Suppression of surface oxygen on nanocarbon film electrodes for maintaining electrode activity

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Abstract

We investigated sputtered nanocarbon films with respect to the effect of suppressing surface oxygen on their electrochemical properties. The nanocarbon film consists of nanocrystallites with mixed sp$^2$ and sp$^3$ bonds formed by unbalanced magnetron sputtering. Ultraviolet/ozone (UV/O$_3$) irradiation and electrochemical pretreatment (ECP) were conducted to change the surface oxygen concentration of 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 treatments, 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$_3$)$_6^{3+/2+}$ were investigated. Some electrochemical measurements of zinc ions (Zn$^{2+}$) and hydrogen peroxide (H$_2$O$_2$) showed that the electrochemical reaction was improved by suppressing the surface oxygen. These results clearly indicated that the low surface oxygen concentration plays an important role in these electrochemical reactions.

Keywords: nanocarbon, nanocrystallites, low surface oxygen concentration, ASV, Zn, H$_2$O$_2$
Introduction

Carbon materials have attracted much interest because of structural differences of their various allotropes such as graphite, glassy carbon (GC), boron-doped diamond (BDD), diamond-like carbon (DLC), carbon nanotube (CNT), and graphene. These carbon materials have been widely studied\(^1\text{-}\text{5}\) as possible electrodes for electrochemical applications such as measurement of biomolecules\(^6\text{-}\text{7}\) and heavy metal ions.\(^8\) It is known that electrode activity for carbon materials depends on not only carbon structures but also electrode surface properties including surface roughness and surface oxygen. In general, it is difficult to evaluate the effect of each factor on the electrode performance because each factor often changes in tandem with the other. For example, with graphite electrode, when increasing the surface oxygen concentration, the surface roughness is also increased at the same time. Therefore, controlling the carbon surface is crucial in terms of providing superior carbon-based electrodes.

One of our coworkers has recently studied the carbon film composed of nanocrystallites with mixed sp\(^2\) and sp\(^3\) bonds formed by the electron cyclotron resonance\(^9\) or the unbalanced magnetron\(^10\) sputtering method. The sputtered carbon film (nanocarbon film) has some superior properties such as controllable sp\(^2\)/sp\(^3\) ratio, extremely flat surface, low surface oxygen concentration and stable structure. These film characteristics provide excellent electrochemical properties such as a wide potential window, low background current, and low surface fouling,\(^9\text{-}\text{12}\) and aim to offer highly sensitive electrodes with high productivity. More recently, we also reported that controlling the surface oxygen concentration (typically 0.1 of O/C) on the nanocarbon film allowed us to measure inosine triphosphate and uridylic acid with higher oxidation potentials.\(^13\) On the other hand, we consider that not all the analytes prefer oxygen-rich nanocarbon surface.
In this study, we investigated the effects of lower surface oxygen concentration (typically below 0.1 of O/C) controlled by ultraviolet/ozone (UV/O₃) and electrochemical pretreatment (ECP) on the electrode characteristics for some species, namely zinc ions (Zn²⁺) and hydrogen peroxide (H₂O₂). Heavy metal pollution causes serious problems for environmental and human health. This can be attributed to rapid urbanization, land-use change and industrialization in developing countries, where various heavy metals have been reported to have an impact on ecosystems.¹⁴ In particular, humans are indirectly affected by aquatic ecosystems and drinking water, and therefore rapid detection and quantification of trace heavy metals are very important. H₂O₂ is a byproduct of many enzyme reactions, acts as a reactive oxygen species in the body, and is a byproduct of reactions in industrial processes. Direct detection of H₂O₂ is difficult using carbon-based electrodes due to high overpotentials.¹⁵ Therefore, evaluation of the effect of surface properties including surface oxygen concentration is crucial because these insights enable us to provide good feedback with respect to the design of carbon-based electrode materials.

