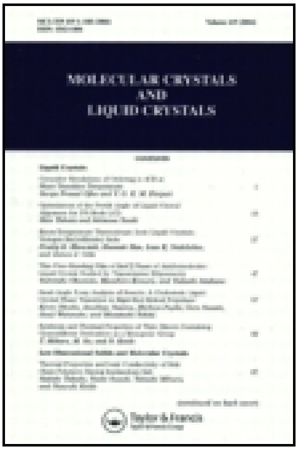

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Film Structure-Induced Resonant Oscillation Changes in a Poly Acrylic Acid Modified Quartz Crystal Sensor

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Film Structure-Induced Resonant Oscillation Changes in a Poly Acrylic Acid Modified Quartz Crystal Sensor

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A poly acrylic acid (PAA) film has been fabricated on a quartz crystal microbalance to study the dynamic property changes induced by different pH values. The experiment has been performed by a two-step. First, using the self-assembly procedure, the gold surface of quartz crystal was chemically modified to allow the graft copolymerization with PAA. Secondly, the resonant frequency response of the PAA-modified QCM was investigated by varying the pH values. The result shows an interesting oscillation property change nearby pH 5.5, and a possible mechanism for the change is proposed considering the oscillation properties of quartz crystal and the physical properties of PAA. Finally, a polymer film complex of PAA/collagen was also used to confirm the proposed mechanism.

Keywords: collagen; pH effect; poly(acrylic acid); QCA; QCM

1. INTRODUCTION

The advantages of conceptual simplicity, relative ease of modification, chemical inertness of the substrate, low cost and ready availability of piezoelectric quartz crystals have encouraged the development

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of various analytical applications. For example, quartz crystal microbalance (QCM) has been used in immunoassay [1], phase transition phenomenoa of liquid crystals [2] and polymer blends [3], electrochemistry [4] and other various sensors [5] using the relation between the resonant frequency and the mass change.

The resonant frequency of the quartz crystal in contact with liquid has been derived as follows [6]:

$$\Delta F = -F^{3/2}(\rho_L \eta / \pi \mu \rho_Q)^{1/2}$$

Where ΔF is the resonant frequency shift, F is the resonant frequency, μ and ρ_{Q} are the shear modules and the density of quartz crystal, η is the liquid viscosity and ρ_{L} is the liquid density.

But the resonant frequency of the quartz crystal can be also changed by various additional factors such as roughness, mass-loading, hydrophilicity/hydrophobicity especially in liquid environment [7]. These topic-related results still requires more exact interpretation because there are many unsolved questions for QCM experiments.

Polyelectrolyte is the term used to classify macromolecules that have many charged or chargeable groups in a polar solvent. Because of the potential applications in smart catalyst separation technologies, controlled drug delivery and release, polyelectrolytes have become one of the key knots in connecting material science, biochemistry and polymer science [8,9]. One of the polyelectrolytes, poly acrylic acid (PAA) and its block copolymers, have been widely used in the construction of organic–inorganic hybride materials, nano structured materials, and self-assembled materials.

In this work, we investigate the dynamic property change of a PAA film with respect to pH values using the QCM technique. We discuss the possible resonant oscillation change induced by the film-structure change using a PAA-modified quartz crystal.

2. MATERIALS AND METHODS

2.1. Instruments

A 9 MHz AT-cut quartz crystal (dimension:$8 \times 8 \times 0.18$ mm) was prepared by forming a pair of gold electrode (thickness about 2500 nm) on both sides of quartz crystal by a sputtering technique with Ti under layers (thickness about 5 nm). In order to remove chemical impurity of the electrode, the quartz crystals were immersed in deionized water for 10 min, and then, were washed continuously in acetone and ethanol for 10 min. The pretreated quartz crystals were dried at room temperature, and the resonant frequency was measured by a quartz crystal analyzer (QCA 917, Seiko Instruments Inc.).

