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Nitrogen-doped metal-free carbon catalysts for aerobic oxidation of xanthene

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Abstract

N-doped carbons were prepared from a commercial activated carbon (AC) by heat treatments in pure NH_3 , an NH_3 -air mixture, and NO and these were used for a model reaction of aerobic oxidation of xanthene to xanthone (XO). The catalytic activity of AC for the title reaction was greatly enhanced by N-doping and the enhancement in the activity depended on the N source gasses used. The effectiveness of the three gases for both N-doping and enhancing the activity was in an order of NH_3 -air > NH_3 > NO . The temperature of N-doping also affected the catalyst activity but not so significantly. X-ray photoelectron spectra indicated the presence of pyridine-type and pyrrole-/pyridone-type N species. The catalytic activity of N-doped carbon was correlated with the ratio of the amount of pyridine type N against that of ether-type O species. The structures of the active sites was discussed on the basis of the XPS and reaction results. Metal-free N-doped AC was less active than a commercial Ru/AC catalyst but more active than a commercial Pd/AC one. The activity of N-carbon slightly decreased after the first recycling but it remained almost the same during the following two-time recycling.

Keywords: carbon; nitrogen doping; oxidation; xanthene; xanthone

1. Introduction

Carbon materials have frequently been used as adsorbents and catalyst supports. They are considered to be chemically less active. However, Bitter et al. and Wang et al. recently reported that N-doped carbon (N-carbon) nanotubes prepared by chemical vapor deposition using N containing compounds of nitriles, pyridine, or amines are effective as solid base catalysts for Knoevenagel condensation reaction [1,2]. Our group has also reported that

N-carbons prepared by ammoxidation of commercial carbon black and activated carbon (AC) can act as solid base catalysts for Knoevenagel condensation and transesterification reactions [3]. X-ray photoelectron spectroscopy (XPS) measurements in these studies showed the presence of several different types of N species on N-carbons prepared. The activity of N-carbon materials tended to increase with the amount of N doped and so the presence of N on their surface is significant for the genesis of the activity for the base catalyzed reactions. Thomas et al. prepared graphitic carbon nitride materials using a well-designed synthetic chemistry, in which the materials were made by polymerization of cyanamide, dicyanamide, or melamine [4–6]. Various materials with different structures and properties can be obtained depending on reaction conditions employed. These carbon nitride materials were shown to be active catalysts for Friedel-Crafts and cyclization reactions. Following those studies, Jin et al. [7] and Xu et al. [8] have also prepared mesoporous carbon nitrides using mesoporous silica materials as templates and indicated that these were active catalysts for transesterification and Knoevenagel condensation reactions.

On the other hand, Ozaki and co-workers found that N- and/or B-doped carbon materials were effective as a Pt-free electrode in proton exchange membrane fuel cells [9–11]. Their computational study [12] revealed that C atoms at edge sites are more tightly interacting with O₂ molecules by the presence of adjacent N atoms, making the chemical nature of N-carbon similar to that of Pt. From these results, one may expect that metal-free N-carbon can be a substitute for metal catalysts that are employed for various organic synthesis reactions.

It is known that aerobic oxidation of xanthene (XT) to xanthone (XO) (Scheme 1) is catalyzed by AC [13] and by supported metal catalysts [14,15] and the latter is more active than the former. This reaction is therefore one of the suitable reactions to examine the above-mentioned expectation that the catalytic activity of AC is increased by N-doping through which its surface becomes similar in nature to that of noble metals. In the present study, N-carbons were prepared from a commercial AC by a heat treatment in pure NH₃, a mixture of NH₃ and air, or NO and tested for the aerobic oxidation of XT to XO. The N-doping to AC has been shown to greatly enhance its catalytic activity depending on the doping conditions used. On the basis of XPS results, the genesis of active sites by N-doping has been discussed.

Scheme 1

2. Experimental

A commercial AC (GL Science Co.) was used as the raw carbon material. A weighed AC sample (c.a. 150 mg) was placed in a quartz reactor and heated to 800°C for 1 h in a stream of pure NH₃, 90 vol.% NH₃-air, or 1 vol.% NO-He at 100 cm³/min. AC was treated at this temperature for 1 h and cooled to 300°C, the treatment gas was then changed to air, and it was further cooled to room temperature. Several N-carbons were also prepared by changing the doping temperature.

