers of bilayers. Top view and cross-sectional images of a film with 5 bilayers are shown in Figs.5 (a) and (b), respectively. The roughness tends to become larger with the number of bilayers and the mean roughness  $R_a$  [22] were 0.65 and 1.91 nm for the film with 5 and 20 bilayers.

Figure 6 shows a C-V curve of the CuPcTs/PDADMAC LbL film (12 bilayers) on ITO electrode in 0.1 M KCl aqueous solution. A pair of peaks for oxidation and reduction of CuPcTs was observed at around + 0.9 and + 0.05 V. The electrochemical changes of the absorption spectra were also observed at applied voltages of + 0.8 and 0 V for the film as shown in Fig. 7. The Q bands decreased and the absorption from around 380 to 550 nm slightly increased. The

absorbance recovered with removal of the voltage, as shown in the broken line in Fig. 7. Figure 8 shows the time dependence of the absorbance at 612 nm against voltage application of 0.8 V and following removal. Transient currents are also shown in the figure. The absorbance changed rapidly after voltage application or removal and became almost stable in about 10 s. Same tendency was observed for the transient current. These changes are considered to be due to the oxidation and reduction of CuPcTs. These phenomena were repeatedly observed and were considered to be due to the redox response of CuPcTs.



(a)



(b)

Figure 5. AFM images of the 5 bilayer film: top view (a) and horizontal cross section (b).

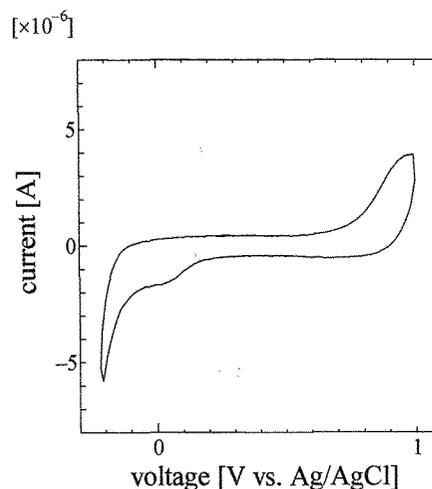


Figure 6 A C-V curve of the 12 bilayer film.

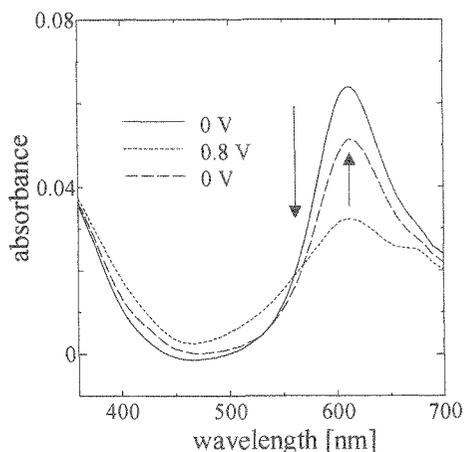


Figure 7 Absorption change of the 12 bilayer film against the voltage applications of +0.8 V and 0 V.

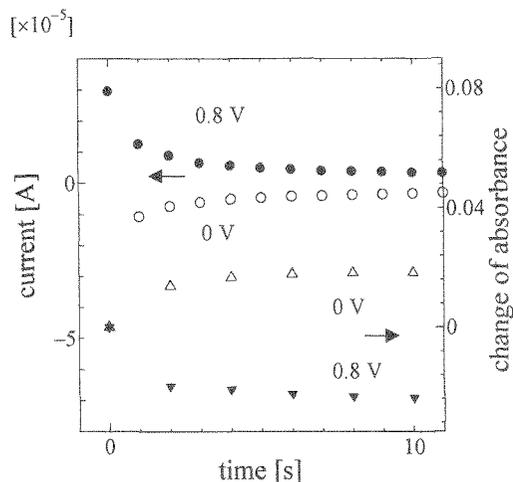


Figure 8. Time dependence of the absorbance at 612 nm and current against voltage application of 0.8 V and following 0 V.

The thickness and the structure of the films can be easily controlled using the layer-by-layer 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 and the plane of CuPcTs molecules are considered to be tilted in the film. The redox responses of CuPcTs molecules were observed in C-V curve at around + 0.9 and + 0.05 V vs. Ag/AgCl. Furthermore, changes of optical absorption were observed repeatedly with voltage application of + 0.8 V and 0 V. These results are considered to be useful for developing electrochemical devices using LbL films containing phthalocyanines.

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