Synthesis of Ultrathin Films of Prussian Blue by Successive Ion Adsorption Technique

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Ultrathin films of Prussian blue (PB) were successfully prepared on substrates by the successive ion adsorption technique that consisted of alternate immersions of a substrate into solutions of Fe^{2+} and $Fe(CN)_6{}^{3-}$. The PB films showed stable electrochemical redox and electrochromic properties.

In recent years, considerable interest has been devoted to the preparation and characterization of polynuclear transition metal cyanides such as Prussian blue ($Fe^{III}{}_4[Fe^{II}(CN)_6]_3$, PB) from viewpoints of interest in the basic aspects of their electrochemistry and of developing devices in technologically relevant fields such as electrochromism,[1] sensor,[2] battery,[3] ion-selective electrode[4] and magnetooptics.[5] Stable films of PB analogues have been prepared so far mainly by galvanostatic and potentiostatic electrodeposition methods after the development by Itaya et al.[1] There are a few studies on chemical (non-electroplating) preparation of ultrathin films of PB analogues.[6] Here we report the chemical synthesis of PB ultrathin films by the successive ion adsorption (SIA) technique. The SIA technique consists of technologically simple processes of alternate immersion of a substrate into a solution of one precursor ion and then that of the other with rinsing in-between.[7–9] The experimental procedure of the SIA is almost the same as that of the alternate adsorption technique, which utilizes the layer-by-layer deposition of oppositely charged ionic species and is applied for the preparation of assembly films of macromolecules[10,11] and inorganic nanoparticles.[12,13] Since the SIA technique is based on the electrostatic interaction between precursor ions in the solution and on the substrate and the successive in situ reaction, it is expected that the film of the in situ reaction product can be grown in a well-controlled manner under ambient conditions. The SIA technique has been so far applied exclusively to the synthesis of metal chalcogenide thin films, the technique for which was so-called successive ionic layer adsorption and reaction.[7–9] In the present study, formation and growth of PB ultrathin film on a substrate have been achieved successfully by the SIA technique using precursor ions of Fe^{2+} and $Fe(CN)_6{}^{3-}$. The electrochemical properties of the PB films were also investigated.

The SIA process for PB deposition was carried out by the following steps unless stated otherwise: (i) immersion of a substrate into 0.1 M aqueous $Fe(NH_4)_2(SO_4)_2$ for 8 min; (ii) rinsing with water for 10 s and drying by an N_2 blast for 30 s; (iii) immersion into 0.1 M aqueous $K_3Fe(CN)_6$ for 10 min; (iv) rinsing and drying as the same manner as (ii). The pH of aqueous solutions was adjusted at 0.5–4.0 by adding a dilute aqueous H_2SO_4. By repeating steps (i)–(iv) n times, Prussian blue (PB_n) ultrathin films were prepared at room temperature onto quartz (Q), mica (M) and ITO substrates with or without pre-modification of the surface by alternate adsorption of poly(diallyldimethylammonium), PD, and poly(styrene sulfate), PS. The pre-modified substrates with anionic and cationic outermost surface layers, substrate-$(PD/PS)_3$ and -$(PD/PS)_2/PD$, were prepared by immersion of well-cleaned substrates into aqueous PD and PS alternately according to the previous reports.[10,11]