Oxidation of XT was carried out in a 100 cm³ Teflon-coated autoclave using 0.1 g of the catalyst sample, 1 mmol of XT, and 8 cm³ of toluene at 100°C for 4 h. Air inside the reactor was used as the oxidant. After the reaction run, the reaction mixture was filtered and the catalyst was washed with dichloromethane. The organic phase was collected, further diluted to 50 cm³ with dichloromethane, and analyzed by a gas chromatograph (Shimadzu14-B) attached with a capillary column (Zebron ZB-50) and a flame ionization detector.

The textural properties of the carbon samples prepared were measured by N₂ adsorption/desorption (Quantachrome NOVA 1000). Surface area was determined by the Brunauer, Emmet, and Teller's (BET) equation. XPS measurements of the samples were made on JEOL JPS-9200 using monochromatic Al-K α radiation. The charge-up shift correction of the binding energy was made by using C_{1s} binding energy at 284.5 eV.

For comparison, commercial Pd and Ru catalysts supported on AC (Wako, 5 wt.% Pd/AC, 5 wt.% Ru/AC) were also used as received for the title reaction. The dispersion values of Pd/AC and Ru/AC determined by CO chemisorption were 30.4 and 37.2%, respectively.

3. Results and discussion

Surface O and N species over the parent untreated AC and N-carbons prepared using NH₃, NH₃-air, and NO were analyzed by XPS. Typical XPS spectra in the O_{1s} and N_{1s} regions are depicted in Figure 1. The O_{1s} spectrum could be deconvoluted into two peaks at 531.8 and 533.3 eV attributed to O species of C=O, O(1), and of C-O-C, O(2), respectively [16,17]. Similarly, the N_{1s} spectrum revealed the presence of pyridine-type N (398.5 eV), N(1), and pyrrole-/pyridone-type N (400.5 eV), N(2) (Scheme 2) [17–20]. Table 1 lists the surface concentrations of those N and O species determined by XPS. N atoms were doped to the

surface of AC by the treatments with NH₃, NH₃-air, and NO. For N-doping at 800°C, the total amount of doped N atoms was in an order of NH₃-air > NH₃ > NO (entries 2–4). Thus, the N-doping with NH₃-air is the most effective for introducing N species on AC. The distribution of doped N species was also changed by the treatment gases. The relative amount of N(1) was the highest with the NH₃ doping. The influence of N-doping temperature was also examined with NH₃-air and with NO (entries 5–8). The total amount of N doped gradually increased with increasing temperature up to 800°C for both the doping methods, (entries 3, 4, 5–8); however, such trend was not significant for the N-doping with NO.

Fig. 1, Scheme 2, Table 1

As shown in Table 1, the surface concentrations of O(1) and O(2) species could also be influenced by the N doping. Exceptions were those with NO at 400°C and at 600°C, which practically did not affect the amounts of O species (entries 7 and 8). Among the other doping conditions, the doping with NH₃-air and with NO at 800°C increased the amount of O(1), but decreased that of O(2) (entries 3 and 4). The rest just decreased the amounts of both O(1) and O(2) species (entries 2, 5, 6).

Untreated AC and N-carbons prepared at various conditions were employed for the title reaction. Under the present reaction conditions, only XO was produced and the catalytic activities were different depending on the N-doping conditions employed. Table 2 represents XO yields obtained with the catalysts along with their BET surface areas. The catalytic activity of the untreated AC was very low and it was significantly enhanced by N-doping. Surface areas of N-carbons were not different so much from that of the untreated AC. Therefore, the surface *chemical* natures of N-carbons should be responsible for their higher catalytic activities. Among N-carbons prepared at 800°C, the catalytic activity was again in the order of NH₃-air > NH₃ > NO (entries 2–4). Thus, the N-doping with NH₃-air is also the most effective for enhancing the activity. For N-carbons prepared with NH₃-air, the XO yield gradually increased with increasing temperature up to 800°C (entries 3, 5, 6). On the other hand, when NO was used, the N-doping temperature little affected the catalytic activity (entries 4, 7, 8). Thus, the influence of N-doping conditions on the catalytic activity of N-carbons is similar to that on the total amount of N species described above.

