

Surface functionalization of single-walled carbon nanotubes using metal nanoparticles

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Received 18 June 2008; accepted 10 March 2009

Abstract: Surface functionalization of suspended single-walled carbon nanotubes (SWNTs) using metal (Au) nanoparticles (NPs) is reported. SWNTs are grown on three-dimensionally patterned substrates by thermal chemical vapor deposition and successfully functionalized with Au NPs. Ethylenediamine is mainly used to functionalize SWNTs surface with amino groups before introducing Au NPs. From Raman scattering spectroscopy of the Au-functionalized suspended SWNTs, enhanced Raman scattering properties are obtained. The results suggest that the attached Au NPs may contribute to the enhancement of resonant phenomena. By measuring the electric properties after each functionalization process, it is found that Au NPs act as electron acceptor to the amine functionalized SWNTs.

Key words: carbon nanotubes; surface functionalization; metal nanoparticles; Raman spectroscopy

1 Introduction

Surface functionalization of carbon nanotubes has been extensively carried out to modify their intrinsic properties and develop applications in various areas[1]. Many functional species, such as biomolecules or metal nanoparticles (NPs) have attracted much attention since they enable us to make nanotubes for sensors, fuel cells, and templates for novel structure construction. Especially, Au NPs have been actively studied due to their interesting optical properties and strong affinity to biomolecules[2]. A lot of methods for attaching Au NPs to carbon nanotubes have already been reported. JIANG et al[3] used cationic polyelectrolyte for negatively charged Au NPs to nitrogen-doped multi-walled carbon nanotubes (MWNTs). CARILLO et al[4] attached Au NPs noncovalently by coating nanotube surfaces with multilayered polymeric films. Similar results with electrostatic attachments using cation-modified[5] or polymer-coated MWNTs have also been reported[6]. Functionalization of single-walled carbon nanotubes (SWNTs) is certainly more beneficial than that of MWNTs due to its versatility toward wide applications. Suspended SWNTs are especially important for understanding the intrinsic properties of nanotubes

because their floating geometry can exclude environmental effects, such as substrates. The high surface to volume ratio of suspended tubes is also an important feature for sensor applications.

In this study, we synthesized suspended SWNT networks and directly functionalized them with amine group and Au NPs subsequently.

2 Experimental

SWNTs were grown using a cold-wall CVD chamber. Ar and methane were the carrier gas and carbon feedstock, respectively. Plane and patterned SiO₂ (100 nm)/Si substrates were used for SWNT growth. All substrates were rinsed thoroughly with a piranha solution, a mixture of H₂SO₄ and H₂O₂ (with volume ratio of 70%:30%), before ferritin spincoating. The ferritin solution (Sigma-Aldrich) was diluted using deionized water (18.2 MΩ) and the final concentration was adjusted to 0.05 and 5 mg/mL. To obtain catalytic nanoparticles, ferritin solution was dropped onto the substrates using a spinner with a rotation condition of 600 r/min for 30 s and 4 000 r/min for 3 min. After then, substrates were rinsed with deionized water and calcined at 450 °C for 5 min in air. Typical growth was carried out at 900 °C for 5 min at 6.7×10^4 Pa under the constant

flow of 300 mL/min. Details are described elsewhere[7]. After growth, we confirmed that the SWNTs formed network structures on patterned substrates, as shown in Fig.1.

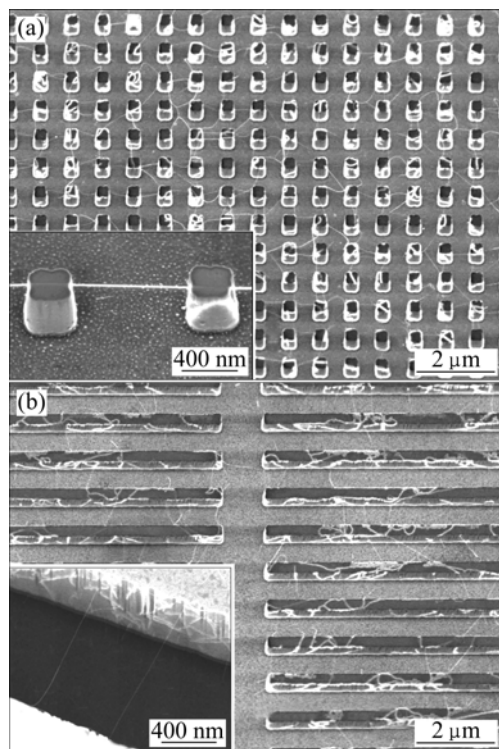


Fig.1 HRSEM images of as-grown suspended SWNTs: (a) Pillar-patterned substrate; (b) Line-patterned substrate (Insets are magnified images)

To chemically oxidize the sidewall of the suspended SWNTs, as-grown samples were immersed in a mixture of $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ for 3 min. After rinsing with deionized water, the suspended SWNTs were immersed in the mixture of EDC and NHS solution for 5 min. This process produces NHS esters on the SWNTs surface. To covalently couple with amine groups, the SWNTs were immersed in ethylenediamine solvent for 10 min. Then, the suspended SWNTs were briefly rinsed with toluene and dried at 100 °C for 10 min in air. Finally, 30 μL of aqueous Au colloid was dropped on the suspended SWNTs. After incubation for 2 h, samples were dried by nitrogen-gas blow. Fig.2(a) shows a schematic presentation of functionalization process. Figs.2(b) and 2(c) show HRSEM images of suspended-SWNTs bundles, which are completely covered with Au nanoparticles.

