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Gold Nanoparticle-DNA Conjugate Decorated Double-Walled Carbon Nanotubes Realized by Gas-Liquid Interfacial Discharge Plasma

気液界面プラズマによる金ナノ粒子ーDNA複合物質修飾二層カーボンナノチューブ

Qiang Chen, Toshiro Kaneko and Rikizo Hatakeyma
陳　強,　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

Gold nanoparticle (AuNP)-DNA conjugates are synthesized by reducing an aqueous solution of chloroauric acid trihydrate with DNA using a pulse-driven gas-liquid interfacial discharge plasma. In addition, the synthesized AuNP-DNA conjugates are forced to be encapsulated into or decorated on double-walled carbon nanotubes (DWNTs) by applying a DC voltage which is superimposed on the pulse voltage. The AuNP-DNA encapsulated DWNTs are possible to be utilized in drug delivery systems when DNA is used as drug molecules.

1. Introduction

As a special class of nanotubes, double-walled carbon nanotubes (DWNTs) have a coaxial structure, containing two concentric graphene cylinders and they have higher thermal and chemical stability compared with single-walled carbon nanotubes (SWNTs). The DWNTs can be applied to gas sensors, dielectric devices, nano-electronic devices, and emitters etc. To tune the properties of the DWNTs for further applications, they may be functionalized by decorating their end-caps or the outer sidewall with functional groups or metal nanoparticles. The functional groups, such as molecules [1,2], polymers [3], and metallic particles [4] can be covalently attached on the DWNT end or sidewall. On the other hand, non-covalent functionalizations can be realized without changing the carbon-bond structures on the DWNT end and sidewall [5,6].

Here we shows a decoration of the DWNTs with gold nanoparticle (AuNP~~s~~)-DNA conjugates with the non-covalent functionalizations, which are realized by a pulse-driven gas-liquid interfacial discharge plasma (GLIDP).

2. Experimental

Figure 1(a) presents the schematic of the experimental setup. The GLIDP is generated between the bottom liquid and top stainless steel (SUS) rod in Ar gas by applying a pulse voltage (20 kHz) to the liquid electrode and connecting the top SUS electrode to the ground through a resistor (5 Ω). The liquid electrode consists of aqueous chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$) (0.1 g/l) with DNA, which is put in a glass cell. DNA is used as a stabilizing agent for keeping the AuNPs small by conjugating on their surfaces, and they are 30-mer DNA containing guanine, (denoted as dG_{30}, 0.5 μM). Since the discharge at atmospheric pressure will overheat the liquid electrode and make much loss of liquid by evaporation, we reduce the gas pressure to 20 kPa at which overheating is largely decreased.

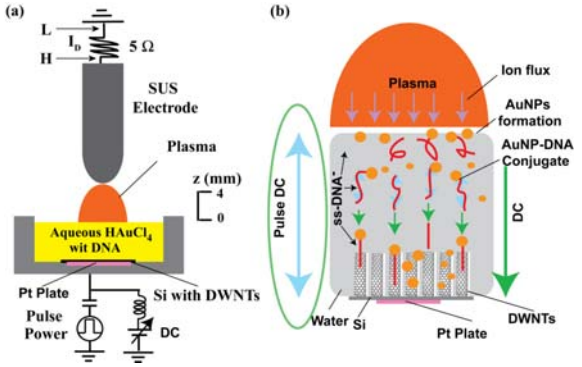

Fig. 1. (a) Schematic of the experimental setup, and (b) mechanism of the synthesis of AuNP-DNA conjugate decorated DWNTs.

For the synthesis of the AuNP-DNA decorated DWNTs, pristine DWNTs are heated in static air at 460 ^{o}C for 30 min to produce the open-ended DWNTs. The AuNP-DNA conjugates are synthesized by reducing gold (III) to gold (0) from the $HAuCl_4$ aqueous solution in the GLIDP as

shown in Fig. 1(b). The plasma provides the reducing agents, such as hydrogen radicals and secondary electrons which are created by plasma irradiation on the liquid surface [7]. A Si substrate covered with the DWNTs is placed on the Pt plate. When the plasma is generated, the AuNP-DNA conjugates are synthesized near the gas-liquid interface as shown in Fig. 1(b). The pulse voltage can stretch the random-coil shaped DNA. The DC voltage superimposed on the pulse voltage can move the charged AuNP-DNA conjugates to the DWNTs by a principle of the electrophoresis. The discharge time is 3 min. After the plasma operation, the collected DWNTs are rinsed by ethanol. The DWNTs with AuNP-DNA conjugates are put in water and rinsed using an ultrasonic bath for 8 h, which will remove DNA attaching outside the DWNTs. Then the DWNTs are extracted from water by a centrifuge for characterization.

3. Results and Discussion

Figure 2 gives the transmission electron microscopic (TEM) images of the synthesized AuNP-DNA conjugate decorated DWNTs. For the sample synthesized with a superimposed DC voltage of +200 V, the most AuNP-DNA conjugates on the surface of DWNTs take on an aggregated form. A few AuNP-DNA conjugates are rod-like and inside the DWNT, meanwhile the AuNP-DNA conjugate caped DWNT exists, as shown with arrow marks in Fig. 2(a). However, for the sample synthesized with a superimposed DC voltage of -200 V, the small-sized (~2.5 nm) AuNP-DNA conjugates are found to be decorated on the DWNTs. In addition, there are non-attached AuNP-DNA conjugates with the size of ~15 nm.

It might be explained as follows. The large-sized AuNP-DNA conjugates are negatively charged and the small-sized AuNP-DNA conjugates are positively charged in the solution. Therefore, the positive DC voltage is possible to transfer the aggregated AuNP-DNA conjugates to the bottom DWNTs, while the negative DC voltage is favorable for the small-sized AuNP-DNA conjugate movement. When the AuNP-DNA conjugates connect with the DWNTs, the DNA part of the conjugates can attach on the DWNT surface by π–π stacking interactions as shown in the SWNT case [8] or the DNA part can be inserted into the DWNTs to form the AuNP caped DWNTs.

4. Conclusions

The GLIDP is used to decorate the DWNTs with AuNP-DNA conjugates. AuNP-DNA conjugates are formed by reducing the gold (III) from the $HAuCl_4$ aqueous solution at the gas-liquid interface. The synthesized AuNP-DNA conjugates are moved toward the DWNTs by the superimposed DC voltage. The large-sized AuNP-DNA conjugates are moved to the DWNTs by the positive superimposed DC voltage, while the small-sized AuNP-DNA conjugates by the negative superimposed DC voltage. We believe that the decoration of the DWNTs by the AuNP-DNA conjugates can vary the electronic and optical properties of the pristine DWNTs, such as the carrier type and light response.

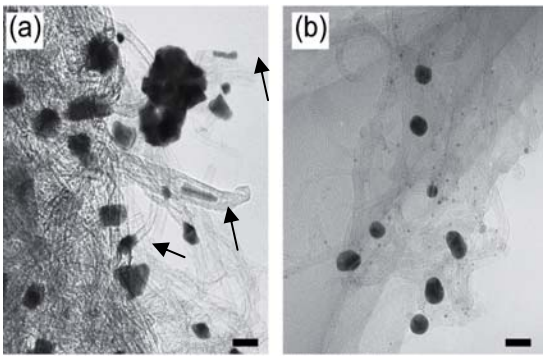

Fig. 2. TEM images of samples with superimposed DC voltage of (a) +200 V and (b) -200 V. Scale bar is 20 nm.

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