Structure and Electroanalytical Application of Nitrogen-doped Carbon Thin Film Electrode with Lower Nitrogen Concentration

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We studied a nitrogen-doped nanocarbon film electrode with a nitrogen concentration of lower than 10.9 at% formed by the unbalanced magnetron (UBM) sputtering method. The sp³ content in the nitrogen-doped UBM sputtering nanocarbon film (N-UBM film) slightly increases with increasing nitrogen concentration. The nitrogen-containing graphite-like bonding decreases and pyridine-like bonding increases with increasing nitrogen concentration. The N-UBM film has a very smooth surface with an average roughness of 0.1 to 0.3 nm, which is almost independent of nitrogen concentration. The N-UBM film electrode shows a wider potential window (4.1 V) than a pure-UBM film electrode (3.9 V) due to its slight increase in the sp³ content. The electrocatalytic activity increased with increasing nitrogen concentration, suggesting that the electroactivity is maximum when the nitrogen concentration is around 10.9 at%, which is confirmed by the peak separation of Fe(CN)₆⁴⁻. The hydrogen peroxide (H₂O₂) reduction potentials at the N-UBM film electrode shifted about 0.1 V, and the peak current of H₂O₂ increased about 4 times.

Keywords Nitrogen doping, carbon electrode, thin film, H₂O₂ detection

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Introduction

Nitrogen-doped carbon materials, including nanotubes, nanocups, nanofibers, as well as thin films, have attracted great attention because of their excellent mechanical and electrocatalytic properties in a variety of applications.¹⁻⁴ It is well known that the carbon-nitrogen bond changes the mechanical and electrocatalytic properties of the carbon film because the carbon-nitrogen bond plays an important role as an active site for oxygen reduction reaction (ORR). In particular, carbon alloy which is also a nitrogen-doped carbon containing a nanoshell structure, has been studied to develop low-cost non-platinum catalysts for fuel cell cathodes.³ More recently, nitrogen-doped nanocarbons including nitrogen-doped carbon nanotube (CNT) and graphene with high electrocatalytic activity for ORR have been reported.⁵⁻⁷ In spite of the high electrocatalytic activity of the above nanocarbon materials, these materials are not always suitable as electrodes for electroanalysis. This is because a large surface area of these powder, flake or fiber-like materials increases the background noise level, which is inconvenient as regards improving the detection limit (or improving the S/N ratio). In contrast, carbon film electrodes have more advantages for electroanalytical applications because relatively high electrochemical activity with low background and capacitive current could be realized by optimizing film fabrication conditions. The film electrodes can be fabricated with excellent reproducibility using low-temperature processes such as the sputtering method. The film form is also advantageous for fabricating any shapes or sizes of electrodes by conventional micro or nanofabrication processes.

Recently, we have developed a nitrogen-doped carbon film electrode formed by using electron cyclotron resonance (ECR) sputtering.⁸ This method offers high-density ion irradiation at the growth surface of the film that allows us to form an ultraflat nanocrystalline carbon film at a relatively low temperature.⁹ The film surface remained very smooth when the nitrogen concentration was increased. We also reported that the electrochemical activity was changed by changing the nitrogen concentration while maintaining a low O/C ratio. Nitrogen-doped carbon contains pyridine-like and graphite-like structures and ORR activity is varied with the ratio of both structures. Indeed, there have been some discussions about which nitrogen containing structures, including pyridine-like and graphite-like structures, contribute to improve electrocatalytic activity such as ORR.¹⁰⁻¹⁴ In our previous report, the relationship between the electrochemical activity such as ORR and the concentrations of pyridine and graphite type nitrogen were studied by changing the nitrogen concentrations from 8.9 to 30 at% in the ECR nanocarbon films. In this concentration region, the electrocatalytic activity decreased with increasing pyridine-like structure (or decreasing graphite-like structure). However, the structural dependence in a different concentration region should be studied since the carbon structure is less disordered in the low nitrogen concentration region. In this paper, we studied the structure and electrochemical properties of the nitrogen-doped nanocarbon film electrode formed by using unbalanced magnetron sputtering (N-UBM film) with very low nitrogen concentration by using some redox species. We also investigated

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the relationship between the structure of N-UBM film electrodes and the electrocatalytic performance, including the ORR activity. Finally, we demonstrated the electroanalytical advantages of N-UBM film electrodes with improved sensitivity for detecting the H$_2$O$_2$.

