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FABRICATION AND ELECTROCHROMIC PROPERTIES OF LAYER-BY-LAYER SELF-ASSEMBLED ULTRATHIN FILMS CONTAINING WATER-SOLUBLE PHTHALOCYANINE

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Alternate ultrathin films of 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 self-assembly technique. Linear depositions of the bilayers were observed from the UV-vis absorption spectra and ellipsometry. The average thickness of the CuPcTs monolayer obtained from ellipsometry was about 1.2 nm and CuPcTs molecules were estimated to be tilted to the film surface. The cyclic votammogram (C-V) of the fabricated films in aqueous solution containing 0.1 M KCl suggested the oxidation and reduction of the CuPcTs at around +0.9 V and 0.05 V 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 reversible absorption changes were observed.

Keywords: cyclic voltammetry; electrochromis; layer-by-layer self-assembly; phthalocyanine; poly(diallyldimethylammonium chloride).

INTRODUCTION

Phthalocyanine dyes have been studied for many electrical and electronic applications [1]. For example, efficient organic solar cells [2] and field effect

transistors [3] have been fabricated using various phthalocyanine derivatives. In organic light emitting diodes, phthalocyanines are useful as anode buffer layers [4] and can be also used as emitting layers [5]. Moreover, sensors against toxic gases can be developed using the conductivity changes of phthalocyanines [5,6]. For secondary batteries, phthalocyanines are quite useful for developing electrodes [7,8]. Furthermore, electrochromism of phthalocyanines have been investigated for developing new type displays [9,10].

The electrostatic layer-by-layer (LbL) self-assembly deposition technique [11] of electrolytes is very useful for developing ultrathin films with thickness in the nano-meter order. This technique can be applied for various kinds of charged materials such as polyelectrolytes, clay [12], nano-particles [13] and so on. Phthalocyanine derivatives with proper ionic groups can be also deposited using the technique [14]. However, only a few studies have been reported for electrochromic properties of phthalocyanine LbL self-assembled films until now [15]. 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.

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. PDADMAC is transparent in the visible light region and is useful to fabricate ultrathin films with well-ordered structure using LbL deposition technique. The CuPcTs molecule has sulfonic acid groups and can be also deposited using LbL deposition technique [14]. 3-aminopropyltriethoxysilane (APS) [16] 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 (CuPcTs/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. Water with resistivity higher than 18.2 MΩ was purified using a Milli-Q purification system (Milli-Q Academic, Millipore Corp.). Freshly cleaned glass substrates with ITO electrode or Si wafer were used for the deposition. The ultrathin 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

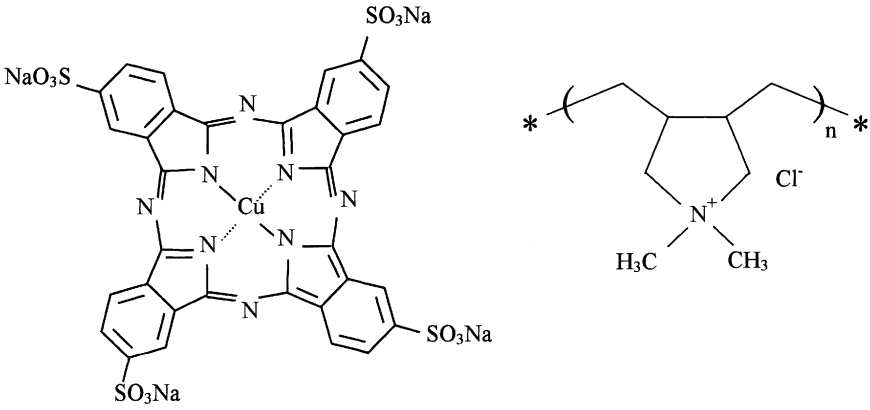

FIGURE 1 Chemical structures of the molecules used in this work: (a) CuPcTs and (b) PDADMAC.

deposited by immersion to the aqueous solution of CuPcTs, PDADMAC or PSS for 30 min.

The UV-*vis* absorption measurements were carried out using a spectrophotometer system (USB2000, Ocean Optics). Thicknesses of the deposited films on Si wafer were obtained using ellipsometry (Multiskop, Optrel GbR) with He-Ne laser ($\lambda = 632.8$ nm).