For structural characterization, a high-resolution scanning electron microscope (HRSEM, Hitachi S-5200) and a transmission electron microscope (HRTEM, Hitachi H-9000) were used. SEM images were mostly taken with a 30°–40° tilt angle. HRTEM images were obtained from direct observation of functionalized samples

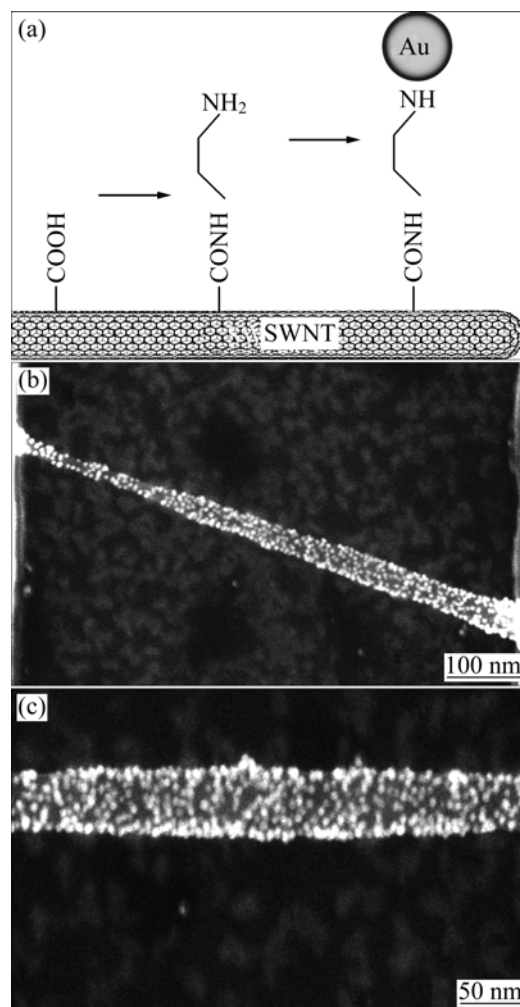


Fig.2 Schematic presentation of Au-attachment via covalent coupling using ethylenediamine (a) and HRSEM images showing suspended-SWNTs bundles completely covered with Au nanoparticles (b) and (c)

after the substrates had been cut. The SWNTs were optically characterized by micro-Raman scattering spectroscopy (Jobin Yvon HR800) using three lasers with excitation wavelengths of 532, 633 and 785 nm. For SWNT-FET fabrication, SWNTs were firstly grown on the plane substrates, which were boron-doped Si wafers with a 500 nm thermal oxide layer and acted as a backgate. Source and drain electrodes were designed by electron-beam and photolithography and made by consecutive electron-beam evaporation of Ti (10 nm-thick) and Au (40 nm-thick). Channel length was 1 μm . All electrical measurements were performed in air with a semiconductor parameter analyzer (Agilent 4156 C). In this study, we measured 72FET devices. The majority of them (54 devices, 75%) were semiconducting and the others (18 devices, 25%) were metallic. Of the 54 semiconducting SWNT-FETs, 38 devices showed p-type

and the others had ambipolar characteristic.

3 Results and discussion

We have firstly investigated the optical properties of Au-attached suspended SWNTs since Au NPs are known as excellent Raman enhancers and SWNTs also show a strongly surface-enhanced Raman scattering (SERS)[8] phenomena when they are in contact with specific metals. The high intensity ratio of the disorder-related D-band (around $1\,300\text{ cm}^{-1}$) to the G-band (around $1\,590\text{ cm}^{-1}$) means that as-grown SWNTs have high quality (Fig.3)[9].

In lower frequency region of Raman spectra, we observed enhanced peak frequency and strong peak intensity in the non-resonant region after Au functionalization (not shown here). In addition, we also observed a drastic change in the high frequency region when we used the 633 nm laser. Representative Raman spectra from the pristine and Au functionalized SWNTs (Fig.3) showed a clear difference in the line shape before and after Au attachment. The pristine samples produced sharp G-band and Breit-Wigner-Fano (BWF) shoulder, which are characteristics of semiconducting and metallic tubes, respectively. In contrast, suppression of the semiconducting component (around $1\,590\text{ cm}^{-1}$) and a significantly enhanced G-peak intensity (around $1\,590\text{ cm}^{-1}$) were observed after Au functionalization. The enhancement has already been reported in the SWNTs/SERS-related works[10], where they explained the enhancement in terms of a charge-transfer enhancement effect. Although the details of the charge-transfer assisted SERS mechanism is not fully understood yet, we can at least expect that our results are closely related to the charge-transfer-enhanced SERS phenomena between amine-covered SWNTs and attached Au NPs, on the basis of their similarity with the previous works. The estimation of the quantitative contribution of each SERS mechanism to the observed enhancement is beyond the scope of this study.

