報告番号	甲　第　14500　号

主　論　文　の　要　旨

論文題目　**Multivariate Analysis of Synthesis Process and Material Structure for Carbons containing Nitrogen using Solution Plasma**
（溶液プラズマを利用した窒素含有炭素の合成プロセスと材料構造の多変量解析）

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論　文　内　容　の　要　旨

Nitrogen doped (N-doped) carbon materials have been widely studied and present their potential use for various energy conversion applications. For the synthesis of N-doped carbon materials, conventional methods with high temperatures, such as thermal annealing and solvothermal methods, are mainly used. The high temperature can significantly promote the reaction by providing large energy to starting organic molecules, leading to the activation of starting organic molecules to undergo the reaction. Nevertheless, the high-temperature process usually causes the evaporation of nitrogen, a lightweight element, resulting in a small amount of nitrogen contained in the carbons. To overcome this problem, low-temperature processes are necessary. However, for the conventional methods, when the temperature is lowered, the reaction becomes much slower because only a small number of activated species can go through the reaction. Recently, solution plasma (SP), a non-equilibrium plasma, have developed and drawn much attention due to its ability to form numerous activated species and promote reactions at low temperature. SP was found to be an effective low-temperature process for the synthesis of N-doped carbons with relatively high doping concentrations. Since SP involves a multidisciplinary of physics, chemistry, and materials science, there have been several unsolved questions. The intensive investigation of SP should lead to a solution and clear understanding, which can bring advantages to further improvement. In this research work, a correlation between the process parameters of SP and the structural parameters of carbon products was discovered by using multivariate analysis. Moreover, the improved SP method was also proposed to synthesize the N-doped carbon with significantly high doping concentration and a well-structured planar framework.

In Chapter 1, the general introduction, including the information on SP and their applications in material synthesis, mainly carbon synthesis, was first provided. Moreover, the information on critical process parameters (*i.e.,* active chemical species from plasma phase, intermediate species from liquid phase, and electric potential from plasma phase to liquid phase) and the structural parameters of carbons (*i.e.,* N content, defect index, and crystallinity) was explained. Finally, the objective and concept design of this research work was described. The selection of fifty-three organic molecules with σ- and π-bonded five- and six-member ring and containing nitrogen components was proposed as the investigated raw materials.

In Chapter 2, the correlation between patterns of optical emission spectroscopy (OES) with different dominations of activated chemical species in SP reaction field and structural parameters of carbon products was discovered. Four patterns with H^*, C_2^*, CN^*, and C_2^*/CN^* dominations were categorized. H^* and C_2^* were important species for the formation of amorphous carbon and graphite, respectively. Nevertheless, CN^* was important species for the synthesis of N-doped carbon with high doping concentration.

In Chapter 3, the correlation between the intermediate species in SP reaction field and the structural parameters of carbon products was discovered. The σ-bonded organic molecules, including five- or six-member ring molecules, dominantly formed intermediates with linear structures. Both π-bonded five-and six-member ring organic molecules mainly maintained ring structure during SP. The linear intermediates were found to produce carbon with lower nitrogen content but higher crystallinity. Oppositely, the intermediates with ring structure could produce carbon with relatively higher nitrogen content. Accordingly, the synthesis pathway of N-doped carbons could be altered depending on the organic molecules as the raw material.

In Chapter 4, the correlation between the electric potential in SP reaction field and the structural parameters of carbon products was investigated. The electric potential at different phases (*i.e.,* plasma, interface, and gas phases) was evaluated by an electrostatic probe technique. As a result, the reaction field with the high electric potential in the plasma phase could result in the formation of graphite-like carbon. However, there was an unclear correlation between the electric potential and nitrogen content in the carbon products.

In Chapter 5, according to the multivariant analysis of critical process and structural parameters from the above chapters, the modified SP system was proposed and successfully produced graphitic N-doped graphene with a high nitrogen content of 18.79 at.%. The proposed system could reduce the excessive current, resulting in stabilizing the glow plasma and maintaining the overall temperature to be at room temperature. It successfully preserved nitrogen atoms in the organic molecules from evaporation during the synthesis process and promoted the formation of a graphitic carbon framework.

In Chapter 6, the correlations of all critical processes and structural parameters in the synthesis of N-doped carbons using SP by multivariate analysis were concluded. The multi-correlation could reveal the connections between the chemical structure of raw materials, activated chemical species, intermediates, electric potentials during SP, and chemical and physical structures of the obtained carbon products. The systematic multi-correlation proved that it could provide direction for designing and modifying SP to achieve the synthesis of graphitic N-doped graphene with significantly high nitrogen content. Moreover, other possible directions for carbon-based material synthesis by SP were proposed in this thesis to guide process designs for chemists, materials scientists, and engineers who are dedicated to the research of carbon-based materials.