EFFECTS OF METAL AND NITROGEN ON THE FORMATION OF NANO-SHELL CONTAINING CARBON

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Introduction

When a mixture of a polymer and a transition metal compound was heat-treated in an inert atmosphere, we found a carbon consisting of shell-like and amorphous carbons. Such carbons showed a catalytic activity for oxygen reduction reaction (ORR). We named the carbon "nano-shell containing carbon" (NSCC) and have continued the researches. NSCC can be platinum replacement for ORR catalyst used in polymer electrolyte fuel cells. The ORR activity was enhanced by addition of nitrogen-containing compound to the mixture of carbon precursor. However, roles of metal and nitrogen for the formation of nano-shells and ORR activity have not been clearly elucidated. To examine the effects of metal and nitrogen on the formation of NSCC, iron oxide and uracil were used as a metal and a nitrogen sources, respectively. The effects of nitrogen contents on NS structure and ORR activities were examined.

Materials and Methods

Novolak type phenol formaldehyde resin (PF), iron oxide (Fe_2O_3, M), and uracil (UR) were used as carbon, metal and nitrogen sources, respectively. Particle sizes and concentrations of M and nitrogen contents were changed. PF was dissolved in acetone and other chemicals were added to the solution, condensed using a rotary evaporator, vacuum dried and then subjected to the experiment. The dried sample was heated to 800 °C at 20 °C/min and then cooled to room temperature in a nitrogen stream. The carbon was ball-milled and sieved to collect carbon particles with diameters less than 106 μm. The carbons were washed with 1 mol dm^{-3} at 70 °C and filtered. This procedure was repeated 3 times to remove iron compounds.

The names of the carbons are expressed as aMbN, meaning a% Fe and b% N in precursors.

Characterization of the samples were performed using a transmission electron microscope (TEM, JEM2010, JEOL), an X-ray diffractometer (XRD, XRD-6100, RIGAKU) and an X-ray photoelectron spectrometer (XPS, AXIS-NOVA, Shimadzu). TEM images were taken before acid washing of the carbons. Average size of iron particles, thickness of NS wall, and NS particle sizes are obtained by examining at least 100 particles on TEM images and averaged. XRD profiles were taken before and after acid washing of the carbons. Other characterizations were carried out after acid washing.

ORR activities of the carbons after acid washing were evaluated using a rotating ring disk electrode apparatus (RRDE-3A, BAS) connected to a potentiostat (Electrochemical analyser Model 710E, ALS). 0.5 mol dm^{-3} was used as an electrolyte. Carbon ink was prepared by mixing 5 mg carbon, 150 μL distilled water, 150 μL ethanol and 50 μL Nafion solution (Aldrich 510211). The ink was applied to a glass-like carbon electrode; the amounts of carbon and Nafion were 200 and 100 μg per cm^2 electrode, respectively. ORR voltammograms were obtained by sweeping the potential from 1 to 0 V vs. RHE with rotating the working electrode at 1500 rpm in N_2 or O_2 saturated electrolyte.

Results and Discussion

Typical TEM images of the carbons before acid washing are shown in **Figure 1**. Without metal, NSs were not formed as shown in left two images in **Figure 1** (0M0N, 0M20N). Therefore, metal is essential to form NS. NS formed without uracil (3M0N) had highly oriented graphitic layers of NS. Addition of uracil to precursors made the graphitic layers of NS warped and NS particle sizes smaller.

Most of the particles owing to metal compounds were attributed to Fe particles by XRD analyses.

Average Fe particle diameters, NS's diameters and NS graphitic layer thicknesses are summarized in **Table 1**. All of them were averaged values of particles on TEM images. N contents in carbons examined by XPS increased with increase of N contents in precursors. With increase of N contents in carbon, Fe particles became smaller and NS's diameters and thickness of NS graphitic layers became smaller and thinner, respectively.

ORR voltammograms of the carbons are shown in **Figure 2**. Carbons having higher N contents showed higher ORR onset potentials and higher ORR activities.

Comparing NS structure and ORR activities of the carbons, warped graphitic layers of the carbons seems to be responsible for ORR activities as we have proposed 1,2. Introduction of nitrogen to carbon layers easily promoted carbon to have such warped graphitic layers.

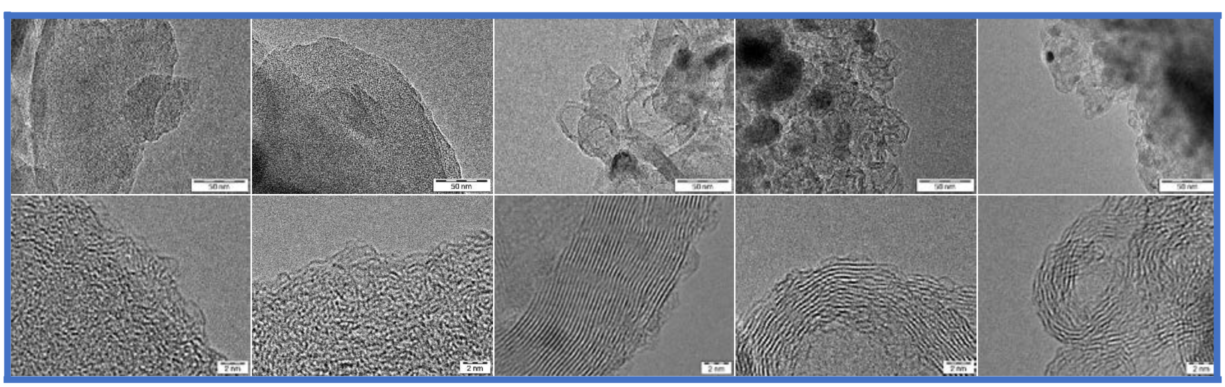

Figure 1. TEM micrographs of carbons. From left to right; 0M0N, 0M20N, 3M0N, 3M20N, 3M24N. Upper and bottom images are for lower and higher magnifications.

Table 1. Effects of N on Fe particle size and NS.

Sample	Fe particle	NS	
	Diameter (nm)	Diameter (nm)	Thickness of graphitic layer (nm)
3M0N	29	41	8
3M6N	32	40	8
3M15N	27	34	6
3M20N	14	21	5
3M24N	8	12	3

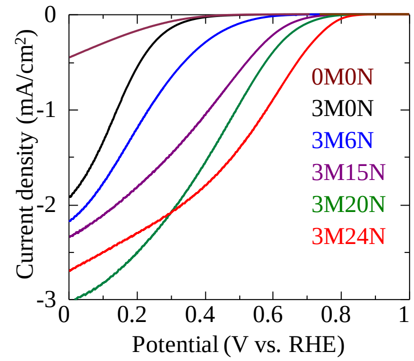

Figure 2 ORR voltammograms of carbons containing different amount of nitrogen

Conclusions

Metal compounds are essential to form NS. When nitrogen content increased, NSs had warped graphitic layers, became smaller, had thinner carbon graphitic layers and showed higher ORR activities. We concluded that warped graphitic layers of the carbons are responsible for ORR activity. Addition of nitrogen assists the carbon to have warped graphitic layers easily.

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