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Carbon Nanotube Network Conjugated by Nanoparticles with Defined Nanometer-Scaled Gaps

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1. Introduction

Carbon nanotubes (CNTs) have been attracting broad interest in many research fields including molecular sensing and nanometer-scaled electronics because of their unique physical and electronic properties. Here we report a nanostructure fabrication process in aqueous solution using a cage-shaped protein. Previously, a peptide named NHBP-1 (DYFSSPYYEQLF) has been identified as an aptamer with an affinity for carbonaceous materials [1]. Utilizing the aptamer, semiconductor nanoparticles (NPs) inside the proteins were attached to CNTs with nanometer-scaled gaps, which could function as tunneling gaps [2].

Changing the size of a protein and the materials mineralized inside, NPs with different sizes and properties can be incorporated in the nanostructure [3]. Metallic or semiconductor materials inside the protein can act as charge storage nodes, and the nanostructure network is expected to show intriguing properties in electric conductivity. We report here our attempt to characterize the electronic properties of the structure.

2. Materials and Methods

Protein purification

An engineered protein that has the NHBP-1 peptide fused to the N-terminus of the *Listeria innocua* Dps (LiDps) protein was expressed in *E. coli* [2]. The cells were lysed and the supernatant was subjected to a thermal denaturation at 75°C for 20 min. After centrifugation at 6,000 g for 10 min, the supernatant was subjected to salt dialysis with a final concentration of 0.5 M NaCl. After centrifugation at 6,000 g for 10 min, the precipitate was suspended in 50 mM Tris-HCl (pH 8.0). The salt dialysis was repeated 2 times, and protein purity was confirmed with sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) and transmission electron microscopy (TEM: JEM-2200FS, JEOL, Tokyo) analysis.

Cobalt oxide mineralization

The NHBP-LiDps protein (0.1 mg mL^{-1}) was dissolved in 100 mM HEPES-NaOH (pH 8.2) and incubated in the presence of 0.5 mM $(NH_4)_2Co(SO_4)_2$ and 1 mM H_2O_2 at 50°C for 15 min. The reaction solution was centrifuged at 30,000 rpm on a 45Ti rotor (Beckman), and the supernatant was applied to a filtration column (NMWC: 30K, Amicon Ultra) and centrifuged at 3,000 rpm at 4°C, then washed by adding H_2O. The protein was further purified through S-300 XK26x100 column (TOSOH), and applied on top of a layer of 15%, 25% and 50% sucrose. After centrifugation at 30,000 rpm on an SW32Ti rotor (Beckman), fractions with high 400 nm/280nm absorbance ratio were collected. TEM and energy dispersive X-ray spectroscopy (EDS: JED-2200 analyzer, JEOL, Tokyo) confirmed the existence of Co oxide cores inside the proteins.

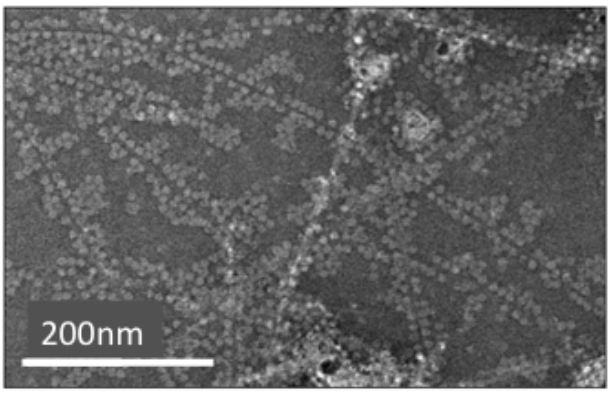

Fig. 1 A TEM image of NHBP-LiDps proteins aligned along SWNTs. Stained with 3% phosphotungstic acid.