2.2. Surface Modification and PAA Graft Polymerization

The quartz crystals were immersed in toluene containing a 2 wt. % of (3-mercaptopropyl)-trimethoxysilane (Fluka, japan) for 1 hr to fabricate a self assembled monolayer prior to PAA graft copolymerization. (3-mercaptopropyl)-trimethoxysilane of about 300 ng was assembled on the quartz crystal, which was calculated from the simple measurement of the resonant frequency difference before and after assembly. After the assembling, the graft copolymerization with acrylic acid (M_W: 250,000, Fluka, Japan) was performed in a 10 wt.% aqueous acrylic acid solution (100 ml) with the addition of a 1 ml portion of N, N, N′, N′-Tetramethyl-2-butene-1,4-Diamine(Aldrich). The reaction was performed at 50°C in a nitrogen gas environment for 1 hr. After the reaction, the quartz crystal was washed with toluene for 1 hr to remove any graft-free polymer on the surface. The washing process was been carefully performed in a toluene solution by applying the agitating speed of 3000 rpm. The removal of the graft-free polymers was confirmed by a stability test of the polymer coated quartz crystal in a toluene solution. When the graft-free polymers were fully removed, the stability of the resonant frequency was measured sub-±25 Hz/h. In the case of the quartz crystal just after the graft polymerization, the stability of the resonant frequency maintains about ±100 Hz/h. The amount of graft polymerization (5.7 μg) was also calculated by the same measurement technique with the self assembly. The detailed mechanism and procedure of the graft polymerization are well documented in a previous report [8].

Using the PAA modified quartz crystals, the dynamic property changes of the PAA film with respect to pH values were investigated through an experimental setup shown in Figure 1. After the quartz

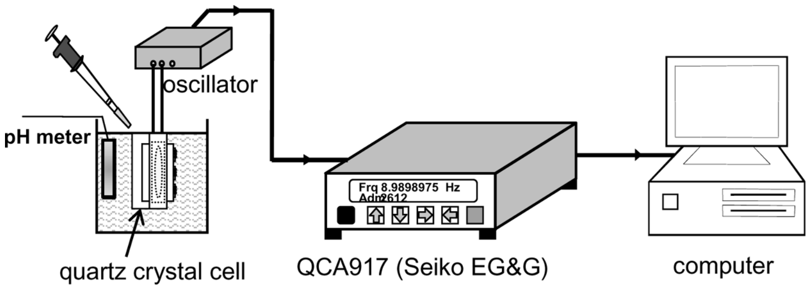
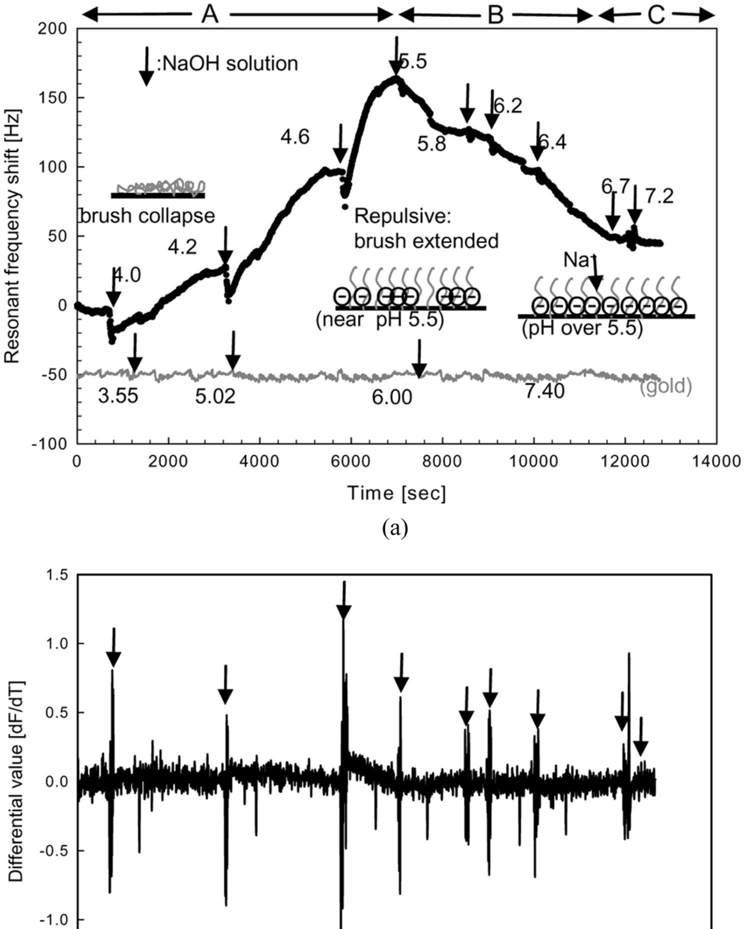


