

Hybrid Nanomaterials for Active Electronics and Bio-Nanotechnology

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ABSTRACT

In this paper, the metallization of single-walled carbon nanotube/single stranded DNA has been reported. At first, SWCNT-ssDNA conjugation is produced, using a well-known chemical pathway which is based on attaching amino compounds to carboxyl-terminal carbon nanotubes. Then the conjugation is metallized with platinum particles. We prove that although the addition of platinum particles has an effect on DNA by Raman spectrum, we still get perfect metallized SWCNT-ssDNA hybrid, which is characterized by SEM, TEM and FTIR. In addition, we have analyzed the metallization mechanism of SWCNT-ssDNA assemblies with HOMO-LUMO calculations.

Keywords: DNA, hybrid, metallization, platinum

1 INTRODUCTION

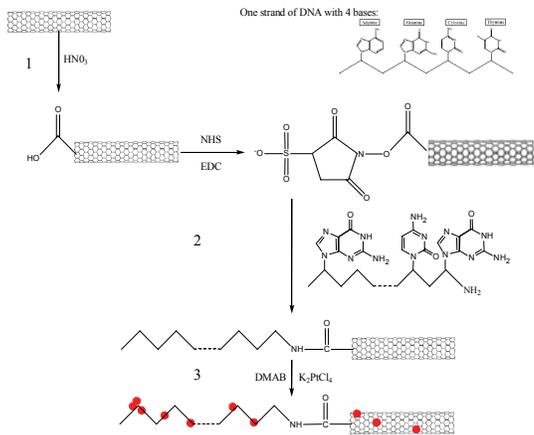
Single-walled carbon nanotubes (SWCNTs) exhibit special structural features and unique electronic properties that have focused interest in their application as active components in future solid state nanoelectronics¹ and optoelectronics². However, the difficulty in precise localization and interconnection of nanotubes impedes further progress toward larger-scale integrated circuits. Self-assembly based on molecular recognition provides a promising approach for constructing complex architectures from molecular building blocks, such as SWNTs, bypassing the need for precise nanofabrication and mechanical manipulations³. DNA is a naturally occurring polymer that plays a central role in biology. Many unique properties of DNA have inspired a search for non-biological applications for it. Molecular recognition between complementary strands of a double-stranded DNA has been used to construct various geometric objects at the nanometer scale⁴. The stacking interaction between bases in DNA has prompted the exploration of its electronic properties for possible use in molecular electronics⁵. So far, building nanoscale structures with DNA is getting more and more attention. It is stimulated by the enormous progress in utilizing DNA either for the controlled self-assembly of molecularly designed nanostructures⁶, or as template for thoroughly engineered inorganic structures⁷. These studies illuminate our work focusing on developing a controllable assembly system about metallization of SWCNT-ssDNA

conjugation. In our work, we report the first time for metallizing SWCNT-ssDNA assembly with platinum. Considering there will be some effect on DNA structure after being metallized, we first synthesized the SWCNT-ssDNA assemblies and then metallized them. Metallized SWCNT-ssDNA complex will get more electrical properties. This will be largely stimulated by many proposed applications of SWCNT-ssDNA assemblies in future nanoscale electronic devices based on their unique electrical properties, biological properties and nanometer sizes.

2 EXPERIMENT AND DISCUSSION

Single wall carbon nanotubes are purchased from Nanolab, INC. One strand DNA is from Sigma Genosys with nine bases 5' (NH₂)GCATCTACG. Single wall carbon nanotubes are oxidized in HNO₃. Oxidization will produce enough carboxyl groups at the end of CNTs, which changes the ends of the CNTs from hydrophobic to hydrophilic. DNA will react with carboxylic acid groups on SWNTs by the amine group at the end. Scheme 1 illustrates the basic chemical pathway which we have used in this work. For the SWCNT-ssDNA conjugation, we use 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC, Pierce Chemicals, Inc.) in the presence of N-hydroxysuccinimide (sulfo-NHS, Pierce Chemicals, Inc.) in DI water. SWCNT-ssDNA conjugates are characterized by scanning electron microscopy and transmission electron microscopy. Figure 1A, B shows SEM images of SWCNT-ssDNA conjugates. The ends of the oxidized SWCNTs produce multiple carboxylic groups, which results in the conjugation of DNA at the ends. SWCNT-ssDNA conjugation metallization is accomplished in a two-step chemical reduction and deposition of metallic colloids⁸. Metallic clusters are first formed on the DNA, and then used as nucleation sites for selective metal deposition. Second, metal ions are reduced into metallic particles. The metallization process is uniform over the entire DNA. Fig1C, D shows SEM images of SWCNT-ssDNA conjugates metallized by platinum. We notice that a lot of small particles distribute along the sidewall of CNTs, which might be Pt particles absorbed on or inserted in CNTs. In order to prove this, we take TEM images and EDS analysis. From Fig2A, DNAPt cluster is located at the end of CNT. Except that, there are many black particles at the surface of CNTs. From the high resolution image, Fig2B, it is clear to see ssCNT is

