Synthesis of functional carbon nanocomposites by gas-liquid interfacial plasma

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Plasma irradiation on liquid surfaces or plasma discharge in solutions enables the high-speed and low-cost synthesis of various nanomaterials such as nanoparticles and nanotubes, and their functionalization. Recently, we have established a high-speed synthesis method of nanographene materials with high crystallinity by a plasma discharge at gas-liquid interfaces with alcohol sources [1]. By this method, a synthesis rate of nanographene over 1 mg/min and higher crystallinity of nanographene than the reduced GO have been realized. Furthermore, we have also found functionalization and structural control of nanographene materials by additive agents to alcohol sources at in-liquid plasma processes [2-3].

In recent years, heteroatoms-doped carbon nanocomposite materials that exhibit catalytic activity are attracting much attention as non-platinum catalysts. Especially, nitrogen (N)-doped nanographene materials are well-known to have high catalytic activity. Pyridinic-N is known as a key component to express catalytic activity [4]. There are two ways to obtain nitrogen-doped carbon nanomaterials. One is the addition of N into carbon nanomaterials during their synthesis, and the other is the post-nitridation after the synthesis, which often used nitrogen plasma. Especially in the latter case, the synthesis method of nanographene itself can be divided into two types of methods. One is the direct synthesis of the powder, and the other is the exfoliating from graphene oxide (GO) or bulk graphite by physical or chemical ways. Hydrothermal treatment using microwaves is one of the effective methods for simultaneous exfoliation, three-dimensional nanopore structuring, and nitrogen addition [5]. While electronic device applications generally need high-quality graphene sheets synthesized by epitaxial growth, or chemical vapor deposition (CVD) methods at high temperatures up to 1,000°C, some kinds of applications, such as sensors, batteries, additives to polymers, and so forth, need a large amount of nanographene power. For that purpose, a reduction of GO is well known, but the quality of the synthesized graphene is not high enough.

For these purpose, in-liquid plasma synthesis is good way to synthesis nanomaterials with high synthesis rate and low process cost. However, there is a trade-off relationship between the synthesis rate and crystallinity, when different types of alcohols were used as a feedstock gas. When ethanol,1-propanol, and 1-butanol were used, it was found that the higher synthesis rates were obtained by the higher-molecular weight alcohols, while its crystallinity was lower. In the comparison between hexane (C_6H_{14}) and hexanol ($C_6H_{13}OH$), in the case of hexane, the synthesis rate is about twice as high as that in the case of hexanol, but the crystallinity is lowered. These results indicate that this trade-of relationship is attributed to a ratio of carbon (C) and oxygen (O) atoms. O-related radicals (O, OH, etc.) in plasma could have etching effects of amorphous or low-crystallinity carbon components. According to the results of plasma diagnostic measurements and residual liquid analyses, it was found that crystallinity of nanographene materials degraded with decrease in OH intensity in plasma. Furthermore, small radicals such as C_2 and CH_x contribute to the synthesis of nanographene rather than by-products with a six-membered ring structure. Using an iron phthalocyanine with ethanol, size of carbon nanosheets increased up to micrometer. And they showed excellent catalytic characteristics thorough 4-electron reduction pathway. According to the verification results of dependence on synthesis conditions such as the type of additive, such the catalytic activity is induced by pyridinic C-N bonds. In the case of this way, to increase pyridinic C-N bonds and improve catalytic performance, iron phthalocyanine is much better than Hemin, even which also included Fe and N.

The in-liquid plasma process is generally used to synthesize powder materials, but if it can be used to construct three-dimensional structures, it will be extremely useful for many device applications. Recently, we have been working on in-liquid plasma using flat substrates and Ni foam as the lower electrodes and have confirmed the deposition of carbon thin films on flat substrates and their conformal coating on Ni foam.

These knowledges obtained in this study will open the way to the next-generation green energy solutions, such as high-performance catalytic electrode for the fuel cell.

References

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