Grafting of phenylboronic acid on a glassy carbon electrode and its application as a reagentless glucose sensor

Grafting of phenylboronic acid on a glassy carbon electrode and its application as a reagentless glucose sensor

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Abstract

Phenylboronic acid (PBA) was covalently grafted to the surface of glassy carbon (GC) electrodes using electrochemical reduction of *in situ* generated diazonium cation. The grafting of GC surfaces was controlled by varying both the concentration of precursor 3-aminophenylboronic acid and the number of potential cycling during the grafting procedure. Cyclic voltammetry (CV) and eletrochemical impedance spectroscopy (EIS) were used to confirm the grafting of the PBA group to the GC surface and formation of multilayer. The barrier properties of the grafted GC electrodes were studied in the presence of a redox probe such as $Fe(CN)_6^{3-/4-}$ by CV. Additionally, the resultant PBA multilayer on the GC electrode was applied for glucose detection utilizing the EIS technique in the presence of a redox probe molecule. Then, the complexation ability of the grafted layers with glucose was also confirmed as an increase of total impedance at non-faradic EIS measurement.

Keywords: *in situ* generated diazonium cation, glassy carbon, impedance spectroscopy, phenylboronic acid, glucose

1. Introduction

Surface modification of a solid electrodes has been paid much attention to confer the chemical functionality to the solid electrodes for applications in chemical and bio-sensors, catalysis, and electronic devices [1]. Several modification methods of a carbon electrodes have been extensively studied [2] and generation of carboxylic acid groups by oxidation of the carbon surface has been one of frequently used methods. However, this method requires strong chemical and/or electrochemical oxidation steps in the pretreatment procedures, which often results in severe surface roughness [3].

Recently, electrochemically assisted covalent modification methods have proved to form a stable organic layer successfully on the carbon electrode [4]. In general, these methods use an electrochemical generation of radicals, followed by formation of covalent bonds between the radicals and the carbon electrode surface. Radical species can be generated by an electrochemical oxidation of aromatic amines [5] or aliphatic amines[6], and reduction of aryl diazonium salts [7]. Among them, reduction of diazonium salts can be achieved by either in acetonitrile[8] or aqueous acid solutions[9] and is easily and rapidly carried out in one step, and the reduction method is applicable to a wide variety of aromatic amines many of which are commercially available [10]. The modification of surfaces by electrochemical reduction of diazonium salts can be applied to carbon [11], metals [12] and semiconductors [13]. Additionally, an aromatic amine can be transformed into a diazonium cation by a standard diazotization procedure in an aqueous acidic solution in the presence of $NaNO_2$ and that the resulting solution can be directly used to modify carbon[14, 15] or gold[16] electrode by electrochemical reduction. Another interesting feature of this method is that high reactivity of aryl radicals enable to give a multilayered structure by attacking phenyl moieties on the pregrafted groups [17, 18]. The continuous generation of radicals generally leads to the formation of the multilayer structure because the radicals can be added not only to the surface carbons but also to the already immobilized molecules. For aryldiazonium salts and

cations, a sort of a polyphenylene structure is formed and the exact structure depends both on the substituents present in the aromatic ring and on experimental conditions used during the electrochemical grafting. Utilizing the multilayer formation, Downard and co-workers [19, 20]prepared micropatterned organic films and microcontact printings on carbon surfaces.

The covalent bond between the modifier and the electrode surface is particularly attractive for construction of chemical-sensor or bio-sensor due to its expected stability in several measurement conditions such as pH and temperature. Additionally, the grafting procedure offers the opportunity of multilayer formation resulting in condensation and integration of recognition sites on the electrode surface. This is in contrast to the self assembly of alkanethiols on Au where a single bonding functionality is solely available. We describe here initial investigations of the formation of covalently grafted multilayers on GC electrodes as chemical- or bio-sensor usage. The purpose of this work is to examine the multilayer formation *via* electrochemical reduction of the *in situ* generated diazonium cation of 3-aminophenylboronic acid (3-APBA) at glassy carbon electrode surfaces in an aqueous acid solution and to demonstrate the utilization of the multilayered structure for the sensory usage. The degree of multilayer formation was controlled by the concentrations of precursor 3-APBA and the number of potential cycling during grafting procedure. Cyclic volammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterize the grafted electrodes. Phenylboronic acid (PBA) group was chosen as the substituent of phenyl ring because complexation between boronic acids and diol molecules is one of the strongest interactions in an aqueous environment that can be readily used for the construction of glucose sensor.