To probe the existence of a provable charge transfer that may contribute to optical enhancement, we made SWNT-FET devices using a standard device fabrication process and investigated their electronic transport properties. Fig.4(a) shows a typical SEM image of the SWNT-FET used. SWNTs with low density were grown so that we could measure the electrical properties from an individual nanotube or a few nanotubes. A typical AFM image ($1.44\text{ }\mu\text{m}^2$) of the device taken after whole functionalization treatments is shown as inset. The nanotube height of 7 nm (inset) implies that the pristine tube ($(1.6 \pm 0.7)\text{ nm}$) is well functionalized by amine ($< 1.8\text{ nm}$) and Au NPs (5 nm) from the height estimation.

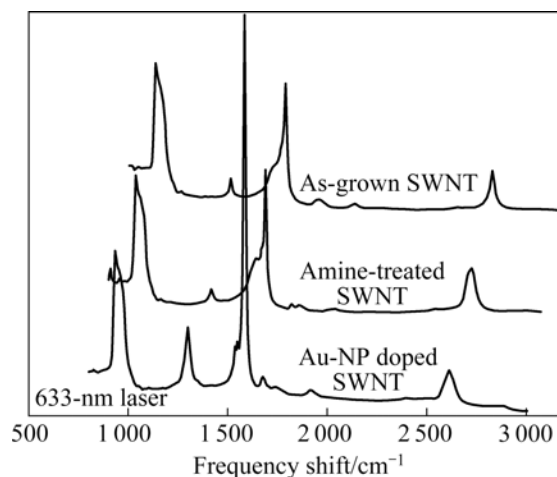


Fig.3 Representative Raman profiles showing drastic changes among as-grown, amine-treated, and Au-functionalized suspended SWNTs in high frequency region (Excitation wavelength of 633 nm)

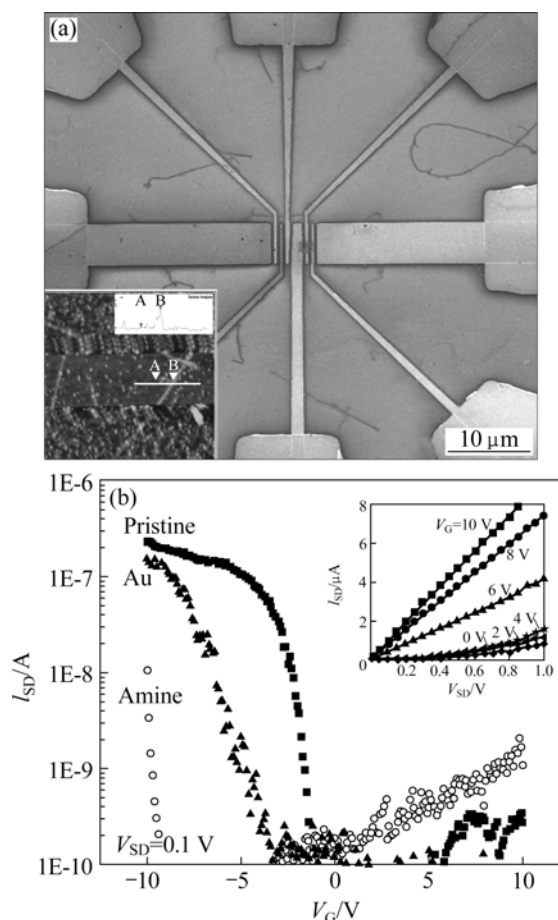


Fig.4 SEM image showing SWNT-FET structure measured (Inset is AFM image ($1.44\text{ }\mu\text{m}^2$) showing detailed view of device after functionalization; Height of individual tube is 7 nm, which implies SWNTs are well functionalized) (a) and evolution of gate dependence of same device (Inset shows source-drain current versus voltage (I_{SD} — V_{SD}) relationship after amine treatment) (b)

A source-drain current (I_{SD}) versus gate-voltage (V_G) curve at room temperature was measured after each functionalization step, and typical results for the same device are shown in Fig.4(b). A starting SWNT-FET showed an ambipolar property with strong p-type transport (full squares); however, the curve shifted to negative gate voltage after amine doping (open circles), where electron donation to the SWNTs from amine groups was expected. The source-drain current (I_{SD}) versus voltage (V_{SD}) curves after amine treatment (inset) indicated that amine had an electron-doping effect on SWNTs. Moreover, it was very interesting that the curve shifted again to positive gate voltage (full triangles) by Au functionalization, which meant that the amine treated SWNTs acted as electron donors to Au nanoparticles.

4 Conclusions

1) Suspended SWNTs were grown on patterned substrates by thermal CVD and successfully functionalized with Au NPs.

2) From the Raman spectra, significantly enhanced peak intensity in the G-band was observed, especially when 633 nm laser was used.

3) By measuring the electric properties after each functionalization process, it was found that Au NPs acted as electron acceptor to the amine-functionalized SWNTs.

Acknowledgements

This study was supported by 2008 Research Grant from Kangwon National University, Korea.

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(Edited by YANG Bing)

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