Controlling surface oxygen concentration of a nanocarbon film electrode for improvement of target analytes

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Abstract

A nanocarbon film consisting of nanocrystallites with mixed sp$^2$ and sp$^3$ bonds formed by unbalanced magnetron sputtering was studied with respect to the changes in characteristics caused by surface oxygen concentration. Electrochemical pretreatment (ECP) was conducted to change the surface oxygen concentration of the nanocarbon film. X-ray photoelectron spectroscopy (XPS) measurements revealed that nanocarbon films with different amounts of surface oxygen could be prepared. In addition, we observed no significant increase of surface roughness ($R_a$) at the angstrom level after ECP, owing to stable structure containing 40% of sp$^3$ bonds. Electrode characteristics including potential window, and electrochemical properties for some redox species such as Ru(NH$_3$)$_6^{3+/2+}$, Fe(CN)$_6^{3-/4-}$ and some biomolecules were investigated. The anodic potential limit became wider and $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ became smaller at the treated nanocarbon film electrode than those of the as-deposited nanocarbon film electrode. Based on these results, we realized to measure uridylic acid (UMP) and inosine triphosphate (ITP) with high oxidation potential by direct oxidation, which was difficult to measure at the as-deposited nanocarbon film electrode.

Keywords: nanocarbon, nanocrystallites, ECP, XPS, AFM, potential window, UMP, ITP
Introduction

Various types of carbon materials, such as graphite, glassy carbon (GC), boron-doped diamond (BDD), diamond-like carbon (DLC), porous carbon, carbon fiber, carbon nanotube (CNT), and graphene, have been widely studied for use in the fields of battery, medicine, separation, catalysis, energy storage, and conversions.\textsuperscript{1-6} Among them, some carbon materials are also widely used for electrochemical applications such as measurement of biomolecules\textsuperscript{7-8} and heavy metals.\textsuperscript{9} For example, GC electrodes, which generally consist of sp\textsuperscript{2} bonds, have been used for such electroanalysis since they exhibit a relatively wider potential window and lower cost than metal electrodes such as Au and Pt. It is known that the electrode activity of graphite electrodes depends on the electrode surface properties such as surface roughness and amount of surface oxygen. It is also well known that electrochemical pretreatment (ECP) of GC electrode enables to improve electrode activity as well.\textsuperscript{10-15} However, excessive treatment of GC causes the increase of background current as result from increase of surface roughness.\textsuperscript{15} From these views, controlling the surface treatment to improve electrode activity of carbon-based electrode is very important. Moreover, the potential window is also an important factor for electrode applications and has been studied for various carbon materials.\textsuperscript{13, 16-18} The wider potential
window of the electrodes we fabricate, the more detectable analytes we expect, leading to improvement of ability of electrochemical measurements. In particular, if the anodic potential limit of the potential window can be expanded, target analytes derived from biomolecules including RNA-constituting bases with high oxidation potentials can be further detected.

BDD electrodes have excellent electrochemical properties such as a wide potential window and a low capacitive current. However, the electron transfer rate at the BDD electrode is slower than that of a conventional carbon electrode for several aromatic analytes (e.g. dopamine or DNA bases) because BDDs mainly consist of sp³ bonds and small grain boundary layers between diamond crystals and so have few oxygen-containing groups on their surfaces.¹⁹⁻²⁰ One of our co-workers has recently studied carbon film consisting of nanocrystallites with mixed sp² and sp³ bonds formed by the electron cyclotron resonance (ECR)²¹ or unbalanced magnetron (UBM) sputtering methods.²² The sputtered nanocrystalline carbon film (nanocarbon film) are controllable of sp²/sp³ ratios in the film and has extremely flat surface. This film electrode exhibited excellent electrochemical properties including a wide potential window, low background current and low surface fouling, compared with the GC electrode.¹⁵,¹⁸ Moreover, we also reported that the potential window of the nanocarbon film electrode became wider by increasing the surface oxygen concentration without losing the surface flatness. However, the
relationship between magnitudes of surface oxygen concentrations and their electrode properties including potential window has yet investigated, and therefore controlling surface oxygen concentration of the carbon-based electrode is very important with respect to the design of carbon electrode suitable for new analytes. In this work, we studied nanocarbon film electrodes with respect to the effect of the surface oxygen concentrations controlled by ECP for electrode properties including potential window and surface roughness. We also investigated the treated nanocarbon film electrode with respect to the electrode properties for biomolecular RNA-constituting bases which are the highest oxidation potentials in DNA/RNA bases.

