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主　論　文　の　要　旨

論文題目　**The Conversion of Pyridine Molecule up to Hetero carbon Nanomaterial by Solution Plasma**
(ソリュションプラズマによるピリジン分子からヘテロカーボンナノ材料への経路と合成)

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論　文　内　容　の　要　旨

The development of carbon nanomaterials such as carbon nanotubes, graphene, carbon dots, and graphene ribbons, various researches has been conducted using them as core materials for advanced technologies. Diverse application areas such as energy storage and conversion, gas storage, smart sensors, targeted drug delivery, catalyst support, field-emission devices, quantum wires are targets of carbon nanomaterials by applying their thermal, electrical, chemical and mechanical properties. However, when the carbon nanomaterials are actually employed in the practical field, they do not show the expected properties. To overcome this problem, hetero-atom doped carbon is focused for candidate material due to high potential to improve a property of pristine carbon. The hetero-atoms as nitrogen, boron, phosphorus, sulfur in the carbon frameworks lead to charge imbalance and polarizes adjacent carbon atoms, creating a net positive/negative charges. Especially, nitrogen atom which has 5 valence electrons and similar size with carbon atom is a best candidate atom among various kinds of hetero-atoms. For instance, when a nitrogen atom is doped into graphene, the spin density and charge distribution of carbon atoms will be influenced by the neighbor nitrogen dopants

and it leads to an improvement of electrical property effectively. In the case of catalyst effect for oxygen reduction reaction, the relative charge of carbon atoms next to the doped nitrogen atom changed to positive charge which is favorable to react with oxygen molecules. Also, the nitrogen atom in carbon quantum dots affects to the improvement of the quantum yield related to energy efficiency of light increased due to effects on the electronic band structure.

Due to these advantages of hetero carbon nanomaterial, many researchers have been focused on the development of effective synthesis methods with containing high concentration hetero atom. Chemical vapor deposition (CVD) methods are commonly used for fabrication of high purity graphene. Owing to synthesize nitrogen atom doped graphene by CVD, the ammonia gas was mixed into hydrocarbon gas source. However, the working temperature of conventional methods could prohibit a presence of nitrogen atoms in the carbon framework because the nitrogen atom which is one of the light elements can volatilize easily and the recrystallization of carbon structure also occur in the high temperature (800 ~ 1300 C°). Thus, the nitrogen contents of products synthesized by conventional method is low.

The solution plasma (SP) is an attractive alternative method for synthesis of nitrogen doped carbon material. Because, for synthesizing, the SP method used the glow discharge in the solution, thus solution temperature do not over the room temperature. And, the electron transfer occurs between plasma phase and hetero cyclic aromatic molecules in the liquid phase and it leads to polymerization of monomers by the C-H activation. Therefore, it is favorable to keep high contents of nitrogen in the carbon structure. Using these advantages of the SP, the previous studies reported that synthesis and analysis of hetero-carbon nanomaterials from heterocyclic aromatic organic solvents such as pyridine, cyanopyridine, and imidazolium ionic liquid. However, the investigation on the formation process from the hetero organic molecule to the hetero-carbon nanomaterials was not yet been clarified. Therefore, in this study, a conversion of hetero cyclic aromatic molecule (pyridine) by SP was investigated for deep understanding how the hetero cyclic molecule change to hetero carbon nanomaterial the SP process.

At first, the initial reaction of pyridine by SP was investigated using gas

chromatography-mass spectrometry (GC-MS). In the GC-MS results, cyanopyridine, bipyridine, and phenanthroline were confirmed after SP 1 second. Also terpyridine which is trimer of pyridine was clearly observed after 5 second of SP. The various molecules were formed by reaction with cyano radicals and pyridine cation radicals occurred by SP. The cyano radicals were generated by dissociation of pyridine molecule due to the plasma and the pyridine cation radical could be formed at the interface between the liquid phase and plasma gas phase by electron excitation. Among the various products, bipyridine was formed mainly, especially 2,2' bipyridine is dominant in the isomer. The energy to forming the reactant to product was calculated by DFT calculation to confirm the reason.

Quantitative diagnostic analysis of both plasma gas and liquid phases of SP in benzene, pyridine and aniline were reported. Until now, emission spectroscopy and chromatography results provide only qualitative information on the detected species. However, qualitative results is not enough to design to synthesis strategy of carbon nanomaterial through SP. Broadband absorption spectroscopy diagnostics method provides a quantitative information of radicals generated during SP. Furthermore, ten to hundred μM of chemical compound such as fluorene, pentaphene, phenanthroline and azobenzene in the liquid was *in-situ* measured by absorption spectroscopy. To form these kinds of arene or heteroarenes, an initiator is nessacary to polymerze and the penyl radical as a main reactant to polymerize the molecules was confirmed by electron spin resonance (ESR) measurement. In addition, the H/C ratio of solid carbon from organic solvent was significantly decreased through graphitizaion and polymerization by SP.

Finally, synthesis of highly N doped carbon dots (NCDs) through SP was presented. Carbon dots (CDs) in the range of a few nanometers of carbon particles are emerging as a new research field of carbon nanomaterials. The CDs have unique optical properties by the quantum confinement effect due to their size. The carbon dots are the intermediate size level between from an organic molecule size to common black carbon size. The SP method has a possibility of synthesizing the carbon dots due to their synthesis mechanism based on a polymerization of monomer by electron transfer. The NCDs was fabricated from pyridine with water by the SP and exhibited bright blue photoluminescence (410 nm) by UV excitation (340 nm). The NCDs showed the high N contents (13 at.%) and the high quantum yield (61 %). The n-pi* transition band was

clearly observed as increasing of N contents in the UV-vis results. Furthermore, as a fluorescence molecule detector for trinitrophenol, the NCDs revealed a high sensitivity and a high selectivity among the nitro group molecules.

In this study, various kinds of conversions from the pyridine monomer to dimer and trimer and several types of molecule by SP were successfully confirmed. Also, a fabricating to nitrogen doped carbon dots was confirmed. The results proved that SP methods can polymerize pyridine molecule rapidly and control the size of hetero carbon nanomaterial. Also, it suggested that suitable hetero carbon nano-material according to purpose can be synthesized by solution plasma. The pyridine as hetero arene is used in this study due to their similarity with benzene structure and their high synthesis rate of carbon nanomaterial. However, other types of hetero molecule also have a large potential to apply for synthesis of hetero carbon nanomaterial with prefer properties. Based on the results of this thesis, a pathway of other types of hetero molecule for hetero carbon nanomaterial will be discovered. Furthermore, it is believed that a molecular design by solution plasma can be achieved by revealing of the conversion procedure in molecular level of various kind molecules.