# In situ Analysis for Initial Formation Process of Gold Nanoparticles in Discharge in Aqueous Solution

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# 1. Introduction

Electrical discharges in an aqueous solution have been intensively studied for several applications, such as metal nanoparticles synthesis [1], water disinfection [2], generation of ozone, oxygen, hydroxyl radicals and other chemically active species [3]. Electrical discharge techniques in the aqueous solution produce active oxidative and reductive species, so they do not require the transfer or disposal of chemicals. Thus, the discharge in water is a promising method to synthesize metal nanoparticles. We successfully synthesized the gold nanoparticles with the discharge in the aqueous solution. However, we have not yet controlled the size of the nanoparticles. In order to control the size of the nanoparticles, it is crucial to elucidate the gold nanoparticles formation mechanism. In addition, it is also important to clarify physicochemical state in the discharge in the water, since the formation process of the nanoparticles strongly depends on the discharge mode.

In this study, we aimed to *in situ* monitor initial formation process of the gold nanoparticles in the discharge in the water using optical spectroscopy. Time resolved optical emission spectroscopy method was used to determine the reactive species generated in the discharge in aqueous solution.

# 2. Experimental set-up

The discharge in the ultrapure water was generated in a plastic vessel in order to determine the evolution of reactive species formed in the water. The measuring equipment is shown schematically in figure 1. The discharge process was initiated between two tungsten electrodes immersed in ultrapure water. The electrodes diameter was in the range of 0.5 - 2.5 mm. The interelectrode gap can be adjusted from 0.5 mm to 5 mm. Charging voltages in the range of 400V - 2kV were applied



Fig.1. Experimental set-up of the electrical discharge in water

to the water gap between the electrodes. Repetition frequency used was in the range of 10 - 30 KHz. Electrical current values were in the range of 4 - 10 A.

Gold nanoparticles were synthesized using chlorauric acid liquid solution as a gold source material. An electrical discharge in this solution was generated between two cylindrical tungsten electrodes with a diameter of 0.5 mm. The conductivity of the solution used in the experiment was 180 µS / cm. Gelatin was used as a stabilizer. The emission spectra of the reactive species generated in the arc discharge process were analyzed by using a spectrograph type AvaSpec-2048. The absorption spectra of the gold colloidal solution were obtained from ultraviolet visible spectroscopy (UV-vis). The gold nanoparticles were observed by transmission electron microscope (TEM) with energy dispersive spectrometry (EDS).

### 3. Results

The breakdown voltage and the electrical current applied in the discharge were measured using different experimental conditions. Physicochemical state in the discharge in the water changed depending on the electrodes diameter, and interelectrode gap. Using a spectrograph type AvaSpec-2048, we monitored the time-resolved optical emission spectra over the range 200 - 1100 nm as a function of discharge parameters (Figure 2). Optical emission spectra acquired in the ultrapure water (Figure 3) showed five principal lines, originating from atomic hydrogen (the H $\alpha$  line at 656.28 nm, the H $\beta$  line at 486.13 nm, and the H $\gamma$  line at 434.04 nm), the hydroxyl radical (OH band at 306.4 nm), and atomic oxygen (the O line at 777.9 nm, 844.6 nm and 926.2nm). In the spectra were also observed molecular oxygen (at 393.8 nm) and hydrogen (616.1 nm.). The dominant line is the Balmer H $\alpha$  line emitted by the atomic hydrogen. These lines come from the water molecules dissociation in the electrical discharge process. Optical emission spectra after the discharge for 30 s in the aqueous solution containing chlorauric acid is shown in figure 4. The hydrogen lines (H $\alpha$ , H $\beta$ ) have been used for electron temperature calculation. The electron temperature obtained for the electrical discharge in water (0.6 eV) was different from that calculated for the electrical discharge in the solution containing chlorauric acid (0.8 eV).



**Fig. 2.** Time evolution of the reactive species in a high voltage discharge in ultrapure water using tungsten electrodes



Fig.3. Optical emission spectrum of a high voltage discharge in ultrapure water using tungsten electrodes



**Fig.4**. Optical emission spectrum of a high voltage discharge in chlorauric acid liquid solution

The formation of gold nanoparticles was confirmed by the UV-Vis spectra of the resulting gold colloidal solution (Figure 5). An absoption peak was located at 540nm, indicating the formation of gold nanoparticles.



Fig.5. UV-Vis spectra of the aqueous gold solution

## 4. Conclusions

Plasma composition and time evolution of the reactive species formed in the discharge process were studied in dependence with discharge voltage, pulse width, repetition frequency. Gold nanoparticles were successfully synthesized by using an electrical discharge process in chlorauric acid liquid solution. The electron temperatures calculated from the hydrogen lines for the discharge in the ultrapure water and in the solution containing chlorauric acid were 0.6 and 0.8 eV, respectively.

#### References

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