surrounded by black grains. And its Energy Dispersive Spectroscopy (EDS) tells us those black grains are Pt particles. Pt particles on ssDNA and ssCNT help to increase the electrical conductivity of SWCNT-ssDNA conjugates. Our future research will focus on the electrical characterization of metallized SWCNT-ssDNA.



Scheme 1: Chemical synthesis of metallized SWCNT-ssDNA hybrid. Step 1 is the selective oxidation of CNT at ends to produce carboxyls. In step 2, DNA is chemically connected with CNTs at the end by amide group. Step 3 shows that in the presence of the reductant DMAB, Pt nanoparticles are bound to both DNA and CNT.

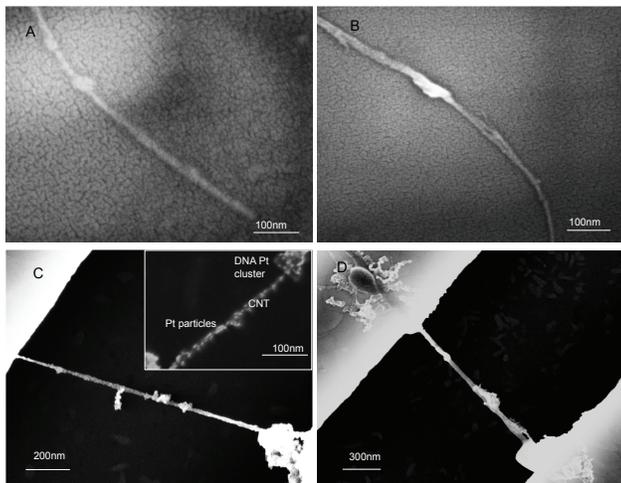


Figure 1: SEM images of SWCNT-ssDNA conjugation (A, B) and metallized SWCNT-ssDNA hybrid (C, D). (A, B) Two CNTs are connected by DNA, and only CNT's end functionalization occurs. (C, D) Metallized SWCNT-ssDNA hybrid traverses across interconnect lines on a Si/SiO₂ substrate, and its high-resolution SEM image.

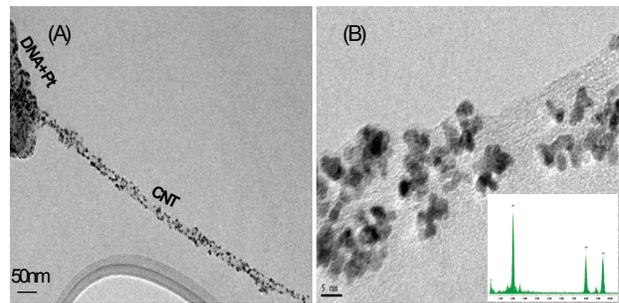


Figure 2: (A) TEM image of metallized SWCNT-ssDNA hybrid. The end of CNT is connected by DNAPt cluster and Pt particles locate on SWCNT-ssDNA surface. (B) High resolution of metallized SWCNT-ssDNA. Its EDS shows that except of carbon and copper, there are two strong platinum peaks. So we can tell the sample is made up of Pt and C.