**Experimental**

*Nanocarbon film fabrication*

Nanocarbon films were fabricated on highly doped silicon (100) substrates at room temperature by unbalanced magnetron (UBM) sputtering. Briefly, the base pressure of the deposition chamber was $7.0 \times 10^{-7}$ Pa. Argon (Ar) gas was used and the deposition pressure was maintained at $6.0 \times 10^{-1}$ Pa. No special catalyst metal was used during the deposition. The target power was 400 W, and the substrate bias voltage was -75 V.
**XPS measurement**

XPS measurement was performed on a Shimazu/Kratos model AXIS Nova (Al Kα 1486.6 eV) spectrometer. The data were obtained at room temperature, and to determine the elemental composition and the quantity of chemical bonds in the carbon electrode surfaces.

**AFM measurement**

AFM measurements were performed with a NanoScope V MultiMode 8 (Bruker, Inc.). The images were acquired in the tapping mode, scan rate is 0.996 Hz. Measurements were made with the Si cantilever in air at room temperature.

**Electrochemical measurements**

All electrochemical studies were performed using electrochemical analyzer Model 760B (CH Instruments Inc., USA). A platinum wire and a Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively. The nanocarbon film was used as the working electrode. The nanocarbon film electrode area was defined by using masking tape in which there was a 2 mm diameter hole. In order to obtain nanocarbon film electrodes with different surface oxygen concentrations, electrochemical pretreatment (ECP) was performed with a cyclic
voltammetry (CV). The CV condition was changed for the number of cycles (n=0, 5, 8 and 15) between 0 and 2.3 V at scan rate of 0.1 V s\(^{-1}\) in a 50 mM phosphate buffer (PB) solution (pH 7.0) at room temperature. Here ECP0 is defined as an as-deposited nanocarbon film electrode (without ECP). The measurement of the potential window was performed with CV in a 50 mM sulfuric acid aqueous solution with Ar purge at room temperature with a scan rate of 0.1 V s\(^{-1}\). The electrochemical measurements of Ru(NH\(_3\))\(_6^{2+/3+}\), Fe(CN)\(_6^{3-/4-}\) and Fe\(^{2+/3+}\) were conducted using CV. The electrochemical measurements of UMP and ITP were performed square-wave voltammetry (SWV) with an amplitude of 25 mV and \(\Delta E\) of 5 mV at 10 Hz.

**Chemicals**

Hexaammineruthenium (III) chloride (Ru(NH\(_3\))\(_6^{2+/3+}\)), potassium ferricyanide (Fe(CN)\(_6^{3-/4-}\)), ammonium iron (II) sulfate hexahydrate (Fe\(^{2+/3+}\)), uridylic acid (UMP) and inosine triphosphate (ITP) were purchased from Sigma-Aldrich.

**Results and Discussion**

*Film properties of the nanocarbon film with different surface oxygen concentration*

First, we estimated the film properties including the surface structure and oxygen
concentration of the nanocarbon films before and after ECP cycles. Fig. 1 shows the typical XPS spectra of the nanocarbon films before and after ECPs. The main components of these nanocarbon films were C (C 1s, 284.5 eV) and O (O 1s, 530.2 eV). The oxygen concentrations of these nanocarbon films were estimated from the peak area ratio of the O 1s and C 1s (O/C). The peak area of O 1s was gradually increased with increasing ECP cycles. From these results, we obtained the calculated O/C ratio as summarized in Table 1. The ratio of sp² bonded carbon atoms to sp³ bonded carbon atoms (sp²/sp³) of carbon film electrode influences the electrode properties especially potential window. As described in Introduction, the potential window of the BDD (sp³-based carbon) electrode is much wider than that of the GC (sp²-base carbon) electrode. Moreover, some of our co-workers also reported that the nanocarbon film electrodes with different sp³ contents (13~53 %) fabricated by UBM sputtering exhibited the wider potential windows with increasing the sp³ contents. Therefore, evaluation of the sp²/sp³ ratio of the nanocarbon film electrode is important to understand the electrode property. The both sp² and sp³ contents were estimated from the XPS spectra (Fig. 1) by using Shirley’s method because XPS is a more suitable approach for our films than Raman measurement as reported previously. Table 1 summarizes these values obtained by XPS analysis of four types of the nanocarbon films treated with different ECP cycles. With the as-deposited film (without ECP),
the sp³ content was 40.7 %, and the O/C ratio of was 0.04. As the ECP cycle was increased from 0 to 15, the sp³ content was increased from 40.7 to 54.1 %. At the same time, the O/C ratio was also increased from 0.04 to 0.10. At the nanocarbon film with ECP15, about 2.5 times higher O/C ratio than that of the as-deposited film was observed.