**Experimental**

**Nanocarbon film fabrication**

Nanocarbon films were fabricated on highly doped silicon (100) substrates at room temperature by unbalanced magnetron sputtering.¹⁰ Briefly, the base pressure of the deposition chamber was 7.0 × 10⁻⁷ Pa. Argon (Ar) gas was used and the deposition pressure was maintained at 6.0 × 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. The film thickness was about 40 nm.
Controlling surface oxygen concentration

In order to obtain nanocarbon film electrodes with different and lower surface oxygen concentrations, we used two treatment methods. One is an ECP that has already been reported, and the other is UV/O3 treatment. The ECP treatment was conducted using cyclic voltammetry (CV) 15 cycles 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. On the other hand, the UV treatment was performed by irradiating Hg lamp (20 mW cm\(^{-2}\)) (SEN Lights Corp. Japan) for 10 s at a distance of 1 mm. We controlled the O/C ratio by optimizing the irradiation time. Ar milling treatment of the ECP-treated nanocarbon film was performed using ion milling equipment (3-IBE, Hakuto Co.) to remove the surface oxygen. Ar gas pressure was 4 × 10\(^{-2}\) Pa, and the treatment time was 40 s.

XPS measurement

XPS measurement was performed using a Shimazu/Kratos model AXIS Nova (Al K\(\alpha\) 1486.6 eV) spectrometer. Data were obtained at room temperature and used to determine the elemental composition and the number of chemical bonds in the carbon electrode surfaces.

AFM measurement

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

All electrochemical studies were performed using an electrochemical analyzer Model 900 (CH Instruments Inc., USA). A platinum wire and an Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively. 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. The measurement of the potential window was performed with CV in a 0.1 M ammonium buffer (pH 8.0) at room temperature with a scan rate of 0.1 V s⁻¹. Electrochemical measurements of Ru(NH₃)₆²⁺/³⁺, Fe(CN)₆³⁻/⁴⁻ and Fe²⁺/³⁺ were conducted using CV under the same conditions as in the previous report. The electrochemical measurements of H₂O₂ (0.2 mM) were conducted using CV, measured in deoxygenated 50 mM phosphate buffer (PB) (pH 7.0). This electrolyte solution was purged with pure Ar gas for 20 min prior to the measurement.

Detection of trace zinc ions was carried out by means of anodic stripping voltammetry (ASV). The preconcentration potential was -1.4 V and the preconcentration time was 240 s. After preconcentration, we carried out square-wave voltammetry (SWV). All the SWV measurements were performed with an amplitude of 25 mV, and a ΔE of 2 mV, at 40 Hz.

**Chemicals**

Hexaammineruthenium(III) chloride (Ru(NH₃)₆²⁺/³⁺), potassium ferricyanide (Fe(CN)₆³⁻/⁴⁻), ammonium iron(II) sulfate hexahydrate (Fe²⁺/³⁺), were purchased from Sigma-Aldrich. Zinc ions (Zn²⁺) and hydrogen peroxide (H₂O₂) were purchased from FUJIFILM Wako Chemicals.
Results and Discussion

Film properties of nanocarbon films with different surface oxygen concentrations

In this study, we focused on the effect of lower surface oxygen concentration on electrode activity, so we used two types of treatment methods, namely ECP and UV treatment as described in the experimental section. The ECP treatment can significantly increase the surface oxygen concentration, whereas the surface roughness also increases gradually as the number of cycles increases.13 In contrast, the UV treatment could not significantly increase the surface oxygen concentration of the nanocarbon films, but could give low surface oxygen concentration without losing the surface flatness.16 The fact is attributed to the difference in the amount of energy given to the electrode surface.

