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Physical and Chemical Behaviors of Nano-Bio Non-Equilibrium Plasmas at the Gas-Liquid Interface

ナノ・バイオ非平衡プラズマの気液界面における物理・化学的挙動

Toshiro Kaneko and Rikizo Hatakeyma
金子 俊郎, 畠山 力三

Department of Electronic Engineering, Tohoku University
6-6-05 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
東北大学 大学院工学研究科 電子工学専攻 〒980-8579 仙台市青葉区荒巻字青葉6-6-05

Density-controlled gold nanoparticles (AuNPs) conjugated with carbon nanotubes are synthesized by a novel non-equilibrium plasma technique combined with ionic liquids using the chemical reactions which are enhanced by the physical actions at the gas-liquid interface. Furthermore, the gas-liquid interfacial discharge plasma is also used for the synthesis of a DNA-AuNP conjugate, where the size and morphology of the AuNPs are simply tuned by varying the concentration of DNA which acts as a stabilizer through conjugating on the surface of the AuNPs.

1. Introduction

Recently, many works on gas-liquid interfacial discharge plasmas (GLIDPs) have been performed as fundamental and application researches [1], because the non-equilibrium plasmas in gas phase can produce the various kinds of chemically active ions and radicals which react with nano- and bio-materials stably existing in liquid. Furthermore, the physical phenomena such as convection and transport in the gas and liquid phases, and formation of potential structures at the gas-liquid interface are expected to enhance the chemical reaction and play important roles in the synthesis of novel nano-bio conjugated materials.

As one of the promising applications of the GLIDPs, the synthesis of various kinds of nanoparticles [2] is advantageous in that toxic stabilizers and reducing agents are unnecessary and the synthesis is continuous during the non-equilibrium plasma irradiation. In addition, the nanoparticles conjugated with carbon nanotubes (CNTs), which are very fascinating materials in electronic, magnetic, and optical applications, could constitute promising nanoelectronics devices.

On the other hand, the GLIDPs are also used in the biomedical field, for example, the synthesis of nanoparticles conjugated with biomolecules such as DNA. The DNA conjugated nanoparticles work as vectors to deliver DNA into living cells because the nanoparticles can be manipulated by a light field. For this purpose, we synthesize the gold nanoparticles (AuNPs) in association with DNA in the aqueous solution using the reaction at the gas-liquid interface by the assist of the non-equilibrium plasma irradiation.

2. Experimental Apparatus

Figure 1 shows the schematic diagram of an experimental setup for the GLIDP [3,4]. A cathode electrode composed of liquid (an ionic liquid (IL) or water) is located inside the glass cell and DC or pulse power is supplied to the cathode electrode. On the other hand, a grounded anode electrode composed of a stainless steel (SUS) plate is set in the gas-phase region at a distance of 60 mm from the surface of the cathode electrode. This discharge configuration is defined as “A-mode”. To examine the effects of the power supplied to the liquid electrode on discharge-related phenomena, the cathode electrode is switched to the SUS plate in the gas phase, and the liquid electrode is grounded instead, which is defined as “B-mode”. Argon gas is adopted as a discharge gas, and the gas pressure P_{gas} is varied from 20 Pa to 40 kPa.

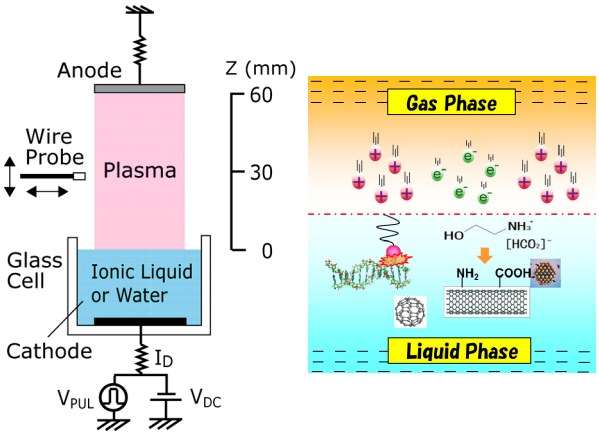

Fig. 1. Schematic of the experimental setup and model of the interaction between charged particles in the non-equilibrium plasma and the nano-bio molecules in the liquid.

3. Results and Discussion

We successfully generate a plasma incorporated with IL (2-Hydroxyethylammonium formate) at low gas pressures with high stability. It is found that the secondary electrons are emitted from the IL more efficiently than the SUS electrode by the irradiation of the high energy ions to the cathode electrode in A-mode and electrons to the anode electrode in B-mode. [3] Therefore, it is expected that the liquid electrode enhances the chemical reactions at the interface between the plasma and the IL, and is effective for the synthesis of nanomaterials [5].