2. Experimental

2.1. Reagents and equipments

3-Aminophenylboronic acid (3-APBA) and other chemicals were purchased from Wako Pure Chemicals Industries (Tokyo, Japan) and were used as received. All aqueous solutions were prepared using Milli-Q water (Millipore Corp., Bedford, MA). Prior to use, all solutions were deoxygenated by purging N_2 gas for at least 10 min and all measurements were carried out under a N_2 atmosphere. Electrochemical measurements were carried out using a electrochemical analyzer (model 650A, BAS, Tokyo, Japan) with a standard three-electrode configuration. A platinum wire (99.98%, Nilaco, Tokyo, Japan) and an Ag/AgCl (sat. KCl) reference electrode (BAS, Japan) were used as the counter and reference electrodes, respectively. A glassy carbon electrode (GC, 3 mm diameter, BAS, Japan) was used as the working electrode. Before each experiment, GC electrodes were polished successively by 1.0 and 0.05 μm alumina slurries (Buehler, Lake Bluff, IL) with Milli-Q water on polishing cloths (Buehler). After polishing, the electrodes were rinsed with Milli-Q water several times and sonicated in Milli-Q water three times for 20 s each.

2.2. Electrode grafting procedure

A schematic illustration of the grafting phenylboronic acids to the glassy carbon electrode is shown in Figure 1. Precursor 3-APBA was dissolved in a 1 M HCl solution at 4 °C, then an ice-cold $NaNO_2$ (5 equiv.) aqueous solution was added. After stirring the mixture for 10 min at 4 °C, a GC electrode was immersed into the mixture and the potential cycling was carried out from the positive potential limit (Fig. 2A). Several grafting conditions were performed for a series of precursor 3-APBA concentrations ranging from 1 to 20 mM and numbers of potential cycling ranging from 1 to 30. Hereafter, the grafted electrode is denoted as [*m, n*]PBA/GC, where *m* is the concentration (mM) of precursor 3-APBA in the reaction mixture, *n* is the number of potential cycling during grafting procedure. The resultant [*m, n*]PBA/GC electrode was thoroughly rinsed with Milli-Q water several times and sonicated in Milli-Q water three times for 20 s each.
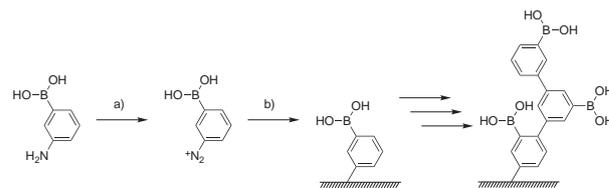
Figure 1: Schematic illustration of the grafting of the GC electrode by the electrochemical reduction of *in situ* generated 3-APBA diazonium cation. a) 5 eqiv. $NaNO_2$, 1 M HCl, 4°C; b) potential cycling between +0.6 and -0.4 V vs. Ag/AgCl, 4°C, formation of submonolayer to multilayer structures dependent upon the grafting procedure.

2.3. Electrochemical measurements

To investigate the apparent acid dissociation constant (pK'_a) of the phenylboronic acid group on the [*m, n*]PBA/GC surface, $Fe(CN)_6^{3-/4-}$ redox couple was used as a probe molecule. To adjust pH values of aqueous

solutions from 2 to 10, a Britton—Robinson buffer solution was used, in which adequate amounts of 1 M KOH solution were added to a solution containing 10 mM acetic acid, 10 mM boric acid, and 10 mM phosphoric acid. To adjust pH values between 1 and 2, dilute HCl solutions were used. The ionic strength of the buffer solutions was adjusted by using 0.1 MKCl. CV and EIS measurements were carried out at room temperature (25 $\pm$ 1 °C).

3. Results and discussion

3.1. Grafting of in situ generated diazonium cation by electrochemical reduction to GC surface

Fig. 2A shows the CVs for the reduction of diazotized 3-APBA in the reaction mixture containing 20 mM 3-APBA and 100 mM NaNO$_2$. A broad irreversible cathodic peak is observed at around +0.0 V in the first cycle. The peak current gradually decreases according to the further potential cycles and reaches a steady state after 30 cycles, reflecting the formation of the PBA layer on the GC surface and the progressive blocking of the electrode [21]. Fig. 2B shows the peak current intensity in the first cycle as a function of the concentration of precursor 3-APBA. It is easily recognized that the peak current intensity monotonically increases and reaches a constant value at around 20 mM.