FIGURE 1 A schematic diagram for the experimental system.

crystal was immersed in deionized water, the pH value required in this experiment ($4 < \text{pH} < 7$) was adjusted using HCl and NaOH solutions, and resonant frequency was monitored to investigate the mechanism occurred in the film by the pH variation. As a support experiment for the dynamic property change of the film, we have investigated a PAA-collagen film complex using the same method. For this experiment, type I collagen from calf skin (Sigma Chem. Co.) was used. The sample preparation of the PAA-collagen film was followed by the previous report [8].

3. RESULT AND DISCUSSION

Figure 2a shows the resonant frequency shift of a bare and a PAA modified quartz crystals in different pH values. For easy explanation, the resonant frequency shift of the bare gold crystal is artificially shifted in Figure 2a. As shown in Figure 2a, any noticeable frequency shift of the bare quartz crystal is not obtained in the used pH range. In the case of the PAA-modified quartz crystal, the resonant frequency is dynamically changed by the injection of a NaOH solution (10 mM, 1 μl) as shown in Figure 2a. In the first injection of the NaOH solution (pH 4.22), the resonant frequency is slightly increasing. This tendency is continuously obtained when the solution pH value reaches to about 5.5 (region 'A'). From this point, the injection of the NaOH solution decreases the resonant frequency. As shown in the Figure 2a, the pH value of 5.5 can be an interesting point for the film property changes. Nagasawa *et al.* [10] have reported that the ionization degree of PAA is about 0.8 at $\text{pH} = 6$ where as 0.5 at $\text{pH} = 4$, in other words, most of the carboxyl groups of PAA are in the COO^- form at $\text{pH} = 6$. *i.e.* the net charge of the PAA molecule is strongly negative. Thus in the region 'A', the injection of the NaOH solution increases the negative charge density of the PAA molecules, and the static charge interactions between the neighbored PAA molecules are changed to a strong repulsive interaction by the accumulation of the injection. In this way, each PAA molecule changes its structure of the brush collapse state (general in lower pH) [8], and brush extended PAA molecules are possibly induced by the injection of the NaOH solution. This phenomenon is similar with the brush shape of short DNA molecules in liquids. Because the DNA molecules have a strong negative charge in liquids, DNA molecules shows a brush extended shape in a liquid phase by a static charge interaction between them. The extended polymer chain has the effect of mass unloading whereas the collapsed PAA structures produce a mass loading effect because the mass sensitivity of QCM directly relates to the bulk wave



(a)

(b)

FIGURE 2 Resonant frequency response of the quartz crystal by the continuous injection of the NaOH solution (a), and the differential values of the resonant frequency response (b). The response of the bare gold quartz crystal is artificially shifted to about −50 Hz in (a).

propagation distance (sub-micron) [7]. Thus, a continuous increase of the resonant frequency is obtained in the region 'A' by the decrease of the QCM mass sensitivity. Because the chain end of the PAA molecules is strongly attached on the quartz crystal by the graft-copolymerization, the removal of the PAA does not occur in the region 'A'. In the region 'B' ($5.5 < \text{pH} < 6.7$), the resonant frequency is decreasing by increasing pH values. It seems that two possible mechanisms are involved in current result [7]. First, Gerlach *et al.* [12] have investigated the possible transportation of hydroxide ion into the film structure in a acidic solution. In a similar way, the Na cation can be parted in the transportation because the PAA molecule is strongly negative net charge in the region 'B'. Thus, more injection of NaOH solution produces more negatively charged PAA. Thus the transportation of the cation can be continuously induced by a charge compensation process. In this way, the gradual decrease of the resonant frequency is induced by increasing the pH values. When the pH value reaches over 6.7 (region 'C'), further change in resonant frequency is not obtained. This means almost neutral PAA/Na complexes are finally achieved by the charge compensation process. For easy understanding, we have calculated the differential values of Figure 2a, and the results are represented in Figure 2b. Normally, the differential value is changed when an additional mechanism is involved in the resonant frequency change [7]. As shown in Figure 2b, the differential values show a clear change near by $\text{pH} = 5.5$, thus imply a different mechanism compared with other areas is involved in the film property change [3].