To synthesize size- and density-controlled AuNPs, we attempt to use single-walled carbon nanotubes (SWNTs) functionalized under the control by the irradiation of the GLIDP. The SWNTs are dispersed in the IL which consists of carboxyl groups, and the plasma is irradiated to the IL. Since we use A-mode in this experiment, the plasma ions with high energy can dissociate the IL and the dissociated carboxyl groups bond to the surface of the SWNTs. Then, the Au chloride ($HAuCl_4$) dissolved in the IL is reduced and the AuNPs are selectively synthesized on the carboxyl groups. Since the density of the carboxyl groups on the SWNTs can be controlled by the plasma ion irradiation parameter, such as irradiation energy, flux, time, and so on, the density of the AuNPs can also be controlled.

Figure 2 shows transmission electron microscope (TEM) images of the AuNPs synthesized on the SWNTs as a function of plasma irradiation time. It is found that the mono-dispersed Au nanoparticles are synthesized on the SWNTs when the SWNTs are previously treated by the plasma irradiation. In

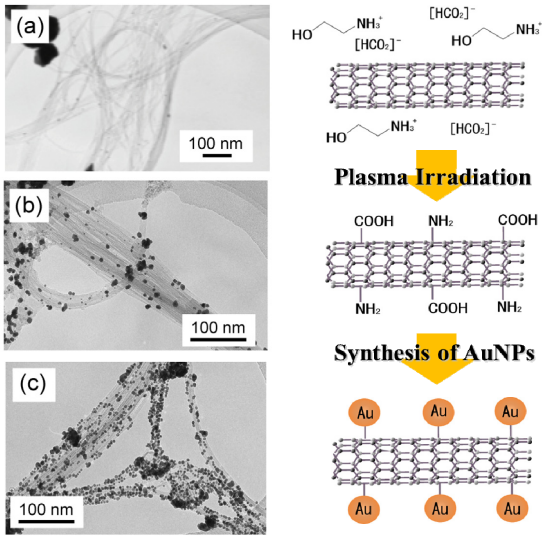

Fig. 2. TEM images of the AuNPs synthesized on the SWNTs as a template. (a) no plasma treatment, (b) plasma treatment for t = 1 min, (c) plasma treatment for t = 10 min. A-mode, P_{gas} = 60 Pa, I_D = 1 mA.

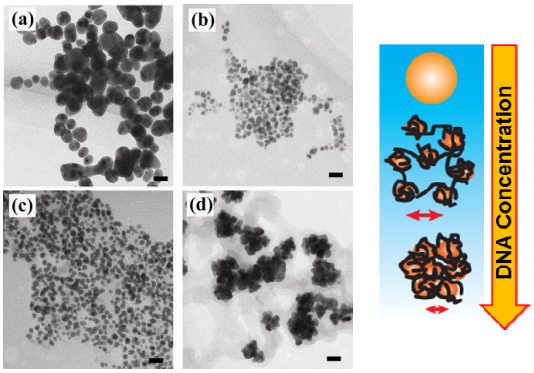

Fig. 3. TEM images of AuNPs synthesized with DNA concentrations of (a) 0, (b) 0.35, (c) 0.7, and (d) 1.75 μM. Scale bar is 20 nm.

addition, the density of the AuNPs becomes large with an increase in the plasma irradiation time. This result means that the AuNP density can be controlled by functionalization of the SWNTs using the plasma ion irradiation in the IL.

For nano-bio application of the GLIDP, we synthesize the AuNPs conjugated with DNA using pure water and a pulse power source in place of the ionic liquid and DC power source, respectively. Figure 3 gives the TEM images for products synthesized at different DNA concentrations. In the presence of DNA, the AuNPs drastically change to water-soluble products, which consist of the dispersedly small-sized AuNPs (~7 nm) covered with DNA. However, the AuNPs take on an agglomerated form for DNA concentrations lager than 1.5 μM. Since DNA covers the surface of the AuNPs during the synthesis by the plasma irradiation, the competition between the AuNP synthesis rate and DNA covering rate can determine the size and morphology of the DNA-AuNPs conjugate.

4. Conclusions

The irradiation of the non-equilibrium plasmas to the liquid surface can realize the density-controlled synthesis of AuNPs on the SWNTs by the chemical reactions which are enhanced by the physical actions at the gas-liquid interface. In addition, the size- and morphology-controlled AuNPs covered with DNA are also synthesized using the GLIDP, where DNA prevents the AuNPs from further clustering, resulting in the small-sized AuNPs.

References

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