Electrochemical cells were fabricated 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 cyclic voltammetry (C-V) experiments were carried out using an Amel 2049 potentiostat/galvanostat and Power lab system. The scan rate for the measurement was 20 mVs^{-1}. The spectra of the samples were also measured *in situ* while electrochemically color changing of the LbL self-assembled film on ITO plate in a quartz cuvette ($l = 1$ cm).

RESULTS AND DISCUSSION

The UV-*vis* absorption spectra of the CuPcTs/PDADMAC LbL self-assembled films on glass substrates are shown in Figure 2(a). Absorption peaks at UV and visible light regions are due to B and Q bands, respectively [17]. The relationship between the absorption peak at 332 and 612 nm and the number of the bilayers are shown in Figure 2 (b). Although the plots are almost linear beyond 6th bilayers, the slope of the curve was small until 6th bilayers suggesting poor deposition.

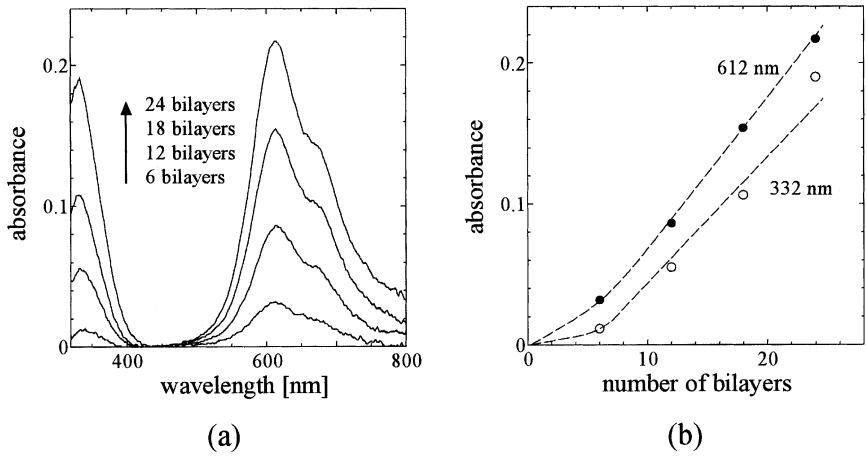

FIGURE 2 (a) Absorption spectrum of CuPcTs/PDADMAC LbL self-assembled films and (b) relationship between absorption at 612 nm and the number of bilayers (not including the precursor films).

The thicknesses of the CuPcTs/PDADMAC films deposited on Si wafer were obtained using the ellipsometry as shown in Figure 3. The refractive index of CuPcTs/PSS film was assumed to be 1.80 + 10.3. A linear relationship was also observed beyond the 12th bilayer. The poor depositions on ITO substrates until 6th bilayers and those on Si wafer until 12th bilayers were probably due to the initial inhomogeneity in the substrate

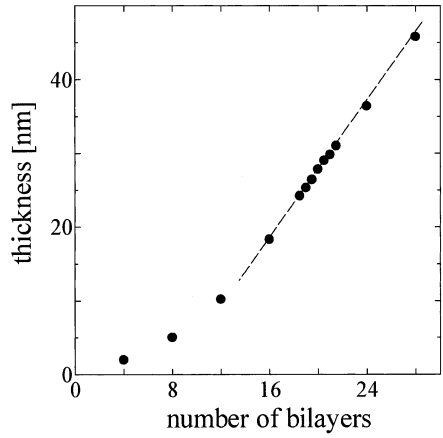

FIGURE 3 Thickness vs. the number of the bilayer relationship of CuPcTs/PDADMAC LbL self-assembled films obtained using ellipsometry.