These voltammetric behavior show the characteristic features of electrochemical reduction of aryl diazonium cations at carbon electrodes [22]. The decrease of the cathodic current indicates that progressive passivation takes place as a consequence of the PBA layer grafting. Although the current is very small, the observation of current in further cycling implies that the formation of PBA layer is not complete after one cycle, and its gradual growth can be expected. Kullapere et al. [23] used electrochemical quartz crystal microbalance to observe a total mass change for a Au electrode during 10 repetitive cycles in the presence of 4-bromobenzenediazonium salt. They found that an increase in mass is observed for the first cycle and a gradual mass increase is also observed on further cycling. Consequently, the gradual mass increase indicates the further growth of the grafted layer (i.e. multilayer growth). Additionally, in the absence of NaNO$_2$, no cathodic peak was observed in the same potential range under the present experimental conditions. It can be, therefore, concluded that the 3-APBA is successively diazotized in the reaction mixture and the PBA layer is covalently grafted on the GC electrode surface.
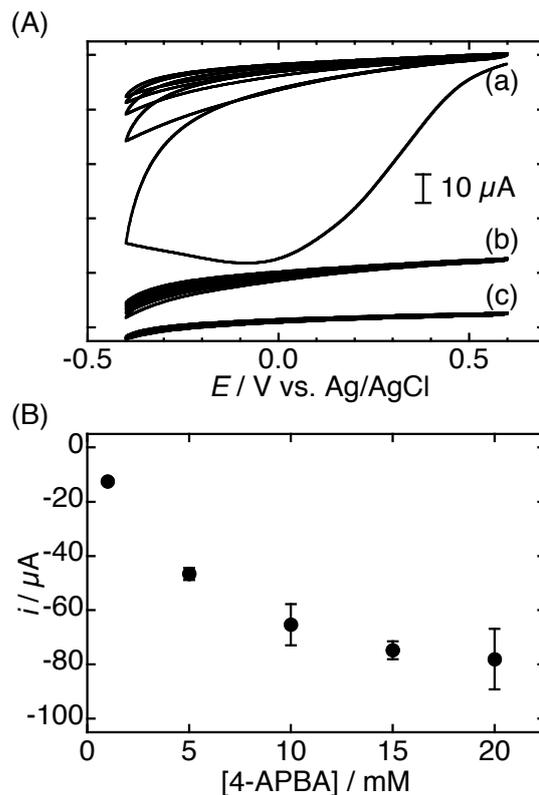
Figure 2: (A) Cyclic voltammograms at a GC electrode immersed in the reaction mixture (20 mM 3-APBA, 100 mM NaNO$_2$ and 1 M HCl). Scan rate = 0.1 V s^{-1}, Temperature = 4°C. (a) 1 - 5 th cycles, (b) 6 - 10 th cycles, (c) 26 - 30 cycles. (B) Peak current intensity for reduction of diazotized 3-APBA as a function of the concentration with an average of three different electrodes.

Furthermore, the formation of the multilayered structure is assessed from the voltammetric behavior shown in Fig. 2A.

3.2. Effect of grafting conditions on the electron transfer kinetics in an $Fe(CN)_6^{3-/4-}$ acidic solution

The grafted PBA layer on the GC electrode surface can be examined by the voltammetric peak separation (ΔE_p) of a redox system. Fig. 3 shows the series of CVs recorded using [5,n]PBA/GC electrodes in a solution of 1 mM K$_3$Fe(CN)$_6$ in 0.1 M KCl buffered at pH 2, where [5, n] denotes the PBA layer formation conditions of 5 mM 3-APBA and the potential cycling number of n as described in Section 2. In this experiment, weak acidic condition was employed to exclude the contribution of charge-charge repulsion between the surface PBA groups and Fe(CN)$_6^{3-/4-}$ as discussed later. A voltammogram for Fe(CN)$_6^{3-/4-}$ redox