Figure 3 shows a resonant frequency response of the PAA modified quartz crystal by the addition of collagen with the continuous injection of a HCl solution (10 mM, 1 μl). In the case of the PAA-collagen system, a static charge interaction occurs to form a polyion complex when the two molecules are oppositely charged. In Figure 3, the resonant frequency does not show noticeable changes until the pH value reaches to 5.5 (region 'A'), and then, more addition of the HCl solution makes the resonant frequency a noticeable decrease (region 'B'). Further addition of the HCl solution at $\text{pH} = 4.9$ makes a large recovery of the resonant frequency (region 'C'). These three steps are interesting, because the isoelectric point of collagen ($\text{pI} = 5.5$, Manufactor's confirmed value) locates in the position of the changes.

In the region 'A', pH value over 5.5, the PAA molecule has the brush extended shape with a strong negative net charge as described previously. Considering the pI value of collagen, both the PAA and collagen molecules have the strong negative net charge, and the attractive interaction between the two molecules is difficult in the region 'A'. In the region 'B', the PAA molecule has a negative net charge (ionization >0.5) whereas collagen changes to a positive net

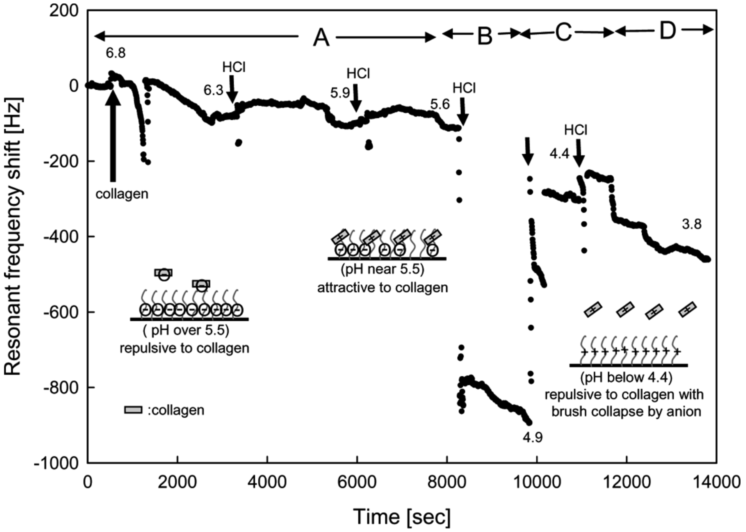


FIGURE 3 The resonant frequency response of the PAA-modified quartz crystal with the addition of collagen. In the region ‘B’, a noticeable frequency change implies the PAA/collagen formation induced by a attractive static charge interaction.

charge because of the isoelectric point. Thus, the amino group of the collagen changes to NH_3^+, and the binding with the PAA molecules can be accomplished. The binding quantity of the collagen molecules can be easily calculated by considering the molecular weight of the collagen (300 kDa). Assuming the elastic film formation on the quartz crystal, the resonant frequency change means the mass change of about 800 ng in the region ‘B’. Thus, the adsorbed quantity of the collagen is approximately estimated as 2.6×10^{-2} M. In the region ‘C’, both the molecules are now changed to a positive net charge, thus a repulsive force between the two molecules makes the separation of the two molecules. In this way, the increase of the resonant frequency is also observed in the region ‘C’. In the region ‘D’ (pH < 4.4), Because the charge polarity of the PAA molecules are changed to a positive net charge, a charge compensation process by Cl anion and the collapse of the brush extended shape are made to form a PAA/Cl complex. In this step, the resonant frequency change is slightly bigger than that of the charge compensation process in Figure 2 (region B). Thus, the collapse of the brush shape can be additional point because the complex is now a neutral net charge by the charge compensation process with the separation of collagen.

4. CONCLUSION

In this work, the effects of pH values on the PAA films and the mechanism for the resonant frequency changes were investigated by the QCM technique. The results showed that the PAA chains were extended in maximum at pH 5.5 and large amount of collagen was absorbed on the extended PAA molecules at the same pH value. Thus we showed the morphological influence on the resonant frequency change of the quartz crystal.

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