Controlled Growth of Polypyrrole Thin Films by Polymerization-induced Adsorption

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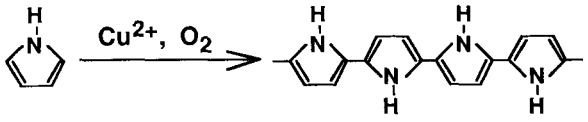
Ultrathin polypyrrole films with a nanometer thickness were prepared by repeating adsorption of polypyrrole from the polymerizarion solution and washing with organic solvents. The thickness of the polypyrrole film linearly increased by using fresh polymerization mixtures at each adsorption step, as confirmed by quartz crystal microbalance and UV spectroscopy.

Fabrication of thin films of conductive polymers is one of the key techniques for designing a wide range of functional materials. Several different methodologies have been studied for this purpose. Electrochemical deposition, spin-coating, and water casting[1] belong to well-known conventional techniques. The first technique is, however, restricted to deposition on conductive materials, and gives films with sub-micron surface roughness.[2] The latter two methods need high solubility of polymers in organic media, and this is not the case for many conductive polymers.

On the other hand, molecular films of conductive polymers have been prepared by build-up of monolayer of long-alkyl derivatives of pyrrole at the air-water interface and subsequent chemical[3] and electro-chemical[4] polymerization. They are also obtainable by extention of alternate adsorption of oppositely-charged polymers[5] to water soluble conductive polymers.[6] These techniques enable us to control the film thickness at nanometer precision. However, additional substituents such as alkyl chains and charged groups that are required for molecular build up often give rise to undesirable properties.

Recently, we found that ultrathin polypyrrole films were formed by direct adsorption from polymerization media and subsequent washing, as monitored by quartz crystal microbalance (QCM). We report herein this polymerization-induced adsorption as a novel technique for layer-by-layer deposition of polypyrrole thin films at nanometer scale.



A gold-coated QCM resonator (9 MHz) was modified with 3-mercaptopropionic acid,[7] and subjected to alternate adsorption of poly(ethylenimine) and poly(styrenesulfonate) to form a smooth precursor layer.[8] The resonator was placed in a pyrrole solution (5 vol% in 2-propanol, 2 mL), and $CuCl_2 \cdot 2H_2O$ dissolved in 2-propanol (10 mg/mL, 100 μL) was added at 20 °C. The resonator was taken out of the reaction mixture at 5 min intervals, washed with methanol, dried by N_2 gas flushing, and immersed again into the reaction mixture within 1 min after measurement of frequency (Figure 1a).

Figure 1b shows QCM frequency shifts (ΔF) during the course of polymerization using the same polymerization mixture. The frequency decreased with repeated immersion and

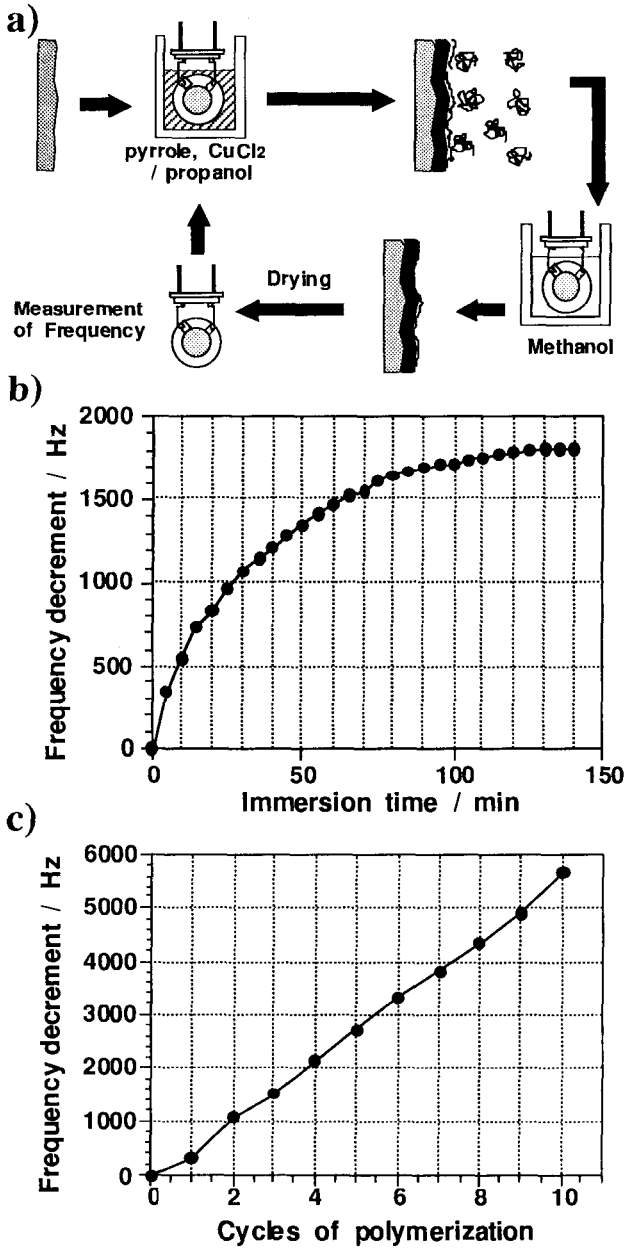


Figure 1. Schematic illustration of polymerization induced adsorption (a), time course of QCM frequency shifts within a single series of polymerization (b), and QCM frequency shifts with cycles of polymerization where the polymerization mixture was renewed at each adsorption cycle (c).