**Experimental**

**Electrode preparation**

A pure-UBM nanocarbon film electrode and an N-UBM nanocarbon film electrode were prepared in accordance with previous reports. Briefly, both film electrodes were deposited on a boron-doped silicon (100) substrate by UBM sputtering at room temperature. A sintered carbon target was used. An argon (Ar) and nitrogen (N$_2$) mixture gas was used with the N$_2$ gas content controlled in the 0 to 3.3% range and the total pressure maintained at 6.0 × 10$^{-3}$ Pa. The film thickness was about 40 nm. No special catalyst metal was used during the deposition.

**Carbon x-ray photoelectron spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) was conducted with a Shimadzu/Kratos Model AXIS Ultra (Al Kα 1486.6 eV) spectrometer to determine the elemental composition and the quantity of chemical bonds in the carbon film electrode surface. The nitrogen concentration of the N-UBM film electrode was estimated from the peak area ratio of the N 1s corrected using instrumental sensitivity factors. The C 1s and N 1s spectra were fitted by Gaussian-Lorentzian sum components after the background had been subtracted according to Shirley’s method.

Atomic force microscopy (AFM) measurements were performed with an SPI4000 (SII Nano Technolgy, Inc.) using a silicon cantilever in air at room temperature. The images were recorded in the dynamic force AFM mode at scan rates of 0.28 Hz with 256 × 256 pixels. The contact angle was achieved using a Drop Master DM 300 (Kyowa Interface Science Co., Ltd.). Milli-Q water droplets were used to characterize the surface hydrophilicity of the carbon electrode.

**Electrochemical experiments**

All electrochemical experiments were performed using an ALS/CHI 730C electrochemical analyzer (CH Instruments, Inc.). A platinum wire and an Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively. The prepared nanocarbon films were 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. Cyclic voltammetry was carried out to estimate the electrochemical properties of the prepared nanocarbon film electrodes. The electrolyte solutions were purged with pure Ar gas for 20 min prior to the measurement and blanketed with Ar during the measurement in the deoxygenated experiments. For an oxygen (O$_2$) reduction reaction (ORR), the solutions were purged with pure O$_2$ for 5 min prior to the measurement. The H$_2$O$_2$ reduction was measured from cyclic voltammograms obtained after adding different amounts of H$_2$O$_2$ to the sample solutions.

**Chemicals**

All the chemicals were analytical grade and were used as received. Hexamaminouruthenium(III) chloride was purchased from Sigma-Aldrich. Potassium ferricyanide was obtained from Wako Pure Chemical Industries, Ltd. (Japan). K$_2$HPO$_4$, Na$_2$HPO$_4$, and sulfuric acid were purchased from Kanto Chemical. We prepared 100 mM phosphate buffer, which contained 100 mM KH$_2$PO$_4$ and Na$_2$HPO$_4$. We prepared a fresh concentration of H$_2$O$_2$ with 0.2 to 28 mM phosphate buffer (pH 7.0). Ultrapure water was used in all the experiments.