Table 2

As shown above, two types of N species, N(1) and N(2), existed on N-Carbons. In Fig. 2, the XO yield is plotted against their amounts. The yield was found to increase with the amount of N(1) species, although there was some scatter in the plot. A similar increasing trend could also be seen in the correlation between the yield and the amount of N(2); however, the scatter was much larger for N(2) than for N(1). Those observations suggest that N(1) species is involved in the active sites for the reaction. Because of the scatter in the plot, further attempts were made to get better correlation between the catalyst activity and the amount of N(1) species by taking into account of O(1) and/or O(2). The yield could not be correlated with the amount of either O(1) or O(2) species alone; however, it was found that a better correlation was observed between the XO yield and the ratio of the amount of N(1) against that of O(2) species (Fig 3). One possible explanation for this is that O(2) species have some negative effects on the catalytic performance of N(1) species.

Fig. 2, Fig. 3

On the basis of the above mentioned results, the structure of active sites for the reaction over N-carbon was considered. Because the N-doping to AC significantly enhanced its catalytic activity for the oxidation of XT to XO, the reaction was also carried out using a few N containing organic compounds (Table 3); however, they showed no or very low activities for the XT oxidation. Thus, it is suggested that the N atoms doped on the surface of AC are unlikely to be active sites by themselves and the presence of N atoms in a large conjugated graphitic structure would probably be requisite. Our previous work showed that, similarly to the cases of the XT oxidation, the catalytic activity of N-carbon prepared with NH_3 -air at 600°C for a base catalyzed reaction of Knoevenagel condensation was much higher than pyridine molecules, revealing that N-carbon has stronger basicity than pyridine [3]. This again suggests the importance of the presence of N atoms in the graphite structure for the catalytic activity of N-carbon. Recently, Kondo et al. showed that N atoms doped on graphite could modify electronic conjugated system of the graphite surface and N(1) species would give Lewis basic nature to neighboring C atoms whose number could be more than 10 [20]. Probably, such Lewis basic sites including both doped N and neighboring C atoms would activate methylene group of XT, which should be responsible for the higher activity in the presence of the larger amount of N(1) species. When O(2) species present near N(1) species, they may perturb electronic state of the graphite surface around N(1) atom and lower the effectiveness of N(1) for influencing the electronic property of neighboring C atoms. As a

result of the promotional effects of N(1) species and the negative ones of O(2) species, the catalytic activity of N-carbon increased with the ratio of N(1)/O(2) as shown in Fig. 3. To discuss the role of O(2) species in more detail, further computational work would be required.

The activation of O₂ molecules may also be a factor determining the overall reaction rate of the XT oxidation. Nishida and Hayashi proposed that O radicals produced from O₂ molecules over AC could initiate the reaction by abstraction of one H atom from the methylene group of XT [21]. Computational studies showed that doped graphite-type N species (Scheme 2) can enhance the ability of adjacent C atoms for the activation of O₂ molecules [12,22]; however, such type N species could not be detected by the XPS measurements for the present N-carbons.

Table 3

For comparison, commercial AC supported noble metal catalysts were employed for the title reaction. The reaction results were listed in Table 4. In spite of a much slower TOF value of N-carbon than those of Pd/AC and Ru/AC, the yield of XO was in an order of Ru/AC > N-carbon > Pd/AC. We think that the present metal-free N-carbon could be a less costly substituent for Ru/AC, although N-carbon needs longer reaction time than Ru/AC to get good conversion levels.

Table 4

Among the catalysts listed in Table 4, N-carbon and Pd/AC were further subjected to catalyst recycling experiments. For the recycling, the catalyst was separated by filtration after a reaction run, washed with dichloromethane, dried in air at room temperature, and then used for the subsequent run. Fig. 4 shows the changes of the catalyst activity by the recycling. The activities of both the N-carbon and Pd/AC slightly decreased after the first recycling but they did not further change during the following two-time recycling runs. To elucidate the reason of the decrease in the activity of N-carbon, XPS spectra of the recycled N-carbon were measured. Fig. 5 compares N_{1s} XPS spectra of the fresh and recycled N-carbons. It shows the appearance of a peak at 402.8 eV ascribable to oxidized N species [18–20] by the catalyst recycling. This suggested that a part of N(1) and/or N(2) species was oxidized during the first reaction run, resulting in the decrease in the activity. But further formation of the oxidized species would not occur during the following reaction runs and so the deactivation was not

observed during the following recycling runs.

Fig. 4, Fig. 5

The present study demonstrates that the heat-treatment of commercial AC with NH₃-air (ammonoxidation) is attractive to prepare *metal-free* oxidation catalysts. Further studies are in progress in our group to employ N-carbons for the oxidation of other substrates having a few reactive groups to evaluate their superiority from the viewpoint of the reaction selectivity. N-carbons have recently been observed to be an interesting catalyst in the chemoselective reduction of 3-nitrostyrene, nitrobenzene, and styrene with hydrazine [24].

