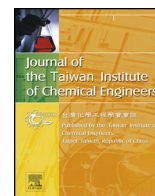




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Influence of the discharge time of solution plasma process on the formation of gold nanoparticles in alginate matrix



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ABSTRACT

Gold nanoparticles (AuNPs) stabilized in alginate matrix were synthesized by applying the plasma into alginate aqueous solution containing gold(III) chloride trihydrate precursor. Effect of the solution plasma process (SPP) discharge time on the physical properties, including shape and size, and the optical absorption properties of the synthesized AuNPs were investigated by varying the discharge times to be 0, 5, 10, 20 and 30 min. Results reveal that the increase in the discharge time leads to a size reduction of the AuNPs. Also, the particles tend to be more spherical. Appearance of the obtained AuNPs–alginate suspensions along with the change in their UV–vis absorption spectra intensity after samples were left standing for several time intervals suggest that alginate solution itself can act both as a stabilizer and a reducing agent for the AuNPs formation while the application of plasma helps to improve the controllability of shape and size of the synthesized particles. Furthermore, the method is simple, reproducible, and does not need any manipulative skill. Since the reducing agent is not required, the method is suitable for utilizing in biomedical application.

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1. Introduction

Owing to their important property to interact with light at a specific wavelength that leads to a phenomenon called surface plasmon resonance (SPR), gold nanoparticles (AuNPs) exhibit powerful potential in medical field as chemical and biological sensing [1]. They have also been widely studied for application in targeted delivery [2] as well as cancer diagnostic and therapeutic agents [3]. Numerous approaches become feasible since the particles are small enough to enter almost all area of the body, for example, blood–brain barrier [4] and blood–retinal barrier [5]. Since the particles would aim to be administered into living organisms, an important issue of utilizing AuNPs in biomedical application is their safety to cells. Biocompatibility of the AuNPs could be improved both by chemical technique through surface functionalization [6,7] or physical passivation through dispersion in biocompatible substances [8,9]. For the latter case, sodium alginate – a natural block copolymer extracted from seaweed – is

an alternative matrix for the dispersion of the AuNPs [10,11]. It is one of the most commonly used substances for the encapsulation of biologicals because of its gel formation ability after dissolution in water. This gel can function to stabilize the AuNPs to prevent particle agglomeration and settlement.

One useful tool for the synthesis of metal nanoparticles is the glow discharge in liquid phase named “solution plasma process (SPP)” [12]. The key of the synthesis is the generation of reactive species induced by the plasma in a liquid environment that can lead to the reduction of ions to nanoparticles. Synthesis of the AuNPs by the SPP was studied in water [13] as well as other media such as liquid nitrogen and ethanol [14]. Previously, we have proposed a one-step production of colloidal AuNPs–alginate aqueous suspension by the solution plasma sputtering (SPS) process [15]. The process was named “SPS” since the AuNPs were produced from sputtering of the gold electrodes. Briefly, the plasma was applied through a pair of gold electrodes which were immersed in alginate aqueous solution. By using the SPS strategy, we obtained spherical AuNPs having diameter ~ 3 – 5 nm which were dispersed well in the alginate matrix within a reasonable period of time (more than six months). Apart from endowing biocompatibility to the AuNPs, utilization of the alginate polymer was of great benefit to the production of AuNPs–alginate suspension by the application of plasma: it can promote the

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generation of plasma in liquid environment and provide colloidal stability to the obtained suspensions. In the present contribution, production of the AuNPs is still based on the application of plasma into alginate aqueous solution. However, the gold(III) chloride trihydrate was used as a gold precursor. We aim to compare this production strategy with the former research [15]. As a first step, influence of the plasma discharge time on the appearance, size, and optical absorption properties of the AuNPs were studied.

2. Experimental

2.1. Chemicals

Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 49.0\%$ Au basis) purchased from Sigma-Aldrich (Buchs, Switzerland) was used as a gold precursor. Sodium alginate was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Alginate aqueous solutions were prepared using ultra-pure water from Aquarius water distillation apparatus, RFD250NB, Advantec (Tokyo, Japan). Sodium alginate aqueous solution was prepared at a concentration of 0.5% w/v while concentration of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ precursor in the solution was 0.2 mM .

2.2. Experimental setup and production procedure

Experimental setup of the SPP used for the production of AuNPs-alginate aqueous suspensions is schematically shown in Fig. 1. Two tungsten rods were used as electrodes. Each electrode was covered with a ceramic tube which was inserted in a silicone stopper. They were then placed in a 100 mL glass beaker having an inner diameter of 43 mm and a height of 75 mm. The distance between the tips of electrodes was set to 0.3 mm . Before the discharge, the glass beaker was filled with 90 mL alginate aqueous solution containing gold(III) chloride trihydrate (0.2 mM). The plasma was generated, at atmospheric pressure and room temperature, using a bipolar-DC pulsed power supply (SPIK

2000A/KT-IDP-1010S). The pulse width and frequency employed during the generation of plasma were $2\ \mu\text{s}$ and 15 kHz , respectively. Solutions were stirred continuously during the operation in order to maintain homogeneity at any instant.