**Results and Discussion**

**Chemical and surface structures of N-UBM nanocarbon film**

We prepared N-UBM nanocarbon films with different nitrogen concentrations by changing the N$_2$ gas content. Table 1 summarizes the variation in the amounts of each chemical bond, the average roughness and contact angle for our pure-UBM and N-UBM films. Each chemical bond was estimated from high-resolution C 1s and N 1s XPS spectra because XPS is a more suitable approach for our films than Raman measurement. The sp$^3$ and sp$^2$ contents in the pure-UBM film were 80.0 and 20.0%, respectively, which are comparable to those in pure-ECR film (sp$^3$: 81.5%, sp$^2$: 18.5%). The N-UBM film (N = 10.9 at%) contained sp$^2$ contents of 63.4 and 64.3%, respectively, indicating that both sputtering methods exhibit similar sp$^3$/sp$^2$ ratios at near nitrogen concentrations. In contrast, the pyridine-like bonding in the N-UBM film was 42.5 to 50.5% at the nitrogen concentration of 7.8 to 10.9 at%, which is slightly higher than that of 36.8% in the N-ECR film (N = 8.9 at%). However, in both films, the graphite-like bonding decreases and pyridine-like bonding increases with increasing nitrogen concentrations.

Figure 1 shows AFM images (3 μm × 3 μm) for the pure-UBM and N-UBM nanocarbon films. No clear surface difference could be observed. Indeed, the average roughness (Table 1) remained almost unchanged (between 0.10 to 0.33 nm) when the nitrogen concentration was increased to 10.9 at%, indicating that the roughness of our N-UBM films did not change with increasing nitrogen concentration. This result is also a similar tendency to our previous report.

We also studied the surface wettability of each film using contact angle measurements. Figure 2 shows contact angles for the pure-UBM and N-UBM nanocarbon films. The contact angle value remained almost unchanged (between 71.8 to 81.4 degrees, also summarized in Table 1) when the nitrogen concentration was increased to 10.9 at%, indicating that these nanocarbon films are relatively hydrophobic. This hydrophobicity is due to the low oxygen concentrations on the

<table>
<thead>
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<th>Table 1</th>
<th>Surface properties of pure-UBM and N-UBM film with different nitrogen concentrations</th>
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<td>Nitrogen gas pressure, %</td>
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<tr>
<td>N concentration, at%</td>
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<tr>
<td>C 1s, %</td>
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<td>N 1s, %</td>
<td>graphite-like bonding</td>
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<td>pyridine-like bonding</td>
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<td>Contact Angle ($^\circ$)</td>
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<tr>
<td>Chemical components of C, N, and O were obtained and analyzed from XPS analysis. Average roughness values were obtained from AFM measurements.</td>
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nanocarbon films. Since the nanocarbon film structures including sp2/sp3 ratio and the ratio of graphite-like and pyridine-like bonding can be changed without changing surface roughness, O/C ratio and wettability, the electrocatalytic activity dependent upon carbon film structures can be systematically studied using N-UBM nanocarbon film electrode.

Potential window and basic electrochemical properties

As previously reported, the electrochemical characteristics such as potential window and electrochemical activity are greatly influenced by changing the carbon film structures.9,16 We also reported that electrochemical properties of pure-UBM nanocarbon film electrodes changed by changing the ion acceleration voltage. When we increased the acceleration voltage during sputtering, the potential window became wider with increasing sp3 bond content.15 Figure 3 shows the variation in the potential window of pure-UBM and N-UBM nanocarbon film electrodes with different nitrogen concentrations (N = 0, 1.8, 6.4, 7.8, and 10.9 at%) obtained in a 0.05 M H2SO4 solution. The potential window is defined as the potential range between current limits that do not exceed ±500 μA/cm2 as previously reported by Swain et al. and our group.9,15,17 The potential windows of the pure-UBM film electrode is 3.9 V and increases to 4.1 V at 1.8 at% nitrogen concentration. We also compared the ratio between oxidation current at 1.7 V (vs. Ag/AgCl) and capacitive current at 0.04 V. The ratio for GC, pure-UBM film and N-UBM film electrodes are 132.9, 25.6 and 7.1, respectively, also suggesting that the N-UBM film electrode has a wider potential window compared with those of the other two electrodes. This increase in the potential window is due to the slight increase in the sp3 bond content caused by nitrogen doping. A similar increase of potential window was observed with a pure-UBM film electrode when we increased the sp3 bond content by changing the sputtering conditions.15 However, the potential window is almost constant between 1.8 and 10.9 at% nitrogen concentrations, although sp3 content is increased from 26.6 to 36.6%. In our previous reports, the potential window of N-ECR film electrode containing 8.9 at% nitrogen shows a wider potential window than those of N-ECR film electrode with higher nitrogen concentrations. By considering the above results, the flat region in Fig. 3 could be due to the balance caused by increasing sp3 content and increasing nitrogen concentration. This is because the former and latter factors make the potential window wider and narrower, respectively.