In order to explore the effect that Pt has on DNA and the metallization mechanism, we use Raman Spectrum, Infrared Spectroscopy, and HOMO-LUMO computation to analyze. Raman spectroscopy provides a powerful tool to identify specific structure in samples. In Fig3, the red line is SWCNT-ssDNA spectrum, while the black one is metallized SWCNT-ssDNA spectrum. There are four peaks in SWCNT-ssDNA conjugation, 1594 cm⁻¹ is the G-band of CNT, 1508 cm⁻¹ is base electronic structure in DNA (stacking, ligation, etc), 1361 cm⁻¹ is the D-band of CNT, and 1153 cm⁻¹ is PO₂⁻¹ interaction in DNA backbone^{9,10}. There are only two peaks in metallized SWCNT-ssDNA hybrid. The peaks of D-band and G-band of CNT still exist. The peaks of base electronic structure in DNA and PO₂⁻¹ disappear. It shows that there are some changes for DNA's structure due to the existence of Pt nanoparticles. With infrared spectroscopy (FTIR), we find pronounced amide peak at 1646.9 cm⁻¹, which means covalent attachment between carboxyls on oxidized ends of CNTs and amine groups on DNA's end. In addition, we also find that 2971.7 cm⁻¹ is the peak of C-H in aromatic ring, 1714.4 cm⁻¹ is the peak of C=O in -COOH¹¹, shown in Fig4. So the addition of Pt does not affect SWCNT-ssDNA assembly.

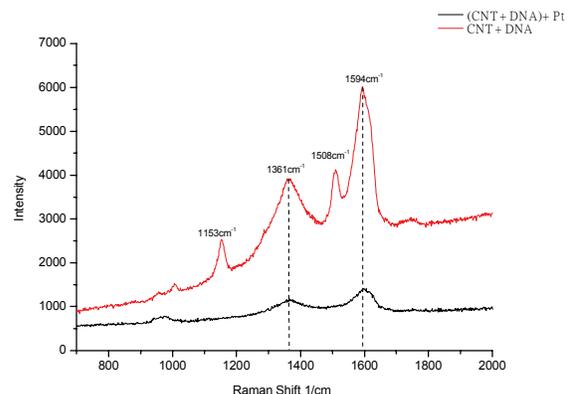


Figure 3: Raman spectrum of (SWCNT-ssDNA)-Pt/SWCNT-ssDNA assembly.

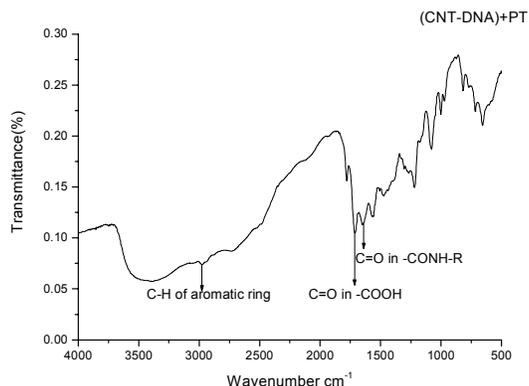


Figure 4: Fourier transform infrared spectra metallized SWCNT-ssDNA hybrids.

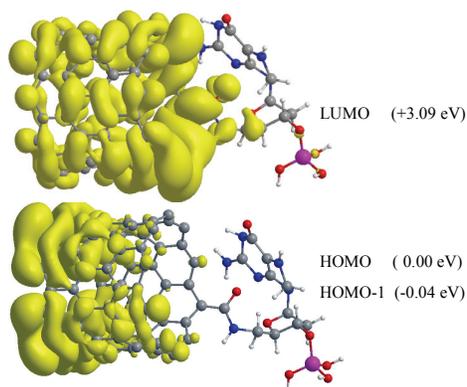


Figure 5: HOMO-LUMO calculation of CNT linked by an amide linkage to a deoxyribose nucleoside with Guanine base

3 CONCLUSION

We have shown that SWCNT/ssDNA is metallized with Platinum successfully. Because of the mild and well-controlled oxidation of the SWCNT, conjugation occurs at the ends of SWCNTs, which is very important in keeping the electronic properties of the CNTs. Although metallization has an effect on ssDNA's structure, it will not destroy SWCNT-ssDNA assembly's structure. Platinum has affinities for both DNA and CNT surfaces. Therefore, metallized SWCNT-ssDNA hybrid can improve the conductivity of SWCNT-ssDNA conjugation and can be used as building blocks for various nanoscale electronic devices.

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