2.3. Characterizations

During the generation of plasma, optical emission spectra were collected using an optical emission spectroscopy (AvaSpec-3648, Avantes, USA), operated with an integration time of 10 ms and average 10 scans within the wavelength range from 200 to 1000 nm . Optical absorption properties of the AuNPs-alginate aqueous suspensions were analyzed with a UV-3600 spectrophotometer (Shimadzu, Japan) in the spectral range from 200 to 800 nm . Samples were prepared by diluting the suspension to reach a concentration of 0.2% w/v (calculated based on the concentration of alginate solutions). Transmission electron microscope (TEM) JEM-2500SE (JEOL, Japan), operated at 200 kV , was used to observe the shape and size of the AuNPs. Samples were prepared by adding ethanol into the suspension which was then dropped onto a copper grid before let it dry by exposure to the air for 24 h . Particle size was obtained by measuring diameters of 80 particles viewed in the TEM images. Zeta potential analysis was carried out using a zeta potential analyzer ELS-7300 K (Photal Otsuka Electronics, Japan). Data were observed from samples which were left standing for 4 months. The pH measurement was conducted using pH/Ion Meter F-53 (Horiba, Japan).

3. Results and discussion

3.1. Reactive species generated during the AuNP formation

Reactive species generated during the plasma discharge in alginate aqueous solution containing gold(III) chloride trihydrate were investigated by optical emission spectroscopy (OES). Results are shown in Fig. 2. Appearance of emission peaks corresponding to excited state of atomic hydrogen (i.e., H_α at $\lambda = 656\text{ nm}$; and H_β at $\lambda = 487\text{ nm}$) and atomic oxygen (i.e., O I at $\lambda = 778$ and 845 nm ; and O II at $\lambda = 743\text{ nm}$) reveals that predominant reactive species occurring in the reaction are H and O species. These species come from decomposition of water molecules, the medium used in this study. Emission peaks corresponding to Na atoms in the alginate polymer are additionally observed (i.e., Na I at $\lambda = 590\text{ nm}$; and Na II at $\lambda = 618\text{ nm}$). The presence of activated Au species is confirmed by the occurrence of Au II emission peak at $\lambda = 401\text{ nm}$. Study reported by Saito et al. [13] indicates that H radical functions

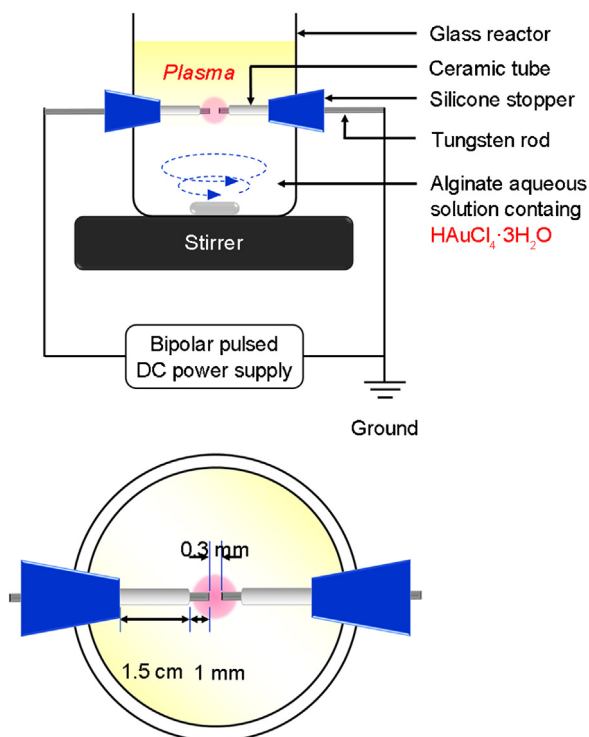


Fig. 1. Schematic illustration of the experimental setup.

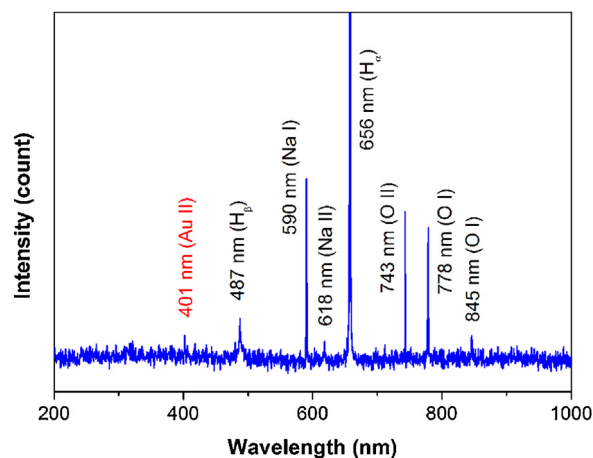


Fig. 2. OES spectra of the plasma generated in alginate aqueous solution containing gold(III) chloride trihydrate.

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