Conclusions

The present study showed that the catalytic activity of AC for the oxidation of XT to XO was greatly enhanced by N-doping and the enhancement in the activity depended on the N source gasses used. The effectiveness of the three gases for both N-doping and enhancing the activity was in an order of NH₃-air > NH₃ > NO. The temperature of N-doping also affected the activity but not so significantly. XPS indicated the presence of N(1) and N(2) species. The catalytic activity of N-carbon was correlated with the ratio of N(1)/O(2). N(1) species was proposed to be involved in the catalytically active sites. Metal-free N-doped AC was less active than a commercial Ru/AC catalyst but more active than a commercial Pd/AC one. Although the activity of N-carbon slightly decreased after the first recycling, it remained almost the same during the following two-time recycling.

Acknowledgements

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Table 1 Surface concentrations of N and O species over untreated AC and N-carbons.

Entry	N doping conditions ^a	Surface concentration (%) ^b					
		N _{total}	N(1)	N(2)	O _{total}	O(1)	O(2)
1	none	0	0	0	8.90	5.23	2.67
2	NH ₃ -800°C	2.63	1.9	0.73	3.09	2.46	0.93
3	NH ₃ +Air-800°C	4.04	2.09	1.95	8.06	6.66	1.4
4	NO-800°C	1.96	1.12	0.84	10.90	9.25	1.65
5	NH ₃ +Air-400°C	2.61	1.77	0.84	6.15	3.81	2.34
6	NH ₃ +Air-600°C	3.75	2.83	0.92	5.42	3.99	1.43
7	NO-400°C	1.56	0.98	0.58	8.41	5.52	2.89
8	NO-600°C	1.58	0.92	0.66	7.92	5.29	2.63

^a Doping gas-temperature.

^b Determined by XPS. N(1), N(2), O(1), and O(2) represent pyridine-type N, pyrrol/pyridine-type N, O of C=O, and O of C-O-C, respectively.

Table 2 BET surface area and the catalytic activities of untreated AC and N-carbons.

Entry	Nitrogen-doping conditions ^a	S _{BET}	XO yield ^b
		(m ² /g)	(%)
1	none	1031	4
2	NH ₃ -800°C	1205	35
3	NH ₃ +Air-800°C	1263	38
4	NO-800°C	1026	21
5	NH ₃ +Air-400°C	971	22
6	NH ₃ +Air-600°C	1000	30
7	NO-400°C	1006	18
8	NO-600°C	1205	24

^a Doping gas-temperature.

^b Reaction conditions: catalyst, 0.1 g; xanthene, 1 mmol; toluene, 8 cm³; 100°C; 4 h.

Table 3. Aerobic oxidation of XT with N containing organic compounds.

Catalyst ^a	XO Yield (%)
Melamine	5
Pyridine	0
2-Pyridone	2

Reaction conditions: XT, 1 mmol; toluene, 8 cm³; 100°C; 4 h.

^a The amount of N atoms contained was the same with that of 0.1 g of AC ammoxidized at 800°C determined by XPS.

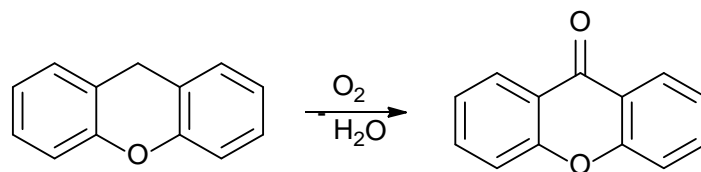
Table 4. Comparison of N-carbon and supported metal catalysts.

Catalyst	XO yield (%)	TOF (h ⁻¹)
N-carbon ^a	38	0.28 ^b
Pd/AC	25	4.54
Ru/AC	98	13.37