Figure 1 shows typical XPS spectra of the nanocarbon films before and after UV or ECP treatments. The main components of these nanocarbon films were C (C 1s, 284.5 eV), O (O 1s, 530.2 eV) and Ar (Ar 2p, 241.0 eV). The surface oxygen concentration of these nanocarbon films was estimated from the peak-area ratio of the O 1s and C 1s (O/C). With UV treatment, the peak area of O 1s was subtly increased compared with that by ECP treatment, as summarized in Table 1. In addition, the ratio of sp² bonded carbon atoms to sp³ bonded carbon atoms (sp²/sp³) of a carbon film electrode influences the electrode properties, especially the potential window. Therefore, evaluating sp²/sp³ ratio of the nanocarbon film electrodes is important for understanding the electrode property. We estimated both sp² and sp³ contents from XPS spectra (Fig. 1) using Shirley's method.10 With the as-deposited film, the sp³ content was 40.3%, and the O/C ratio was 0.03. On the other hand, the UV-treated nanocarbon film had an increased sp³ content of 46.9%, and the ECP-treated nanocarbon film increased to 52.6%. The O/C ratio also increased from 0.03 to 0.07 (UV) and 0.12 (ECP). For the
UV-treated and ECP-treated nanocarbon films, about 2.3 and 4.0-times higher O/C ratio than that of the as-deposited film were observed. As described in a later section, these differences were numerically valid, and therefore, the UV treatment could control the lower surface oxygen concentration than the ECP treatment reported in our previous study.\textsuperscript{13} With the difference in introduced oxygen functional groups between the UV and ECP treatments, we attempted to analyze O 1s spectra, but no large difference in the spectra shape was observed. Therefore, we consider that the types of oxygen functional groups of the both treated nanocarbon films are almost the same. Figure 2 shows the surface morphology of three film samples with different oxygen concentrations using AFM, and average surface roughness (R\textsubscript{a}) obtained from each AFM measurement were 0.07, 0.07 and 0.516 nm for as-deposited, UV-treated, and ECP-treated nanocarbon films, respectively. Vig has demonstrated that UV treatment was an effective method for generating near-atomically clean surfaces, which is able to remove micrometer-thick layers of polymers (e.g. exposed photoresist)\textsuperscript{18} in a cleaning process. In addition to the cleaning process, UV treatment increases the amount of carbon oxides on the surface of GC electrode.\textsuperscript{19} Comparing Fig. 2 (A) and (B) reveals that the surface roughness hardly changes before and after UV treatment. On the other hand, the R\textsubscript{a} values at the ECP-treated nanocarbon film was slightly increased with angstrom order (0.516 nm (5.16 Å)), which was still smoother than that of the untreated GC (2.4 nm).\textsuperscript{12} This is less susceptible to etching against ECP because the nanocarbon film contains greater amounts of sp\textsuperscript{3} bonds. This feature is highly advantageous in terms of evaluating the effect of lower surface oxygen concentration on electrode activity, since the electrode activity of the analyte is generally dependent on the surface structure of the electrode, such as chemical components and the surface roughness.
Effect of low surface oxygen concentration of nanocarbon films on electrochemical measurements

To confirm the effect of low surface oxygen concentration of these nanocarbon film electrodes, we conducted CV measurements of typical redox species such as Ru(NH₃)₆²⁺/³⁺, Fe(CN)₆³⁻/⁴⁻ and Fe²⁺/³⁺. With Ru(NH₃)₆²⁺/³⁺, which is an outer-sphere-type redox species, voltammograms exhibited an almost reversible and similar electrochemical response on all the nanocarbon film electrodes even with different oxygen concentrations (Figure 3 (A)). Indeed, the peak separation (ΔEₚ) values at all the nanocarbon film electrodes were unchanged (about 80 mV) before and after the treatments, which were the equivalent to the previous results. On the other hand, with Fe(CN)₆³⁻/⁴⁻ (Fig. 3 (B)), both treated electrodes showed smaller ΔEₚs and larger oxidation/reduction currents with increasing surface oxygen. In addition, the ΔEₚ value of Fe²⁺/³⁺ (Fig 3 (C)), whose electron transfer is sensitive to surface oxygen concentration, 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 was consistent with previous reports.

