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The direct-current discharge plasma during nanoparticles formation was observed using a high-speed camera. Metallic plates of Au, Ni, Ti, and Zn were used as a cathode, and a Pt wire was used as an anode. Both electrodes were immersed in a 0.1 M NaOH solution. The solution plasma with light emission was generated via the vapor layer surrounding the cathode by applying 190 V. The current concentration occurred at a certain point of the electrode surface, in which the electrode surface was partially melted to produce nanoparticles. According to the high-speed observation, many light-emitting points appeared on the metallic plate and immediately disappeared when a certain point was strongly heated to produce nanoparticles. Additionally, light emission points moved in a chain reaction; after the first emission point was generated, the next emission point tended to be generated in the space surrounding the first emission point. During electrolysis, holes were generated on the cathode. The current concentration strongly heated certain spots on the electrode, and the electrode momentarily melted or vaporized, resulting in the formation of nanoparticles.

In the past decade, in-liquid plasma containing direct-current (DC) discharge,1 high-frequency plasma,2 microwave plasma,3 or pulsed discharge4 has been applied for nanoparticle formation. In certain conditions of plasma in liquid, metallic wires were used as electrodes, the surfaces of which were locally heated to produce nanoparticles. Hattori et al. reported the formation of WO3, Ag, Au, Mg(OH)2, and Zn/ZnO nanoparticles from a rod electrode with a 1- to 2-mm diameter via microwave or radio frequency plasma in liquid.2,3 Gold clusters of diameter less than 2.0 nm were successfully fabricated by solution plasma sputtering in liquid nitrogen, and a gold wire of diameter 1.0 mm was used as a source material.4 Additionally, contact glow discharge electrolysis (CGDE) has been applied for producing Ni, Ti, Ag, and Au metallic nanoparticles using 1-mm-diameter wires.5–7

When the anode is placed above the surface of an electrolyte in an Ar atmosphere and a high DC voltage is applied between the anode and an electrode immersed in the electrolyte, glow discharge occurs between the anode and surface of the electrolyte. An electrode under such conditions was named a “GDE” by Hickling and Ingram.8 When both electrodes are immersed in the electrolyte, the discharge plasma is sustained between the electrode and the surface of the surrounding electrolyte. This discharge is classified as a CGDE.1 As mentioned above, GDE and CGDE have been applied for nanoparticles synthesis and water treatment. However, the plasma-liquid interaction is still not well understood owing to the complex and dynamic nature of the plasma-liquid interface.

To understand how nanoparticles are synthesized from the metallic electrode, plasma diagnostics has become increasingly important. Optical emission spectroscopy is one of the most widely used tools for investigating in-liquid plasma properties. We can calculate the excitation temperatures and electron densities by analyzing the emission spectrum.9,10 Furthermore, the plasma behavior can be clarified through high-speed imaging. High-speed imaging has been applied for observing plasma in liquid.11–15 However, it is difficult to observe the surface of a wire electrode by using a high-speed camera because the surface of conventional wire electrodes is very small and not flat.

In this study, we generated DC discharge plasma on a flat metallic plate to realize the observation of the electrode using a high-speed camera. The experimental setup consisted of two electrodes in a square-shaped glass cell to eliminate the effect of light refraction. When the metallic plate without any covers was directly immersed in an electrolyte, the discharge primarily occurred at the edge of the plate because the current tends to concentrate on the edge of the electrode. To limit the area of plasma discharge on the electrode plane, a quartz glass holder was used to cover the whole surface of the cathode electrode plate, except for the hole on the electrode plate, which had a 14-mm diameter, as shown in Fig. 1. Discharge occurred at this hole on applying 190 V using a direct-current power supply (Takasago ZX-800H). Metallic plates of Au, Ni, Ti, and Zn with thicknesses of 0.2 mm were inserted in this glass holder. The counter electrode was a platinum wire of length 1000 mm and diameter 0.5 mm. A 0.1 M NaOH solution was used as the electrolyte. A high-speed camera (Photon FASTCAM SA3) with a frame rate of 20 000 fps was placed in front of the electrode plate. Light emission from the plasma was measured using a visible light spectrophotometer (USB 2000+, Ocean Optics) with an observation range from 200 to 850 nm. After producing particles in the experiment, the electrodes were characterized using a scanning electron microscope (SEM) and a transmission electron microscope (TEM).
The spot, where the current concentration occurs, is heated exclusively. Eventually, the cathode melts or ionizes at the spot to form nanoparticles.