system on [5,1]PBA/GC is shown in Fig. 3 (a), where small peak separation, ΔE_p (71 mV), is recognized, indicating fairly rapid electron transfer. Subsequent cycles ($n = 5$—20) during the grafting procedure have a significant effect on ΔE_p values from 92 mV to 504 mV summarized in Table 1. The increase in the ΔE_p value reflects a significant decrease in the electron transfer rate from the bare GC electrode due to the blocking by the grafted PBA layer. Based on the treatment of the relationship between ΔE_p and the heterogeneous electron transfer rate constant ($k°$) by Nicholson [24], an increase in ΔE_p from 71 to 504 mV implies a decrease in $k°$ by a factor of *ca.* 3 orders of magnitude. Under higher precursor 3-APBA concentration conditions, the barrier effect was too intense to observe clear voltammetric peaks of $Fe(CN)_6^{3-/4-}$ redox couple.

Similar results were reported by Kariuki and McDermott [25] who utilized electrochemical and scanning probe microscopic techniques to track multilayer formation. They reported that longer electrolysis time of diazonium salt yielded larger ΔE_p for several redox systems in CV, and that the formation of thick films with an average of 20 nm was observed by scanning force microscope. Therefore, the increase in ΔE_p can be ascribed to the PBA groups grafted on the electrode surface, and the dependance of ΔE_p on the number of potential cycling and the concentration effect of precursor 3-APBA indicate the formation of the multilayered structure.
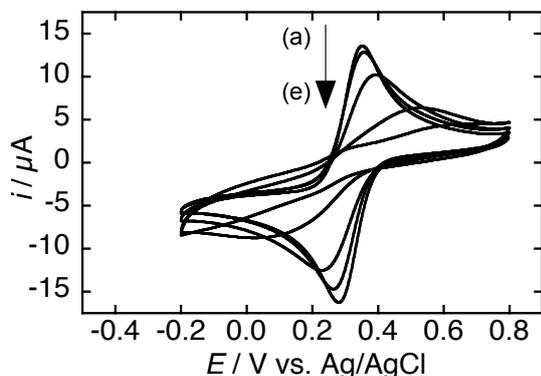
Figure 3: CVs of 1 mM $K_3Fe(CN)_6$ in 0.1 M KCl (pH 2) on [5,*n*]PBA/GC varying *n* during grafting procedure. Scan rate = 0.1 V s^{-1}. (a) - (e) n = 1, 5, 10, 15, and 20, respectively.

3.3. Determination of pK_a' for grafted PBA groups

The surface pK_a' value of the PBA group grafted to the GC electrode surface was examined by utilizing attenuation of the redox response of the charged probe

Table 1: ΔE_p, $k°$ obtained for [5,*n*]PBA/GC in 0.1 M KCl aqueous solution (pH 2) and pK_a' determined by electrochemical titration

n	ΔE_p / mV	$k°$ / cm s^{-1}	pK_a'
1	71	2.1×10^{-2}	5.1 ± 0.1
3	–	–	4.9 ± 0.1
5	92	6.6×10^{-3}	4.4 ± 0.1
10	163	1.8×10^{-3}	3.9 ± 0.1
20	504	$\ll 10^{-4}$	4.1 ± 0.1

molecules [26]. Fig. 4A shows the CV response of $Fe(CN)_6^{3-/4-}$ at the [5,1]PBA/GC electrode under different pH conditions. The redox response of $Fe(CN)_6^{3-/4-}$ is attenuated clearly as the pH value of a solution increases. It is well known that the redox response of a charged probe molecule is attenuated when a charged layer on the electrode surface possesses the same charge as the probe molecule [27]. Hence, observed pH dependent redox response can be ascribed to the electrostatic repulsion between $Fe(CN)_6^{3-/4-}$ and the negatively charged PBA groups on the electrode surface. The decrease of the current response in CVs was used to estimate the pK_a' value of the grafted PBA group. From the definition of the pK_a in a bulk solution, the surface pK_a' value can be defined from the acid-base equilibrium of the surface functional groups. According to the assumption in the literature [28], the peak current of the probe molecule at the modified electrode was plotted against the pH value of a solution and the surface pK_a' value was deduced. The surface pK_a' value for each [5,*n*]PBA/GC was determined by averaging the results obtained from the responses of three different electrodes and results are summarized in Table 1. The surface pK_a value of the PBA group on the [5,1]PBA/GC electrode was estimated as 5.1 ± 0.1 by the best fit of the data in Fig. 4B and the pK_a' values for [5,*n*]PBA/GC show a negative shift as the cycling number *n* increases.