The deposition of PB by the SIA process onto the Q-$(PD/PS)_3$ substrate with anionic surface was monitored at pH 2.5 by means of UV-Vis spectroscopy. The Q-$(PD/PS)_3/PB_n$ films exhibited absorption around 710 nm due to the intervalence charge transfer (IVCT) band of PB[14] (Figure 1). The SIA process was optimized by monitoring the absorbance as a function of substrate immersion time; 8 min and 10 min of immersion times were found to be ideal for (i) and (iii) steps, respectively. The absorbance at 710 nm increased with increasing n linearly after 3 cycles, indicating quantitative formation and/or deposition of PB on the substrate. Similarly, the steady increase in the PB deposition amount was observed when the Q-$(PD/PS)_2/PD$ with cationic surface was subjected to the SIA process which started from step (iii) followed by steps (iv), (i) and (ii). In both cases, the increase in absorbance at 710 nm was observed both after the immersion into aqueous Fe^{2+} and aqueous $Fe(CN)_6{}^{3-}$ except for the first immersion step. The SIA process on a bare quartz substrate was followed by UV-Vis spectroscopy. It was found that the quantitative and regular deposition of PB was observed not at pH 2.0, which is close to isoelectric point of quartz, but at pH 4.0 and 0.5. These results clearly indicated that the either cationic or anionic surface of the substrate is indispensable for the deposition of PB by the SIA process not only at the adsorption of the first ionic layer but also in the steady growth of the film. The events during the SIA process can be postulated as follows. If the anionic substrate is first immersed into aqueous $Fe(NH_4)_2(SO_4)_2$, Fe^{2+} ions are electrostatically adsorbed on the substrate. During the subsequent immersion into aqueous $K_3Fe(CN)_6$, $Fe(CN)_6{}^{3-}$ ions interact and react with preadsorbed Fe^{2+} to form PB. In addition, excess $Fe(CN)_6{}^{3-}$ ions are deposited on the surface, which then react with Fe^{2+} in the next immersion. The reaction and excess adsorption repeat at each immersion step.

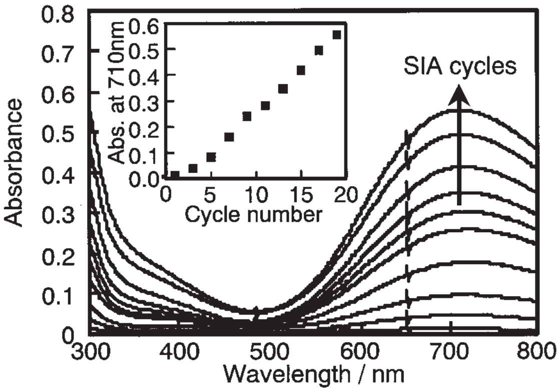

Figure 1. UV-Vis spectra of Q-$(PD/PS)_3/PB_n$ films prepared at pH 2.5. The spectra are of the samples with odd number cycles of the SIA up to the 19 cycles. The inset shows plots of absorbance at 710 nm against n.

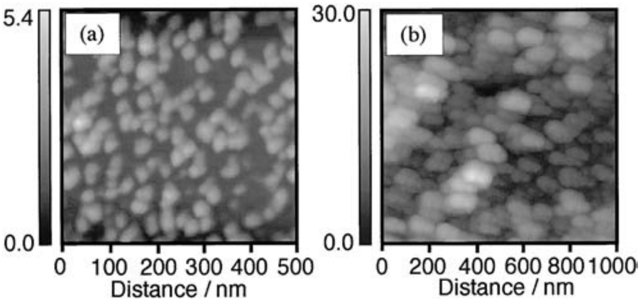

Figure 2. AFM images of surfaces of (a) M/PB_1 and (b) M/PB_2.

The PB deposition with the SIA cycles was also confirmed by a quantitative mass increase in quartz crystal microbalance (QCM) measurements using 2-amino-1-ethanethiol derivertized resonators. The mass increase per each SIA cycle was nearly constant at 650 ± 30 ng when the concentration of the immersing solutions (aq Fe^{2+}, aq $Fe(CN)_6{}^{3-}$) was 0.1 M. X-Ray diffraction (XRD) measurement showed that the PB produced on the substrate was $Fe^{III}{}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$ that is the insoluble form of PB.[15] Assuming that a dense film of $Fe^{III}{}_4[Fe^{II}(CN)_6]_3 \cdot 14\text{–}16H_2O$ (density $= 1.75\text{–}1.81\ g{\cdot}cm^{-3}$)[16] is formed, the average thickness of the PB films per 1 cycle of the SIA is estimated to be 11 ± 1 nm. Observations by scanning electron microscopy (SEM) on the Q-$(PD/PS)_3/PB_{20}$ film showed that a continuous PB film with ca. 0.2 μm thickness was formed throughout the Q-$(PD/PS)_3$ substrate and that the film consisted of densely packed nanoparticulates of PB below 50 nm (the image is not shown here). The 1 cycle thickness of PB estimated from the SEM was ca. 10 nm, which is consistent well with evaluated by the QCM. From these results, it was concluded that the average thickness of the PB film could be controlled of the order of nanometer level by the number of SIA cycles considering the proportional increases in UV-Vis absorbance and mass in QCM. The initial stage of the formation of PB on a mica substrate at the solution conditions of 0.1 M and pH 2.5 was investigated by atomic force microscopy (Figure 2). A lot of nanodomains with 20–30 nm in lateral size and 2 nm in height were produced directly on the surface of mica substrate after 1 cycle of the SIA (Figure 2a). After the second SIA cycle (Figure 2b), the amount and size of nanodomains increased and almost all the substrate surface was covered with PB nanoparticulates. These results indicated that PB nanoparticles formed at initial stage grew with repeating the SIA cycle to yield eventually a continuous nanoparticulate film.