CNT/Co structure Formation

To construct a nanostructure in which the cage-shaped protein surround single-walled carbon nanotubes (SWNTs), 15 mg of SWNTs (Aldrich 519308) were mixed in 50 mL of water in a glass vial. Next, the protein was mixed with the SWNTs in H_2O in a final concentration of 0.3 mg mL^{-1}. The final concentration of SWNTs is roughly 0.2 mg mL^{-1}. Ultrasonication (Sonifer 250; Branson Ultrasonic Corp., Danbury, CT, USA) was applied for 5 min and the solution was centrifuged at 15,000 rpm for 10 min at 4°C. The

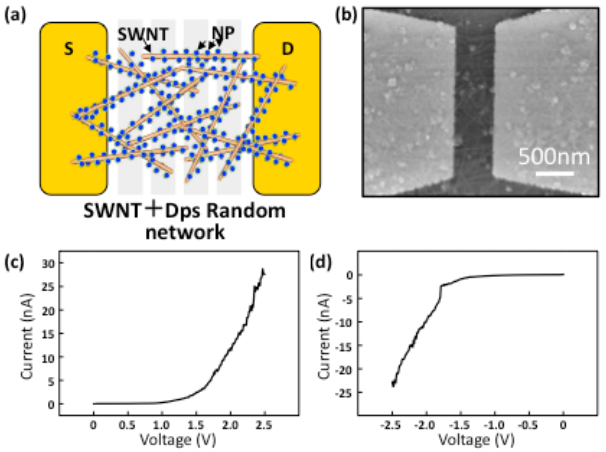

Fig. 2 Current-voltage characteristics of SWNT/NHBP-LiDps(Co) structures bridging a pair of Au electrodes. Schematic (a) and an SEM image (b) of the SWNT/NHBP-LiDps(Co) structures covering a pair of Au electrodes fabricated on a silicon surface. Bias voltage was swept from (c) 0 V to 2.5 V or (d) 0 V to − 2.5 V.

supernatant was put on a Cu TEM grid and stained with 3% phosphotungstic acid (PTA). TEM observation revealed that the NHBP-LiDps proteins were aligned along SWNTs as expected.

Electronic measurements

A pair of Au electrodes, which are 500 nm apart, were fa bricated on a silicon surface using electron beam lithography [2]. Briefly, a 20-nm thick Au layer was deposited onto the silicon surface with a 5-nm Cr layer in between. The silicon surface was cleaned with UV/ozone (UV/ozone cleaner UV-1, SAMCO, Kyoto, Japan) at 110°C with an oxygen gas flow rate of 0.5 L min^{-1} for 10 min.

To eliminate the effect of the buffer and other salts, buffer exchange of SWNT/Co-containing NHBP-LiDps solution was performed using centrifugal devices with an ultrafiltration membrane (Microcon YM-30, Amicon). One μL of SWNT/ NHBP-LiDps(Co) in H_2O was applied onto the substrate and liquid was evaporated by heating at 120°C for 5 min. SEM revealed that SWNT/NHBP-LiDps(Co) structures bridged a pair of electrodes.

3. Results and discussions

Utilizing an aptamer with an affinity for carbonaceous materials, a structure in which SWNTs are surrounded by cage-shaped proteins could be fabricated (Fig. 1) [2]. Various metals or semiconducting materials can be incorporated inside the protein cages, resulting in NPs separated from SWNTs by nanometer gaps. After casting solution with the structure onto a pair of Au electrode (Fig. 2), current-voltage characteristics were measured at ambient conditions using metal probes connected to a semiconductor parameter analyzer (Agilent Technologies, 4156C) (Fig. 2c, 2d).

When bias voltage was swept from 0 V to 2.5 V, current increase was observed (Fig. 2c). When the polarity of bias voltage was changed and swept from 0 V to -2.5 V, the current increased in the opposite direction (Fig. 2d). The electric current suppression observed at low bias voltage may have been caused by the cobalt oxide NPs separated by nanometer gaps from the SWNTs. However, further electronic characterization is necessary to reveal the true nature of the SWNT-protein complex.

4. Conclusions

Utilizing a cage-shaped protein, an electronic device component of SWNTs surrounded by NPs with nanometer gaps could be fabricated. The formed complex can bridge Au electrodes fabricated on a silicon surface. Although detailed characterization of electronic properties of this complex is necessary, tunneling junctions between SWNTs and some of the NPs surrounding them may have been formed. Novel memory effects may emerge as a result of multiple electron pathways in the complex. Combining with other nanometer-scaled structures [4,5], the SWNT-protein complex could be utilized for electronic devices with unprecedented characteristics.

Acknowledgements

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