Next, we evaluated the electrochemical properties of pure-UBM and N-UBM nanocarbon film electrodes by measuring Ru(NH3)63+ and Fe(CN)64–. Voltamograms of these electrodes are shown in Figs. S1 and S2 (Supporting Information). Figure 4 shows peak separation (ΔEp) calculated from voltammograms of both species obtained at pure-UBM and N-UBM film electrodes with different nitrogen concentrations. For Ru(NH3)63+, ΔEp is almost constant (65 mV) at pure-UBM
and N-UBM film electrodes because Ru(NH₃)₆³⁺ is outer-sphere redox couple and less influenced by surface condition. In addition, this result also indicates that the N-UBM film electrode has sufficient conductivity without interference from the IR drop. It is also reported that Fe(CN)₆⁴⁻ is an outer-sphere redox couple but the kinetics are quite complex and dependent both on the surface chemistry and interaction. The ΔEₚ value of Fe(CN)₆⁴⁻ was 146 mV for a pure-UBM film electrode and decreased to 85 mV for N-UBM film electrodes. The ΔEₚ value remained almost unchanged (between 85 to 89 mV) when the nitrogen concentration was increased to 10.9 at%. Swain and coworkers demonstrated that the ΔEₚ of Fe(CN)₆⁴⁻ was dependent upon the sp³ content of the sp² and sp³ mixed carbon films. On the other hand, it is well known that average roughness, surface oxygen-containing groups and wettability often influence the electron transfer rates for some redox species. However, the average roughness, O/C ratio and contact angle of N-UBM film electrodes remained almost unchanged, as summarized in Table 1. From the considerations described above, Fe(CN)₆⁴⁻ behavior in our N-UBM film electrode was dominantly dependent on film structure.

Electrocatalytic reduction of oxygen

Several groups have reported that nitrogen-doped carbon materials exhibit a positive shift of ORR potential. The well-known carbon alloys prepared by pyrolyzing nitrogen containing aromatic polymers exhibited ORR potential close to that of a platinum electrode. A positive ORR shift was also observed at the carbon felt by electrochemically introducing nitrogen containing groups onto the carbon felt surfaces. Some groups have also reported electrochemical responses of nitrogen containing carbon film electrodes. However, very few reports studied the relationship between carbon film structures, particularly about chemical bonds and electrocatalytic properties.

In this work, we studied N-UBM nanocarbon film electrodes with relatively low nitrogen concentration in terms of structural dependence of ORR. Figure 5 shows voltammograms of oxygen reduction at pure-UBM and N-UBM nanocarbon film (N = 0, 1.8, 6.4, 7.8, and 10.9 at%) electrodes. The pure-UBM film electrodes showed the peak reduction currents at –0.75 V (vs. Ag/AgCl). When the nitrogen concentration was increased up to 10.9 at%, the peak potential gradually shifted to –0.48 V. At the same time, the magnitude of the peak current also increased as shown in Fig. 5. Murakoshi et al. reported that pyridine-like bonding is active sites of ORR by studying graphene containing 2.0 to 2.7 at% nitrogen concentrations, which is included in the concentration region we studied with our N-UBM film electrode. Our current results about structural dependence of ORR potential agree well with their results. However, the ORR peak potentials were shifted negatively with increasing pyridine-like structure (or decreasing graphite-like structure) when nitrogen concentrations ranged from 8.9 to 30.4 at%. Previous studies have also reported that graphite-like structure is important to improve electrocatalytic activity such as ORR. Therefore, more studies are needed to further understand the structural dependence of ORR in nitrogen-doped carbon films.