The photographs shown in Fig. 1 display the light emission from the Au, Ni, Ti, and Zn electrodes. From these photographs, it is clear that the discharge plasma was successfully generated on the electrode surface. In the optical emission spectroscopy, strong emissions of H_a (656 nm), H_b (486 nm) (Balmer atomic hydrogen lines), OH A 3Σ^−→X^2Π (0, 0) band (309 nm), and O (777 nm) were detected. Strong emissions of Na (589 nm) were derived from the NaOH electrolyte solution. The emissions from Au (312 nm), Ni (341, 357, 362, and 386 nm), Ti (324 and 334 nm), and Zn (330, 335, 468, 472, and 481 nm) were also detected. This result indicates that the electrode materials were partially ionized during CGDE.

Figure 3 shows sequential images of the electrodes taken using the high-speed camera with a frame rate of 20000 fps (media file in supplementary material^19). In these images, the plasma appears as points, rather than as a layer structure. The total discharge area is very small. These light-emitting points correspond to current-concentration points depicted in Fig. 2(b). The large current is concentrated at a certain point, which induces the ionization of various species. From the videos taken using the high-speed camera, emission disappeared very quickly within a few hundred microseconds and there was regularity in the movement of light emission. After the first emission point was generated, the next emission point tended to be generated in the space surrounding the first emission point. In the Ni case, the light-emitting points moved in a linear manner. The light emission from Zn slowly spread in a circle. These results revealed that the current-concentration occurred in a chain reaction.

We predicted the formation and extinction mechanism of plasma emission, as shown in Fig. 4(a). First, the current concentration occurred at a certain spot, as mentioned in Fig. 2. The increase in temperature at a certain spot induces a large current flow, which increases the temperature further. When the temperature exceeds the melting point of the electrode material, the electrode melts and nanoparticles form (step 1). Second, heat diffusion extends the concentration spot (step 2). Subsequently, the current concentration spot disappears because the temperature distribution becomes uniform owing to the heat diffusion (step 3). Subsequently,
the new current concentration spot is generated near the first emission point because it has a higher temperature than surrounding area. Thus, the current-concentration seems to be a chain reaction.

After producing particles in the experiment, the electrode surfaces were observed through SEM and TEM. According to Fig. 4(b), holes were formed on the surface of Au, Ni, and Ti electrodes. The current concentration strongly heated a certain spot of the electrode, and the electrode momentarily melted or vaporized. In the case of Zn, rod-like structures were attached to the electrode surface. From the TEM and SEM observation of the products, it is clear that the Au, Ni, and Ti electrodes produced nanoparticles. The products were mainly spherical particles. Some particles were agglomerated by attaching to each other during the melting process. From the X-ray and electron diffraction, it can be seen that Au and Ni have a metallic phase. The product from the Ti electrode was oxidized because of high-temperature corrosion. The Zn electrode produced rod-like ZnO particles. As reported previously, the precursor of rod-like ZnO is Zn(OH)$_4^{2-}$, which is formed around the electrode at high temperatures. When the ZnO precipitated,
ZnO crystals grew preferentially along the [0 0 0 1] direction. The ZnO nanorods also grew on the surface of the Zn electrode.

In conclusion, we successfully generated a DC-excited discharge plasma on the flat surface of Au, Ni, Ti, and Zn plates in liquid. The current concentration generated in the vapor surrounding the cathode induced the plasma at a certain point. From optical emission spectroscopy, the emissions of hydrogen lines, OH, O, Na, and elements contained in the electrodes were detected. Our observation using a high-speed camera revealed that the total emission area was small and that the current-concentration occurred in a chain reaction because of the difference in temperature on the electrode surface. During the discharge, nanoparticles of Au, Ni, TiO₂, and rod-like ZnO were synthesized.