It was reported that the pK_a values are 8.8 and 9.2 for phenylboronic acid in solution [29] and 4-mercaptophenylboronic acid self-assembled monolayer on a gold electrode [30], respectively. Several factors can be invoked to explain the shift of the pK_a value of an immobilized molecule on a substrate surface compared to its bulk pK_a in solution and their possible combinations as well as the unknown structure of the surface grafted layer make it difficult to provide a definitive explanation for the phenomenon observed in the present work. Saby *et al.* [31] demonstrated the shift of the pK_a value to a lower value upon grafting the 4-carboxyphenyl group at the surface of a glassy carbon electrode. They pointed out that some specific interfa-

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(A)

(B)
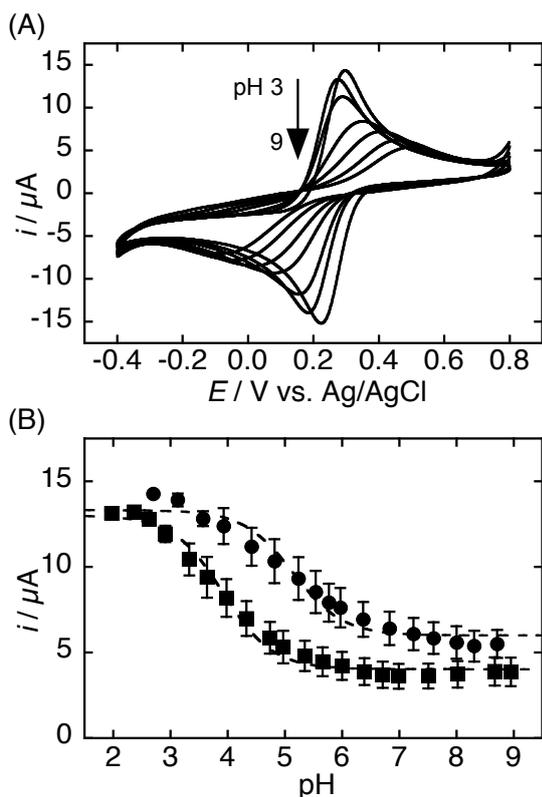
Figure 4: (A) CVs of 1 mM $K_3Fe(CN)_6$ for [5,1]PBA/GC electrode under several pH conditions. Scan rate = 0.1 V s^{-1}. (B) Plot of the anodic peak current of the CVs as a function of the solution pH. CVs were recorded at the [5,1]PBA/GC (solid circle) and [5,10]PBA/GC (solid square) in a solution containing 1 mM $K_3Fe(CN)_6$ and appropriate buffer.

cial effects between the carbon surface and the carboxylate functionalities or the phenyl ring of the layer might play an important role.

Burke and Barrett [32] observed that, in the case of polyelectrolyte layer-by-layer films, the pK_a value of the surface amino group was positively shifted whereas it was negatively shifted for the surface carboxylic group. Moreover, they found that both the acid strength of poly-(acrylic acid) and the base strength of poly(allylamine hydrochloride) increase as the total number of layers in the films increases. This behavior is similar to that observed in the present work, and Burke and Barrett [32] attributed it to inhomogeneous polyelectrolyte coverage or to the influence of the silica substrate. At this moment, mechanistic details are not known for the pK'_a shift found in this study. It is reasonable to assume, however, that negative shift of pK'_a is favorable for glucose detection using the PBA group as a recognition site.[33] It has been commonly believed that the higher the pH, the higher the binding affinity between a boronic acids and diol molecules. It is also expected that boronic acids with lower pK_a values have higher affinities toward sugars. [29] Indeed, there is considerable interest in developing synthetic receptors based on a PBA moiety having lowered pK_a. [34, 35]

3.4. Faradic impedance measurements for PBA/GC in the presence of probe molecule

To elucidate the affinity of PBA/GC electrodes toward glucose, EIS measurements were carried out in the presence of 1 mM $K_3Fe(CN)_6$ at different pH conditions. The EIS plots for [5,5]PBA/GC at pH 3.5 are shown in Fig. 5A and the plots give a typical shape, with a semicircle in the high-frequency domain characteristic of an interfacial charge-transfer mechanism and a straight line with near unity slope in the low-frequency domain characteristic of a semiinfinite diffusion phenomenon. Upon addition of glucose, an increase is observed for the charge transfer resistance (R_{ct}, determined as a diameter of the high frequency semicircle). This increase is due to the electrostatic repulsion between the anionic PBA-glucose complex and negatively charged $Fe(CN)_6^{3-/4-}$.