Fig. 2 shows the surface morphology of four film samples with different oxygen concentrations using AFM, and Fig. 3 exhibits the relationship between average surface roughness (Rₐ) obtained from AFM measurements and the O/C ratio, and ECP cycles. The Rₐ values tends to increase gradually with angstrom order. For example, with ECP 15 cycles, the Rₐ was 0.311 nm (3.11 Å), which was still smoother than that of the untreated GC (2.4 nm).¹⁵ This is probably because the nanocarbon film contains much amounts of sp³ bonds. In general, the sp²-carbon may react during ECP cycling to form CO and CO₂, and then the carbon atom on the surface is removed by gasification,¹³ that induces Rₐ increase. Therefore, our nanocarbon film electrode exhibited less susceptible to etching against ECP. This is highly advantageous in terms of evaluating the effect of surface oxygen concentration for electrode activity since electrode activity of the analyte are generally dependent on the surface structure of the electrode such as chemical components and surface roughness. Moreover, the increased Rₐ of the treated nanocarbon film was at most 3.11 Å, which was smaller than those of the electrochemical
analyte sizes. Indeed, UMP used in this study has a molecular length of approximately 7.5 Å. Therefore, the flat surface of the nanocarbon film after ECP is suitable for use in evaluating the effect of surface oxygen for the electrode activity by suppressing the effect caused by increase in surface roughness. Although the nanocarbon film in this study has sp³ contents of 40 %, the tendency of the gradual change of Rₐ by ECP was similar to that of the nanocarbon film with much amounts of sp³ content (sp³=50 %) electrode fabricated by ECR sputtering. However, the magnitudes of the Rₐ change of the nanocarbon film electrode in this study was different compared with that of the nanocarbon film (sp³=50 %) fabricated by ECR sputtering. When we compared the nanocarbon films treated with the same condition (ECP15), the Rₐ value of the treated nanocarbon film in this study and the treated nanocarbon film (sp³=50 %) were 3.11 and 1.40 Å, respectively. These results clearly demonstrated that the Rₐ change by ECP was dependent on the sp³ content of the nanocarbon film.

Effect of surface oxygen concentration of nanocarbon film electrode on potential window

The potential window is one of the important property of electrodes used in electroanalytical chemistry. We expect that the electrode material with wider potential window can measure more analytes. In this study, we investigated the effect of surface oxygen
concentration in term of change in potential window of the nanocarbon film electrodes. Fig. 4 (A) shows CVs of the nanocarbon film electrodes with different oxygen concentrations. The potential window was defined as the potential range between current limits that do not exceed ±500 μA cm⁻², as previously reported by Swain et al.²⁴ One of the authors previously reported that the nanocarbon film by ECR sputtering (as-deposited) had a wider potential window than DLC or GC.¹⁸ We also observed the wide potential window of the nanocarbon film electrode by UBM sputtering in this study, which was equivalent to the nanocarbon film electrode by ECR sputtering. The potential window especially the anodic potential limits became gradually wider with increasing ECP cycles as shown in Fig. 4 (B). This widening is due to the increase in the apparent sp³ contents caused by ECP as summarized in Table 1. We observed a similar widening of potential window for the nanocarbon film electrode when the sp³ content was increased by changing the sputtering condition.²² With the nanocarbon film (ECP15), the potential window was similar to that of the nanocarbon film (ECP8) despite the fact that the sp³ contents was larger than that of the nanocarbon film (ECP8). This would be due to the slight increase in background current at higher potential regions caused by slight increase of Rₐ. Indeed, the background currents at 2.0 V for ECP0, 5, 8 were 9.34 to 7.63 and 6.99 μA, respectively that were decreased gradually with increasing the apparent sp³ contents. In contrast, the nanocarbon
film (ECP15) exhibited the slight increase of the background current (7.09 µA at 2.0V).