Measurement of hydrogen peroxide

The electrochemical reduction of H₂O₂ is very important in electrodes for electrochemical enzyme biosensors using various oxidase enzymes. Therefore, we evaluated the sensitivity of H₂O₂ response by using pure-UBM and N-UBM nanocarbon film electrodes with different nitrogen concentrations. As shown in Fig. 6(a), the pure-UBM film electrode showed a weak reduction peak current of –28 μA/cm² at –0.74 V. The reduction peak of H₂O₂ gradually shifted to the positive direction and the magnitude of the peak current increased with increasing nitrogen concentration (Figs. 6(a) and 6(b)). With the N-UBM film (N = 10.9 at%) electrode, the peak current was increased to –80 μA/cm² at –0.64 V, indicating electrocatalytic activity for H₂O₂ was also improved with increasing nitrogen concentration up to 10.9 at%. These results agree well with our previous report that the N-ECR nanocarbon film electrode showed the highest electrocatalytic activity at the nitrogen concentration of 8.9 at%. Figure 6(c) shows calibration curves of H₂O₂ at the pure-UBM and N-UBM film electrodes. Both electrodes exhibit good linearity between 0.2 and 28 mM of H₂O₂, and the current of the N-UBM film electrode (N = 10.9 at%) is 4 times larger than that of the pure-UBM film electrode. The oxidation current of H₂O₂ has been commonly measured by using metal electrodes such as platinum. However, the signal faced interference from those of other biochemicals including l-ascorbic acid and uric acid. In contrast, the reductive detection of H₂O₂ will be useful without the effect of such interfering molecules, particularly for biological fluid samples. Our N-UBM nanocarbon film electrode is highly advantageous in terms of measuring lower concentrations of H₂O₂.
Conclusions

In this paper, we studied the structure and electroanalytical performance of N-UBM nanocarbon film electrodes with relatively low nitrogen concentrations. The sp\(^2\) content decreased and sp\(^3\) content increased with increasing nitrogen concentration. The graphite-like bonding decreases and pyridine-like bonding increases with increasing nitrogen concentrations. However, the film surface roughness, O/C ratio and wettability were unchanged when the nitrogen concentration was increased. The electrochemical responses of redox species such as Ru(NH\(_3\))\(_6\)\(^{3+}\) and Fe(CN)\(_6\)\(^{4–}\) at the N-UBM nanocarbon film electrode exhibit a similar tendency to those of the N-ECR film electrode, suggesting that nitrogen-doping improves the electron transfer at the electrode surface. The reduction potential of oxygen (ORR) to shifted positive and its peak height was increased with increasing nitrogen concentration up to 10.9 at%. At the same time, the reduction potential and peak height of H\(_2\)O\(_2\) reduction showed similar tendencies to those of ORR, indicating that the highest electrocatalytic activity of N-UBM nanocarbon film at the nitrogen concentration of 10.9 at% is almost similar to our previous results using the N-ECR nanocarbon film electrode which shows its highest activity at the nitrogen concentration of 8.9 at%. As an electroanalytical point, the N-UBM film electrode shows 4 times higher sensitivity for H\(_2\)O\(_2\) reduction than that of the pure-UBM film electrode with linear range from 0 to 28 mM.

Supporting Information

Cyclic voltammograms of pure-UBM and N-UBM film electrodes in 1.0 mM Ru(NH\(_3\))\(_6\)\(^{3+}\) and Fe(CN)\(_6\)\(^{4–}\) in 1.0 M KCl. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References

10. A. Morozan, P. Jégou, M. Pinault, S. Campidelli, B.