The EIS plots shown in Fig. 5B were obtained at pH 7. There are clear differences between EIS plots obtained at pH 3.5 (near the pK'_a of [5,5]PBA/GC) and at pH 7. First, the semi-infinite diffusion in the low frequency region is no more apparent, and this phenomenon can be explained by the low current involved in the $Fe(CN)_6^{3-/4-}$ redox reaction on a PBA/GC electrode in the potential range studied. Indeed, the CVs for the PBA/GC electrodes for any grafting conditions reveal an electron-transfer-limited process and not a diffusion limitation. Second, the EIS plot of PBA/GC electrodes consists of a depressed semicircle. A similar behavior was reported for 4-carboxyphenyl-modified glassy carbon electrode [31].

It is well known that the complexation of sugar with PBA groups involves a tetrahedral boronate anion form. Thus, the increased amount of tetrahedral boronate induced by the sugar binding causes an enhancement in the density of anionic charge on the electrode surface. Since the EIS and CV responses of a bare GC electrode are not affected by addition of glucose, the EIS changes in Fig. 5 are considered to be caused by binding of glucose with the PBA layer on a GC electrode.

3.5. Non-Faradic impedance measurements for reagentless detection of glucose

The results described above suggest that EIS measurements can be used to confirm the complexation of

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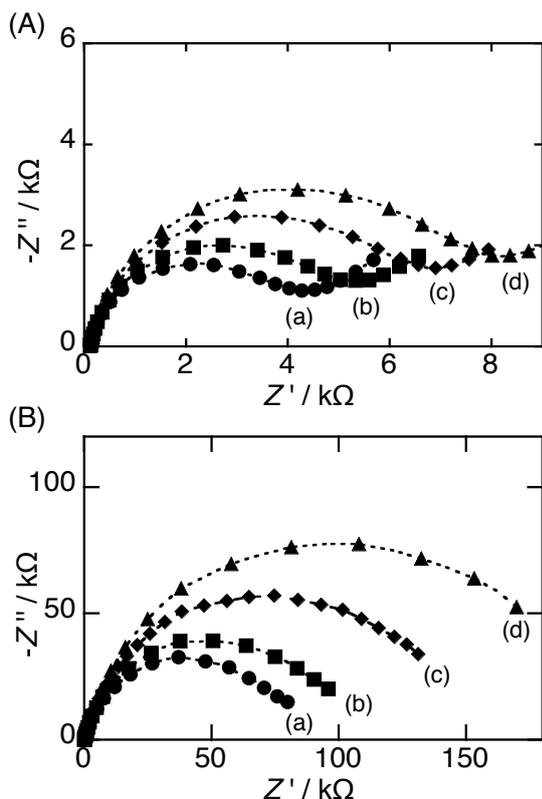
Figure 5: EIS plot of the [5,5]PBA/GC electrode in different glucose concentrations in the presence of 1 mM $K_3Fe(CN)_6$ at (A) pH 3.5 and (B) pH 7.0. E = 0.225 V and the frequency range was 100 kHz - 0.1 Hz. (a)-(d) [glucose] = 0, 10, 30, and 50 mM, respectively.

sugars and PBA groups at PBA/GC electrode in the presence of $Fe(CN)_6^{3-/4-}$. On the other hand, use of a redox probe molecule could be omitted from a sample solution to implement PBA/GC electrodes as a reagentless sensor. In the absence of any redox probe in the electrolyte solution, only non-Faradaic impedance is operative [36]. Non-Faradaic impedance spectroscopy in the absence of a redox probe was applied to follow the biorecognition events at functionalized electrode surfaces. First, impedance measurements were made at a constant frequency in a potential range of −0.2 V to +0.6 V with a potential step of 0.05 V in a pure buffer solution (pH 7). It was found that a U-shaped potential-total impedance (|Z|) curve (figure not shown) was obtained with a local minimum at 0.0 V. Fig. 6 shows changes in |Z| value upon addition of glucose at 0.0 V for [m, n]PBA/GC electrodes. Although the impedance changes were small, they showed the linear response to the glucose concentration, reflecting formation of glucose-PBA complex on the electrode surface. The ef-