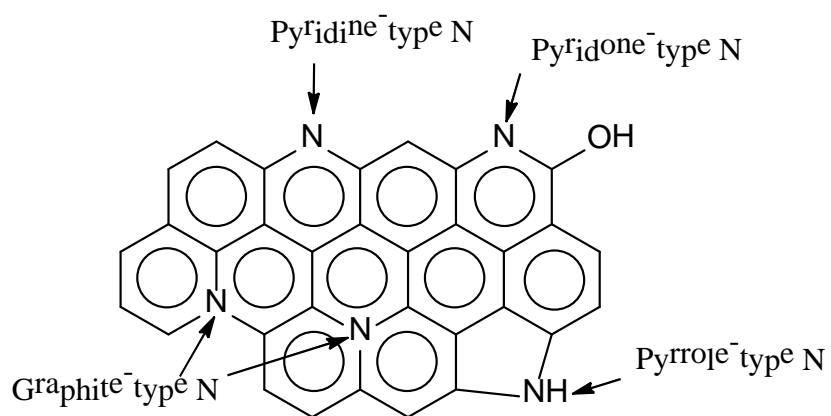
Reaction conditions: catalyst, 0.1 g; XT, 1 mmol; toluene, 8 cm³; 100°C; 4 h.

^a Prepared with NH₃+air at 800°C for 1h.

^b Based on the number of surface N(1) species, which was estimated from BET surface area and surface concentration on the assumption of C–C bond of 0.142 nm [23].



Scheme 1. Oxidation of xanthene (XT) to xanthone (XO).



Scheme 2. Structures of N atoms doped to AC.

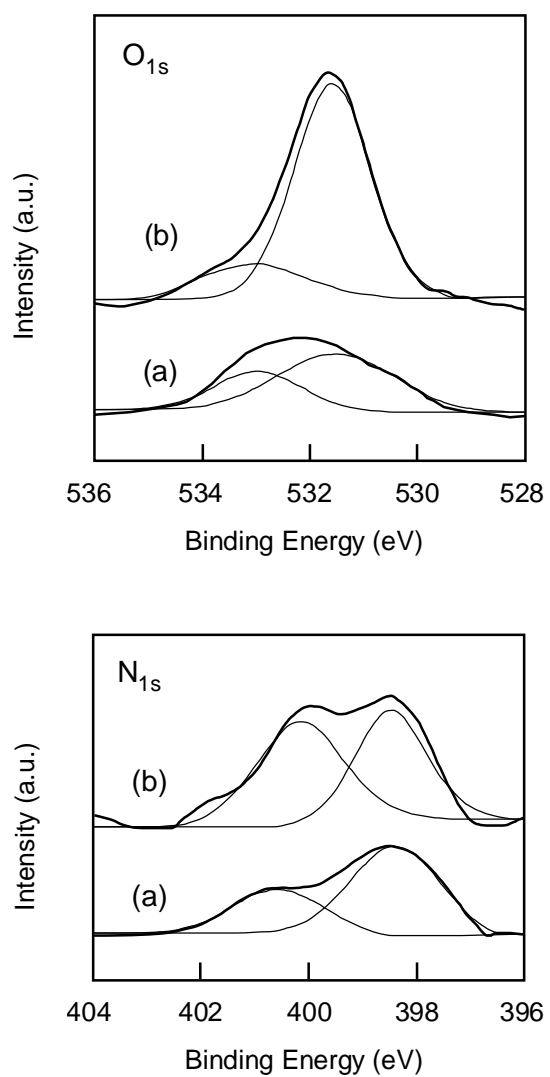


Figure 1. XPS spectra of N-carbons in O_{1s} and N_{1s} regions. The catalysts corresponding to spectra a and b are entries 2 and 3 in Table 1, respectively.

