Attempt of Liquid-Phase Material Processing Using Atmospheric-Pressure Glow Discharge Electrolysis

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Atmospheric-pressure dc glow discharge with liquid electrode is studied aiming the application for material processing in liquid such as metal nanoparticles (NPs) synthesis⁴,⁵ and surface modification⁶. In the synthesis of metal NPs, metal ions in the liquid are considered to be reduced by hydrated electrons or other reductive species⁴,⁵. The surface modification of polymer materials was achieved by glow discharge with electrolyte cathode using KCl, KBr or KI aqueous solutions⁶, although the reaction process is not clearly known. In these systems, the reactions in liquid are started by the electron/ion irradiation of the liquid surface or the dissolution of radical species from gas discharge plasma. Therefore, we can control various parameters in the gas phase as well as the parameters in the liquid for the process optimization. In addition, we can use the smart techniques developed in conventional electrolysis such as ion-exchange membrane. In this work, we report on our recent attempts on the NPs synthesis and surface modification in liquid using atmospheric-pressure glow discharge electrolysis.

The experimental setup is essentially the same as our previous works. An acrylic rectangular container is filled with aqueous solution. A Pt wire is immersed in the solution to connect to the ground; thus, the solution works as a liquid electrode. A nozzle electrode made of stainless steel with inner and outer diameters of 500 and 800 μm, respectively, is set at about 1 mm above the liquid surface. Helium gas is flowed from the nozzle electrode. By applying a dc voltage between the nozzle and liquid electrodes an atmospheric-pressure dc glow discharge is generated stably along the helium flow. By changing the polarity of the applied voltage, electrons or positive ions are exposed to the liquid surface from the glow discharge. For nanoparticle synthesis, HAuCl₄ aqueous solution, AgNO₃ aqueous solution, HPtCl₄ aqueous solution are used for Au NPs, Ag NPs, and Pt NPs, respectively. In the attempt to synthesize NPs with core-shell structure, the acrylic rectangular container was divided into two regions by cation-exchange membrane; the two regions were filled with different aqueous solutions. Only specific cation can pass through the cation-exchange membrane. In the surface modification of polymer material in liquid, a specimen made of polypropylene (PP) was set in NaCl aqueous solution, which also works as liquid electrode of the glow discharge. The surface of PP was investigated by FT-IR after treatment in addition to the measurement of water contact angle.

In each aqueous solution, metal NPs were synthesized. Au-core/Ag-shell NPs were synthesized in the limited experimental condition using cation-exchange membrane with HAuCl₄ solution and AgNO₃ solution; Ag⁺ ions were supplied into HAuCl₄ solution gradually through the cation-exchange membrane. In this case, the color of the HAuCl₄ solution became red, and then changed to yellow. The color change was confirmed by a spectrophotometer in contrast to the color by surface plasmon of Au and Ag.

In the surface modification, we first traced the experiment by Titov et al.⁶. However, we could not clearly reproduce it. The surface modification was not stable. The hydrophilicity of PP surface was improved by advanced oxidation process using H₂O₂ and UV, and Fenton method using Fe²⁺ and H₂O₂. This fact suggests that the OH radical is necessary for surface modification of polymer materials. Therefore, the key will be the production of OH radical close to the surface of polymer materials.

This work is partly supported by JSPS KAKENHI Grant Number 15H03584.