fect of grafting conditions on the |Z| response was examined by varying the number of potential cycling (Fig. 6A) and the concentration of precursor 3-APBA (Fig. 6B) in the reaction mixture during electrode grafting. As shown in Fig. 6A, enhancement in the |Z| response is achieved by increasing n value for [5,n]PBA/GC electrodes. In contrast, a decrease in the |Z| response is observed for [m,30]PBA/GCs as the m value increases, as shown in Fig. 6B. Considering the results for the two types of grafting conditions, the most significant effect on |Z| response is obtained for [5,30]PBA/GC electrode.

It should be emphasized that lowering of the |Z| response is recognized for a higher precursor concentration condition (Fig. 6B-d). It is expected that the thick multilayer with high density is obtained by the use of high precursor concentration and long electrolysis time. It is reported that the microscopic structure of multilayer is relatively inhomogeneous and rough from the observation by probe microscope [16, 25]. From the present results, it can be also expected that the increase of the precursor concentration leads to an increase of the deficiency in the multilayer structure. Thus, the use of higher precursor concentration is not suitable for the construction of multilayer structure for sensor usage.

4. Conclusion

We demonstrated here the possible use of a covalently grafted multilayer for chemical sensor application. Phenylboronic acid was successfully grafted onto the surface of glassy carbon electrode by simple electrochemical reduction of *in situ* generated diazonium cation in an acidic aqueous solution. Cyclic voltammetry and electrochemical impedance spectroscopy have allowed the characterization of the layers on glassy carbon electrodes and estimation of the surface coverage. The latter can be controlled by adjusting the concentration of precursor aryl amine and the number of successive potential cycles in the grafting procedures. Resultant [m, n]PBA/GC electrodes were used as a sensor for reagentless detection of glucose. The formation of glucose-PBA complex was confirmed by an increase in total impedance in a pure background electrolyte. Although a limit of detection can be roughly estimated by SN as a few mM or lower from Fig. 6A, ongoing work is focused on the effect of interference compounds such as ascorbic acid, uric acid, and dopamine as well as determination of the limit of detection, and we are now undertaking such experiments along this direction.
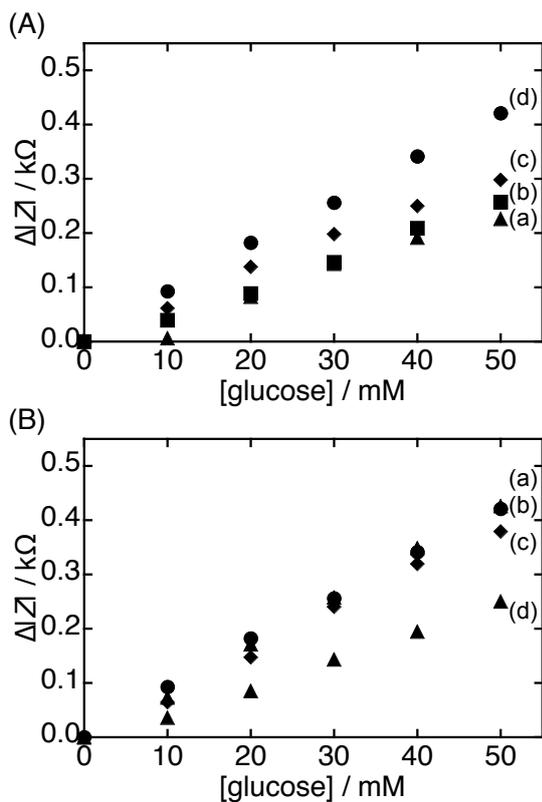
Figure 6: (A) Impedance changes of the [5,*n*]PBA/GC electrodes caused by addition of glucose. (a)-(d) *n* = 5, 10, 20, and 30, respectively. (B) Impedance changes of the [*m*,30]PBA/GC electrodes caused by addition of glucose. (a)-(d) *m* = 5, 10, 15, and 20, respectively.

5. Acknowledgement

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