Therefore, we speculate that the widening of potential window caused by increase in the apparent sp\(^3\) contents and slight increase in background current caused by the slight increase of \(R_a\) were competed at the nanocarbon film (ECP15). Nevertheless, this widening of potential window is very effective for the electrochemical measurements for some biomolecules with higher oxidation potentials, as described later. Although a BDD electrode, one of the carbon-based electrodes having the widest potential window,\(^{25}\) has excellent electrode characteristics such as high physicochemical stability in addition to a wide potential window, it is necessary to use high energy (about 800 °C) such as CVD for film formation. In contrast, our nanocarbon film with wide potential window equivalent to that of BDD, can be formed at room temperatures. This is highly advantageous for film electrode fabrication of superior carbon-based electrode.

Next, CV was measured using Ru(NH\(_3\))\(_6\)^{2+/3+}, Fe(CN)\(_6\)^{3-/4-} and Fe\(^{2+/3+}\) to confirm the effect of surface oxygen concentration of the nanocarbon film electrodes. As shown in Fig. 5 (A), all of the CV results for Ru(NH\(_3\))\(_6\)^{2+/3+} showed almost the same waveforms even when nanocarbon film electrodes with different oxygen concentrations were used. Indeed, the peak separation (\(\Delta E_p\)) is almost constant at about 80 mV at all the nanocarbon film electrodes. This is because
Ru(NH₃)₆²⁺/³⁺ is classified as an outer-sphere redox couple and is relatively insensitive to the surface microstructure such as surface oxide and the monolayers adsorbed on the sp² carbon electrode. On the other hand, with Fe(CN)₆³⁻/⁴⁻ (Fig. 5 (B)), the treated electrode showed a smaller ΔEₚ and an increase in oxidation/reduction current, indicating electrode performance for Fe(CN)₆³⁻/⁴⁻ was dependent on the surface oxygen concentration, which was unlike Ru(NH₃)₆²⁺/³⁺. In addition, the ΔEₚ value of Fe²⁺/³⁺ (Fig 5 (C)), whose electron transfer is sensitive to surface oxygen concentration,¹⁴ was drastically decreased at the treated nanocarbon film electrodes. Therefore, the large decrease in the ΔEₚ of the Fe²⁺/³⁺ at the treated electrode suggests that the oxygen functional groups (such as quinone type) were introduced on the surface, which were coincident with the O/C ratio as summarized in Table 1. These results supported that the electrode activities of Fe(CN)₆³⁻/⁴⁻ and Fe²⁺/³⁺ at the treated nanocarbon film were mainly dependent on the surface oxygen concentration. Moreover, it is noteworthy that background currents obtained in Fig. 5 (A)-(C) were almost unchanged during the potential range of -0.8~1.2 V. This is highly advantageous when we consider the sensitivity of the developed electrodes. Sensitivity in electroanalytical chemistry often refers to an increase in obtained current value per substance concentration. There are many reports that the sensitivity was improved by modification of the nanomaterials such as CNTs, graphene, and porous carbon.
although the background current was also increased at the same time. Such improvement of
the sensitivity is included both effects of not only the high activity of intrinsic nanomaterials but
also increasing geometric area from modification of bulky nanomaterials. Our results at the
nanocarbon film electrodes were observed the increase in the current while maintaining low
background current that caused detection sensitivity (signal to noise) was improved solely by
controlling in the surface oxygen concentration.