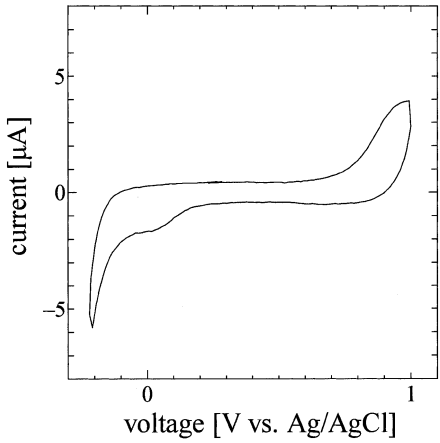

FIGURE 4 Cyclic voltammogram of the CuPcTs/PDADMAC LbL self-assembled film in 0.1 M KCl aqueous solution at scan rate of 20 mV/s.

surfaces, i.e., surface charges, which eventually became homogenous with deposition. The average thickness of one CuPcTs monolayer beyond 12th bilayer was about 1.2 nm and was smaller than the size of the molecular plane of the CuPcTs molecule [14]. The CuPcTs molecule plane was considered to be tilted to the film surface.

Figure 4 shows the C-V curve of the CuPcTs/PDADMAC LbL self-assembled film (12 bilayers) on ITO electrode in 0.1 M KCl aqueous solution. Peaks at around 0.9 V and 0.05 V were observed and they were

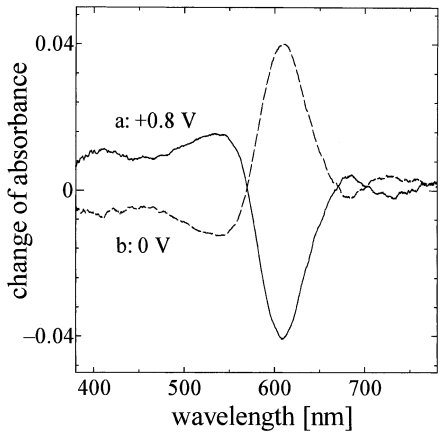

FIGURE 5 UV-*vis* spectra change of CuPcTs/PDADMAC film (12 bilayers) at applied voltage of +0.8 V and 0 V in 0.1 M KCl aqueous solution.

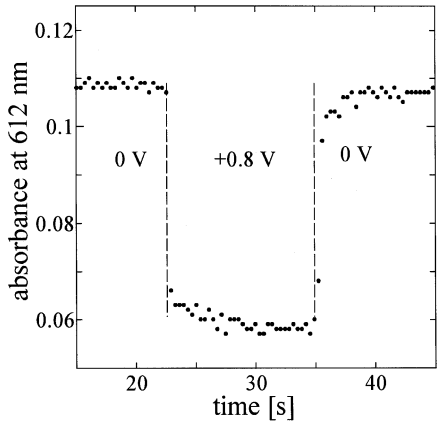

FIGURE 6 Time dependence of absorbance (at 612 nm) of CuPcTs/PDADMAC film with the switching of applied voltage.

considered to be due to oxidization and reduction of CuPcTs, respectively [7–10]. The electrochemical changes of the UV-*vis* spectra were also observed at applied voltages of 0.8 and 0 V for the film. The solid line in Figure 5 (curve a) shows the absorption change of the film after voltage application of 0.8 V for 10 s. The Q band at around 612 nm largely decreased and the absorption from around 400 to 550 nm increased with the voltage application of 0.8 V. The dashed line in Figure 5 (curve b) shows the absorption change after voltage application of 0 V for 10 s and the recovery of the spectrum was observed for the film. The electrochromisms were repeatedly observed and were also considered to be due to the redox response of CuPcTs. The change of absorbance at 612 nm with the switching of applied voltage is shown in Figure 6. The absorbance changed in a few seconds after the switching of applied voltage.

The results in this study are considered to be useful for developing phthalocyanine electrochemical devices.

CONCLUSION

Multilayer films of CuPcTs and PDADMAC were fabricated using LbL self-assembly technique and the structure and fundamental electrochromic properties were investigated. Linear depositions were observed after several bilayers and the plane of CuPcTs molecules are considered to be tilted to the film surface. The redox responses of CuPcTs molecules were observed at 0.9 and 0.05 V for C-V curve obtained in 0.1 M KCl aqueous

solution. Moreover, electrochoromic responses were also observed repeatedly with applied voltage of 0.8 V and 0 V. These results are considered to be useful for fabricating phthalocyanine electrochemical devices.

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