became unchanged after 2 h at a shift of 1800 Hz. The ΔF value is proportional to the polypyrrole mass adsorbed on the

electrode. Adsorption of polypyrrole is fast at the initial stage of polymerization, but it does not occur when the resonator is dipped for more than 2 hrs in the identical polymering solution in which pyrrole has been used up. ΔF value of 1800 Hz corresponds to a film thickness of 33 ± 5 nm, using the density of 1.5 ± 0.2 g/cm^3.[9]

Further adsorption of polypyrrole was achieved reproducibly by renewal of the reaction mixture at each adsorption. The frequency shifts are shown in Figure 1c, where a QCM resonator with the PEI/PSS precursor film[10] was immersed for 10 min into freshly prepared solutions of pyrrole and $CuCl_2$ up to 10 cycles. Linear frequency changes observed here point to regular film growth of polypyrrole at nanometer scale. The frequency change was 580 ± 210 Hz except for the first cycle. This value corresponds to a thickness increase of 12 ± 5 nm, using the above-mentioned density (1.5 g/cm^3). The ΔF value for one cycle is controllable by selection of the concentration of the reaction mixture and immersion time. For example, the frequency change was 142 ± 76 Hz for a polymerization solution of 2 vol% pyrrole (1.5 mL) and $CuCl_2$ (10 mg/mL, 100 μL) with an immersion time of 5 min.

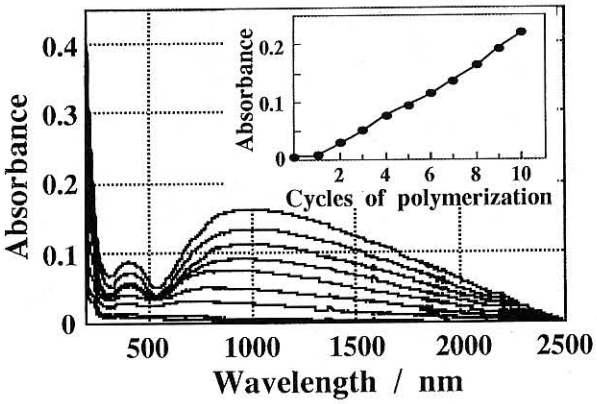


Figure 2. UV-Vis-NIR absorption change with growth of polypyrrole film (polymerization solution: pyrrole; 5 vol% in 2-propanol, $CuCl_2$; 5.3 mM, 20℃). The insert shows the absorbance change at 1002 nm. The precursor layer was formed from poly(allylamine) and PSS.

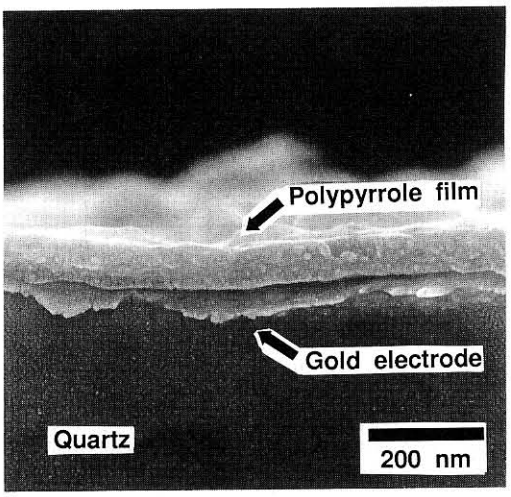


Figure 3. Scanning electron micrograph of a polypyrrole film on Au-coated resonator. Total frequency shifts: 6215 Hz.

Figure 2 shows UV-Vis-NIR spectra of polyprrole films adsorbed onto a quartz plate. The absorbance at 1002 nm linearly increased with adsorption cycles. An FT-IR RAS spectrum of the film prepared on a gold-coated glass plate gave two characteristic peaks of polypyrrole at 1572 and 1493 cm^{-1}.[11] XPS Spectra showed that copper atoms used as oxidation catalyst were incorporated into the film in a ratio of pyrrole : Cu = 9 : 1.

Figure 3 shows a scanning electron micrograph of the cross section of a polypyrrole film deposited onto a gold-coated QCM resonator. The film has a uniform thickness of 90 ± 10 nm with scattered dome-like structures of ca. 40 nm height. The average film thickness becomes 110 nm. The corresponding total frequency shift was 6215 Hz. These data were used for estimation of film density. The high density observed (1.5 g/cm^3) suggests that polypyrrole chains are densely packed in the film, though the correction for copper ions must be made.

Sano and co-workers reported that many kinds of polymers were epitaxially adsorbed on the basal plane of graphite.[12] The growing polymer chains are strongly and epitaxially adsorbed at the graphite surface, but not polymers formed in bulk solution. This phenomenon of the polymerization-induced epitaxy has a common feature with the present observation in that only the growing polymer chain is adsorbed on the solid surface. However, the nature of precursor layers is not crucial to adsorption and there is no evidence for epitaxy.

We demonstrated here that the polymerization-induced adsorption is a novel technique for the preparation of ultrathin polypyrrole films. This technique must be a useful tool for design of polymer thin film, if it is extended to a wide range of functional polymers.

References and Notes

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9 We estimated the density from the film thickness of 110 ± 40 nm observed by scanning electron microscopy (Figure 3) and the corresponding QCM frequency shift of 6215 Hz, as described in the text.
10 Adsorption of polypyrrole was not effected by the type of the precursor layer except for the first adsorption.
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