Next, we confirmed the effect of surface oxygen concentration in terms of change in potential window of the nanocarbon film electrodes. The potential window is one of the important properties of electrodes used in electroanalytical chemistry. Previously, we reported that our nanocarbon film has a wider potential window than other carbon electrodes such as GC and DLC. Figure 4 shows the potential window at the cathode potential limit of nanocarbon film electrodes with different oxygen concentrations, in the same condition for ASV of Zn²⁺. 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.22 As shown in Table 1 and Fig. 2, there are slight variations such as an apparent increase in sp³ content caused by a change in surface oxygen concentration and a slight increase in background current caused by a slight increase in Rₐ. Nevertheless, the potential windows are sufficient to cover the Zn²⁺ preconcentration potential of -1.4 V as described later.

**ASV of Zn²⁺**

ASV is a well-known electrochemical technique for detecting heavy metal ions. ASV has the advantages of high-cost performance and high sensitivity through its use of the electrodeposition of the target metal ion onto an electrode surface from a sample solution. Moreover, it is also easy to be miniaturized measurement systems.23-24 The reason we chose Zn²⁺ as the measurement target in this study is the fact that Zn²⁺ has a higher ionization tendency than hydrogen and one of the lowest preconcentration potentials. Therefore, since ASV measurement cannot be performed with other metal electrodes with narrower potential window, we tried to measure Zn²⁺ with our flat nanocarbon film electrode with wide potential window. Figure 5 shows the result of ASV measurement of Zn²⁺ using nanocarbon film electrodes with different oxygen concentrations. With the nanocarbon film electrode with lower surface oxygen concentrations of 0.03 (as-deposited) and 0.07 (UV-treated), we observed clear oxidation peak currents for the preconcentrated Zn⁰ on the surface around -1.14 V vs. Ag/AgCl, which was the same results of our previous report.17 On the other hand, the oxidation peak at the nanocarbon film electrode with higher surface oxygen concentration of 0.12 (ECP-treated) became broader with the positively sifted peak
position, and the background current was also increased. As a result, the peak current was reduced to approximately 40% of that at the as-deposited nanocarbon film electrode. From these results, we suggest that the surface oxygen concentration plays an important role in detecting Zn$^{2+}$.

The effects of surface oxygen functional groups on carbon electrodes have been extensively studied. These studies have described that the electrochemical reactions at the carbon-based electrodes are dependent on the surface properties including surface oxygen and/or surface roughness. As shown in Fig. 2, the nanocarbon film electrodes with lower surface oxygen concentrations of 0.03 (as-deposited) and 0.07 (UV-treated) exhibited the same surface roughness. Therefore, we can estimate solely the effect of surface oxygen concentration on ASV measurements between them. Concerning the difference in ASV results caused by surface oxygen concentration, these could be due to two potential reasons. One is the fact that the surface oxygen prevents reduction process during preconcentration of Zn$^{2+}$. The other reason could be the effect of oxidation process during detection although Zn$^{2+}$ was preconcentrated on the surface. In order to confirm oxidation process, all the electrodes after ASV measurements were transferred to the blank solution and SWV was performed again. In all cases, no peaks could be detected. These results clearly indicated that Zn$^{0}$ did not remain on the electrode surface after the first ASV measurement. From this result, we consider that surface oxygen influences the reduction of Zn$^{2+}$ (preconcentration) despite the fact that each electrode has sufficient potential window to preconcentrate Zn$^{2+}$ as described above. Indeed, when removed the surface oxygen by short-time Ar milling treatment, the response was recovered to approximately 80% of that at the as-deposited nanocarbon film electrode as shown in Fig. 5.