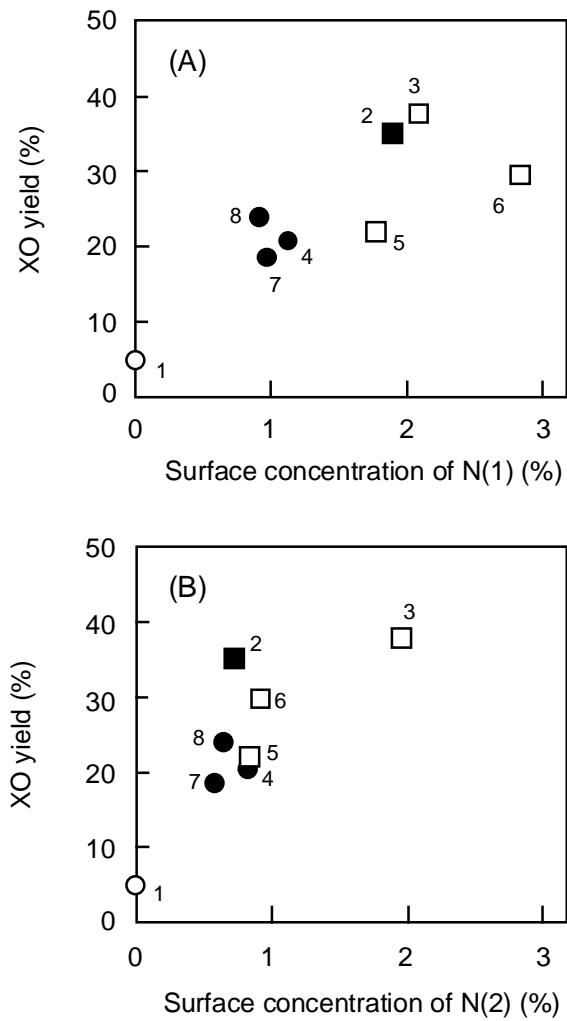


Figure 2. Relationship between the catalyst activity and the surface concentrations (A) of N(1) and (B) of N(2) species. Parent AC (○) and N-carbons prepared with NH₃ (■), NH₃+air (□), and NO (●). Numbers correspond to those in Table 1.

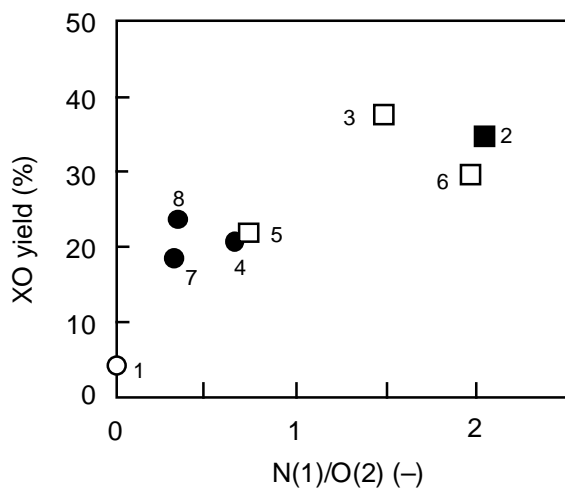


Figure 3. Relationship between the activity and the ratio of N(1)/O(2). Parent AC (○) and N-carbons prepared with NH₃ (■), NH₃+air (□), and NO (●). Numbers correspond to those in Table 1.

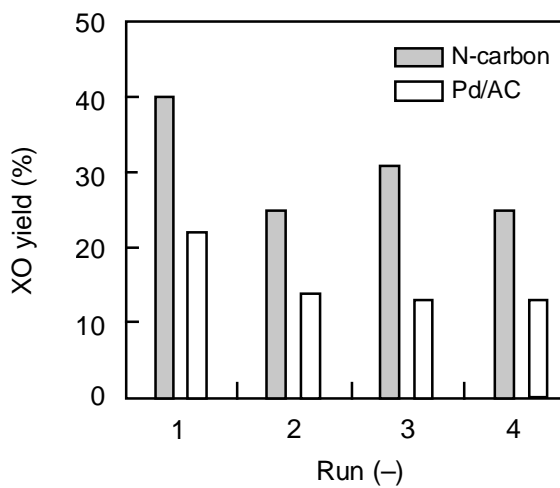


Figure 4. Influence of catalyst recycling on the activities of N-carbon and Pd/AC. Closed and open bars indicate the results with N-carbon and Pd/C, respectively. N-carbon examined was the same with the one in Table 4.

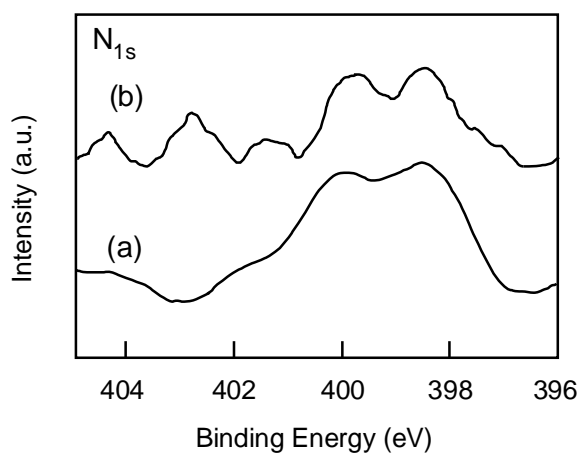


Figure 5. N_{1s} XPS spectra of (a) fresh and (b) 4-time recycled N-carbons. N-carbon examined was the same with the one in Table 4.