The electrochemistry of PB nanofilms deposited on an ITO-electrode was investigated by cyclic voltammetry (CV) in a 0.1 M aqueous KCl solution (25 °C). The PB_{10} film showed two-redox waves at $E_1{}^0 = +0.17$ V and $E_2{}^0 = +0.85$ V (vs Ag/AgCl) at a scan rate of $10\ mV{\cdot}s^{-1}$ as shown in Figure 3a. The redox potentials are in agreement with the reported values[1] of the following reactions for electrochemically deposited PB films. The ratio of the charges consumed for the oxidation of PB at two anodic peaks (E_{pa2} to E_{pa1}) was 0.746, which is consistent with the ratio of 3/4 based on the redox reactions of (1) and (2).

$$Fe^{III}{}_4[Fe^{II}(CN)_6]_3 + 4e^- \leftrightarrow Fe^{II}{}_4[Fe^{II}(CN)_6]_3{}^{4-} \qquad (1)$$

$$Fe^{III}{}_4[Fe^{II}(CN)_6]_3 - 3e^- \leftrightarrow Fe^{III}{}_4[Fe^{III}(CN)_6]_3{}^{3+} \qquad (2)$$

This also agrees with the XRD results that the insoluble form of PB, $Fe^{III}{}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$, was formed. In addition, the peak current increased proportionally with n in PB_n films, confirming again the quantitative PB deposition on the substrate by the SIA process. In situ UV-Vis spectra during the CVs were also investigated. The absorption around 710 nm due to IVCT of PB was changed with the potential sweep as shown in Figure 3b and it was reproducibly observed up to 20 multiple scans (+1.3 V ⇔ −0.3 V). These results indicate that the SIA-derived PB films show a stable electrochromism (coloring dark blue around +0.5 V and bleaching around +1.3 V and −0.3 V).

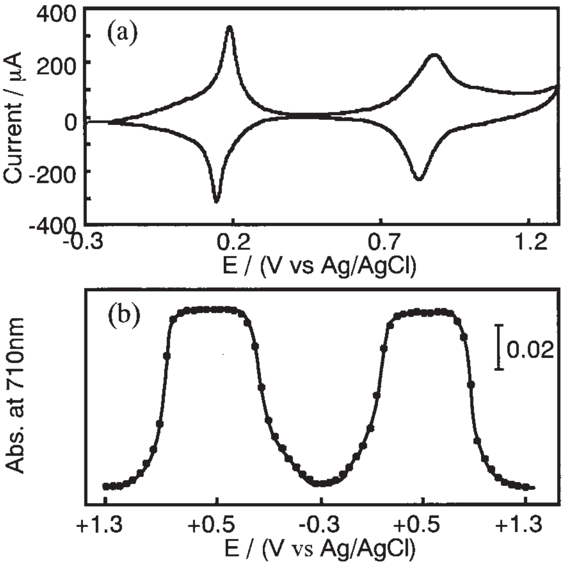

Figure 3. (a) Cyclic voltammogram (CV) of ITO/PB_{10} and (b) absorbance change at 710 nm in ITO/PB_{10} during the CVs, in aqueous 0.1 M KCl (pH 6.5) with a scan rate of $10\ mV{\cdot}s^{-1}$.

The adapted SIA technique is in principle applicable to synthesis of a variety of polynuclear transition metal cyanides. In addition, multilayer films composed of Prussian blue and organic polyelectrolyte layers can be also prepared by coupling with alternate adsorption technique. Therefore, the present study can contribute to a chemistry of Prussian blue analogues as well as a development of functional devices hybridized between Prussian blue analogues and organic materials.

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