The electrode performance was estimated by each calibration curve.
shows calibration curves for Zn\textsuperscript{2+} using nanocarbon film electrodes with different oxygen concentrations. As shown in Fig. 6(a), the as-deposited nanocarbon film electrode exhibited the good linearity in the region of 0-500 ng ml\textsuperscript{-1} of Zn\textsuperscript{2+} (r\textsuperscript{2}=0.988). On the other hand, the obtained current was saturated at the Zn\textsuperscript{2+} concentration over 200 ng ml\textsuperscript{-1} at the UV-treated and the ECP-treated nanocarbon film electrodes. This was due to the decrease in active electrode area by existence of surface oxygen. Compared with three electrodes in the region of 0-200 ng ml\textsuperscript{-1} of Zn\textsuperscript{2+} (Fig. 6(b)), all the electrodes exhibited the good linearity (over 0.92 of r\textsuperscript{2}). The nanocarbon film electrodes with lower surface oxygen concentration of 0.03 (as-deposited) and 0.07 (UV-treated) exhibited the same slopes, indicating the same sensitivity. In contrast, the nanocarbon film electrode with higher surface oxygen concentrations of 0.12 (ECP-treated) exhibited low slope whose value was approximately one-fifth of the as-deposited nanocarbon film electrode. Moreover, the ECP-treated electrode exhibited the poor reproducible results (relatively high error variance). This is probably due to not only the surface oxygen but also the surface roughness in this measurement. Indeed, the R\textsubscript{a} value (0.516 nm) of the ECP-treated nanocarbon film is larger than the Zn\textsuperscript{2+} size (0.134 nm). From these results, we conclude that suppressing the surface oxygen at the nanocarbon film electrodes made it possible to control the analytical performance of ASV measurements of Zn\textsuperscript{2+}.

\textit{Cyclic voltammetry of H\textsubscript{2}O\textsubscript{2}}

We also investigated the effect of the surface oxygen concentration on H\textsubscript{2}O\textsubscript{2} measurements. The concentration of H\textsubscript{2}O\textsubscript{2} in urine can be used as an indicator of the whole-body oxidative stress for regulation of renal function and diagnosis of several
diseases. Hence, \( \text{H}_2\text{O}_2 \) determination is of great significance in biomedical, industrial, and academic applications. Several analytical methods have been reported for the detection and quantification of \( \text{H}_2\text{O}_2 \). However, accuracy in the measurements and detection at low level has been a challenge. Moreover, they also display a few other drawbacks, such as lack of selectivity, long analysis time, use of expensive equipment, and reagents.\(^{31}\) The electrochemical method is regarded as one of the most promising techniques, and various studies using carbon-based electrodes such as CNTs and graphene have been reported.\(^{32-34}\) Figure 7 shows the result of CV measurements of \( \text{H}_2\text{O}_2 \) using nanocarbon film electrodes with different oxygen concentrations. The used electrolyte solution was deoxygenated to exclude the effect of dissolved oxygen. A reduction peak of \( \text{H}_2\text{O}_2 \) was found at -0.86 V vs. Ag/AgCl at the nanocarbon film electrodes with lower surface oxygen concentration of 0.03 (as-deposited) and 0.07 (UV-treated). On the other hand, the reduction peak at the nanocarbon film electrode with higher surface oxygen concentration of 0.12 (ECP-treated) became shift to negative direction (-1.18 V). Moreover, when removed the surface oxygen of the ECP-treated nanocarbon film using short-time Ar milling, the electrochemical response of \( \text{H}_2\text{O}_2 \) was recovered to that of the as-deposited nanocarbon film electrode (Fig. 7) as with the result of \( \text{Zn}^{2+} \). There are two possible reasons for the peak shift at the present stage. One reason could be the sluggish electron transfer to \( \text{H}_2\text{O}_2 \), and the other is that \( \text{H}_2\text{O}_2 \) is difficult to access the electrode surface by existence of surface oxygen. Hsu and coworkers reported the reduction reaction of \( \text{H}_2\text{O}_2 \) at the graphene oxide and reduced graphene oxide electrodes.\(^{34}\) They exhibited both results as reference materials (not main material) but these results indicated reduced graphene oxide could detect \( \text{H}_2\text{O}_2 \) sufficiently than the graphene oxide. Therefore, we suggest that there is a borderline of the surface oxygen concentrations around 0.07 for electrochemical \( \text{H}_2\text{O}_2 \) reduction at
carbon-based electrodes.