Detection ability of biomolecules

The nanocarbon film electrode with high surface oxygen concentration exhibits
wider anodic potential limit that enables to detect some biomolecules with higher oxidation
potential. We previously reported that all the four DNA bases (G, A, T and C) and their
derivatives were successfully measured by using the nanocarbon film electrode. Further
study is important to understand the relationship between the surface oxygen and the electrode
activity of the DNA/RNA bases in term of increasing the numbers of detectable DNA/RNA
bases, especially RNA-derived uridine compound or inosine compounds with higher oxidation
potentials than four DNA bases. Direct detection by oxidation reaction is very important
because RNA-derived substances have been actively researched recently. Moreover, uridic
and inosic acid are also umami components. These food components are typically determined by using HPLC-based techniques. Electrochemical determination offers the simple and rapid analysis if these components will be oxidized at our nanocarbon film electrode. Therefore, we here investigated the ability for electrochemical measurements of ITP and UMP. Fig. 6 (A) shows the SWV results of ITP at the nanocarbon film electrodes before and after the ECP. The oxidation peak of ITP was not observed at the as-deposited nanocarbon film electrode. In contrast, the sharp oxidation peak of ITP could be detected at 1.6 V with the treated nanocarbon film electrode (ECP5). It is noteworthy that background current at higher potential region (over 1.5 V) at the treated nanocarbon film electrodes (ECP5, 8 and 15) were drastically decreased compared with the as-deposited nanocarbon film electrode (ECP0), due to the widening of anodic potential limit as described above. When the background current was subtracted, we obtained much clearer voltammograms at each treated electrode (Fig. 6 (B)). We also observed similar tendency for UMP with higher oxidation potential (E_p=1.86 V, Fig. 7) than that of ITP at the treated nanocarbon film electrodes. These were because the anodic potential limit became wider to the range capable of oxidizing ITP and UMP. With the effect of the ECP cycles, the oxidation currents were slightly decreased (at most 90 % of the treated electrode (ECP5)) as ECP cycle increased despite the fact that oxidation potential was almost unchanged. This would
be due to the slight increase of background current by ECP cycles as result from slight increase of the surface roughness. Nevertheless, the electrode activity for ITP and UMP at the nanocarbon film could be sufficiently improved by 5 cycles of ECP. We are now studying the nanocarbon film electrode to expand further detection substances and improving sensitivity for realizing an important and valuable carbon material for the development of various electrochemical devices.

**Conclusions**

We investigated the effect of surface oxygen concentration of nanocarbon film electrodes to improve the electrode performance. The nanocarbon films with different oxygen concentrations were successfully prepared without losing the significant increase of the surface roughness. Controlling surface oxygen concentration was very effective for widening of the anodic potential limit of the treated nanocarbon film electrode. As results, we realized to measure ITP and UMP with the higher oxidation potentials at the treated nanocarbon film electrode, which was difficult to detect at the as-deposited nanocarbon film electrode.
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Controlling surface oxygen concentration of nanocarbon film electrode for widening potential window

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Table 1 XPS analysis results for the nanocarbon films treated with different ECP cycles

Fig. 1 XPS spectra for the nanocarbon films treated with different ECP cycles.

Fig. 2 AFM images of nanocarbon film surface treated with different ECP cycles. ECP cycle; 0 cycle (as-deposited) (A); 5 cycles (B); 8 cycles (C); and; 15cycles (D).

Fig. 3 Relationship between Rₐ and number of ECP cycles.

Fig. 4 (A) CVs of the nanocarbon film electrodes treated with different ECP cycles, measured in a 50 mM H₂SO₄ solution at a scan rate of 0.1 V s⁻¹ and (B) anodic potential limit obtained from (A).

Fig. 5 Voltammograms of three kinds of redox systems at the nanocarbon film electrodes treated with different ECP cycles: (A) 1.0 mM Ru(NH₃)₆²⁺/³⁺ measured in 1.0 M KCl. (B) 1.0 mM Fe(CN)₆³⁻/⁴⁻ measured in 1.0 M KCl. (C) 1.0 mM Fe²⁺/³⁺ measured in 0.1 M HClO₄. Scan rate is 0.1 V s⁻¹.

Fig. 6 (A) SWVs results of 100 μM ITP at the nanocarbon film electrodes before and after ECP (solid lines). The dashed lines are background scans. (B) Background subtracted SWVs of 100 μM ITP at the nanocarbon film electrodes treated with different ECP cycles.

Fig. 7 (A) SWVs results of 100 μM UMP at the nanocarbon film electrodes before and after
ECP (solid lines). The dashed lines are background scans. (B) Background subtracted SWVs of 100 μM UMP at the nanocarbon film electrodes treated with different ECP cycles.
Table 1 XPS analysis results for the nanocarbon films treated with different ECP cycles

| ECP cycle | O/C | sp² / % | sp³ / % |
|-----------|-----|---------|---------|
| ECP0      | 0   | 0.04    | 59.3    | 40.7    |
| ECP5      | 5   | 0.08    | 51.8    | 48.2    |
| ECP8      | 8   | 0.08    | 50.1    | 49.9    |
| ECP15     | 15  | 0.10    | 45.9    | 54.1    |
Fig. 1 XPS spectra for the nanocarbon films treated with different ECP cycles.
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Fig. 7 (A) SWVs results of 100 μM UMP at the nanocarbon film electrodes before and after ECP (solid lines). The dashed lines are background scans. (B) Background-subtracted SWVs of 100 μM UMP at the nanocarbon film electrodes treated with different ECP cycles.