Conclusions

In this study, we investigated the effect of low surface oxygen concentration of the nanocarbon film electrodes. We succeeded in producing nanocarbon films with different and low oxygen concentrations while maintaining a high electrode activity and surface roughness, thanks to the very stable structure made by possible by the sp²/sp³ mix bonds. We found that suppressing the surface oxygen concentration made it possible to measure Zn²⁺ and H₂O₂ more sufficiently. Taking accounts of these results (low O/C) together with our previous reports (large O/C)¹³, ³⁵-³⁹, controlling surface oxygen concentration on the nanocarbon film electrode led to an expansion of the measurable analytes as shown in Figure 8. We believe that these findings will be a significant and general insight into the design of carbon-based electrode materials.

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Graphical Index

Suppression of surface oxygen on nanocarbon film electrodes for maintaining electrode activity

Electrode activity

\[ \cdot \text{Zn}^{2+} \]
\[ \cdot \text{H}_2\text{O}_2 \]

0.03  O/C  0.12

Biomolecules (DNA/RNA bases)

low  O/C  high
**Figure captions**

Fig. 1 XPS spectra for nanocarbon films with different surface oxygen concentrations. (A) as-deposited, (B) UV-treated, and (C) ECP-treated nanocarbon films.

Table 1 XPS analysis results for nanocarbon films with different surface concentrations.

Fig. 2 AFM images of nanocarbon films with different surface oxygen concentrations. (A) as-deposited, (B) UV-treated, and (C) ECP-treated nanocarbon films.

Fig. 3 CVs of three kinds of redox systems at the nanocarbon film electrodes with different surface oxygen concentrations. (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. 4 CVs of nanocarbon film electrodes with different surface oxygen concentrations, measured in a 0.1 M ammonium buffer (pH 8.0).

Fig. 5 Typical ASV results of Zn²⁺ (75 ng ml⁻¹) at nanocarbon film electrodes with different surface oxygen concentration, measured in 0.1 M ammonium buffer (pH 8.0).

Fig. 6 (a) Calibration curves of Zn²⁺ at as-deposited (black circle), UV-treated (white circle), and ECP-treated (black square) nanocarbon film electrodes. (b) Enlargement of Fig. 6a.
Fig. 7 CVs of $\text{H}_2\text{O}_2$ (0.2 mM) at nanocarbon film electrodes with different surface oxygen concentrations, measured in deoxygenated 50 mM PB (pH 7.0).

Fig. 8 Schematic outline of the relationship between the analytes that are compatible with each O/C region on the nanocarbon film electrode.
Fig. 1
Table 1

|                  | O/C | $sp^2$, % | $sp^3$, % |
|------------------|-----|-----------|-----------|
| As-deposited     | 0.03| 59.7      | 40.3      |
| UV-treated       | 0.07| 53.1      | 46.9      |
| ECP-treated      | 0.12| 47.4      | 52.6      |
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
**Fig. 8**

- **H$_2$O$_2$** [This study]
- **DNA/RNA bases**
  - G/A/T/C [ref. 9, 35], 8OHdG [ref. 36]
  - 5mC/5hmC [ref. 37, 38], UMP/ITP [ref. 13]
- **heavy metals**
  - Zn$^{2+}$ [This study, ref. 17]
  - Cd$^{2+}$/Pb$^{2+}$ [ref. 8, 29]
- **kynurenic acids** [ref. 39]

**O/C on nanocarbon film electrode**