Bio-assembly of Nanoparticles for Device Applications

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ABSTRACT

Conjugation of carbon nanotubes (CNTs) with biomolecules results in highly functionalized CNTs which serve as the templates for self assembly of nanostructured materials and as elements of nanoelectronic circuits. Here, we report the synthesis of novel nanocomponents by conjugating single walled carbon nanotubes (SWNTs) with peptide nucleic acid (PNA), an artificial DNA analogue by using carbodiimide coupling. Raman spectroscopy was employed as initial characterization technique for these SWNT bio-conjugates. Finally, their formation was confirmed by using transmission electron microscopy (TEM).

Keywords: self assembly, carbon nanotubes, peptide nucleic acid, electron microscopy, nanodevices.

1. INTRODUCTION

Due to their excellent chemical and electrical properties, carbon nanotubes (CNTs) have been used to realize a number of nanodevices [1, 2], but there is a need for integrating these devices into large structures. Self assembly by molecular recognition provides us a robust yet cost effective alternative for this purpose [3]. Nucleic acids especially DNA, because of their inherent molecular recognition, nanoscale dimensions and easy chemical manipulation are the best candidates for imparting molecular recognition to CNTs [4, 5]. But use of DNA is limited due to its charged backbone, low thermal and chemical stability. To overcome these limitations of DNA, this work aims to utilize the superior chemical and structural properties of its artificial analogue, peptide nucleic acid (PNA). PNA has an uncharged backbone, which is made from repeating N-(2-aminoethyl)-glycine units linked by peptide bonds [6]. Few of the advantages of PNA are shorter probe length, stronger hybridization, higher thermal stability, greater resistance to acidic conditions and enzyme degradation, and higher shelf life [7]. In this work we synthesized and characterized SWNT-PNA nanocomponents.

2. MATERIALS AND METHODS

There is very little work done to realize the potential of PNA outside the scope of conventional biology [8]. This work aims to exploit PNA's ease of functionalization by conjugation to develop SWNT-PNA bioconjugates. As received SWNTs (Sigma Aldrich) were oxidized by refluxing with 1 M HNO_3 for 12 hrs. After sonication in acidic mixture and filtration, the CNT cake was suspended in dimethylformamide (DMF, 99.5%) and incubated for 30 min in 2 mM 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride and 5 mM *N*-hydroxysuccinimide (NHS) to form SWNT bearing NHS esters [8].

The PNA (sequence: NH_2-Glu–GTGCTCATGGTG-Glu-NH_2) probe purchased from Applied Biosystems Inc. was functionalized on both the ends by glutamate amino-acid residue (Glu) as amine present on PNA backbone is not sufficiently reactive for the conjugation purposes. The SWNT-PNA bioconjugates were formed by reacting SWNT-NHS esters with PNA in DMF for 1 hour. For further characterization these nanocomponents were transferred to water.

3. RESULTS AND DISCUSSION

In this work we attempt to find characterization techniques which are simple, less costly but effective as well. We decided to use Raman spectroscopy as our primary characterization technique as it is a powerful, quick, nondestructive yet simple tool for identifying specific materials in complex structures. A high-resolution micro-Raman spectrometer Renishaw 2000 was employed for this study. The spectral resolution of the instrument was about 0.01 cm^{-1}. The spectra were taken under the visible (λ = 488 nm) laser excitation and 1800 gratings at room temperature. All spectra were taken using the backscattering geometry setup.

The obtained Raman spectra of SWNTs, SWNT-PNA are shown in Fig. 1. One can identify in the SWNT spectrum

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the radial breathing mode (RBM), disorder induced D-band and G-band at 157.78 cm^{-1}, 1346 cm^{-1} and 1582.4 cm^{-1}, respectively. In SWNT-PNA conjugation spectrum the D-band and G-band of SWNT are observed at 1354.6 cm^{-1} and 1592.4 cm^{-1}, respectively. A possible reason for the disorder peak shift is the conjugation of SWNTs with PNA. The observed peak at 1569.8 cm^{-1} characterizes the basic electronic structure of nucleic acid [9], in our case PNA. The presence of PNA is further indicated by the absence of peak(s) for phosphate backbone, 1050-1150 cm^{-1}[9], which differentiates it from DNA. A very weak RBM band of SWNT is observed in this case, which is reasonable since the low-frequency radial breathing mode is expected to be sensitive to the SWNT conjugation with other nanomaterials. Since the SWNT-PNA sample was prepared on Si substrate, a strong Si peak was also observed.

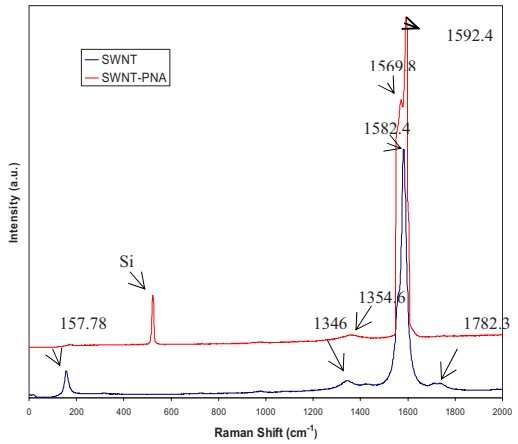

Figure 1. Raman spectra of SWNT (blue) and SWNT-PNA bioconjugates (red). The observance of a new peak (1569.8 cm^{-1}) and shifting of D- band and G- band of SWNTs indicate the conjugation of SWNTs with PNA molecules.

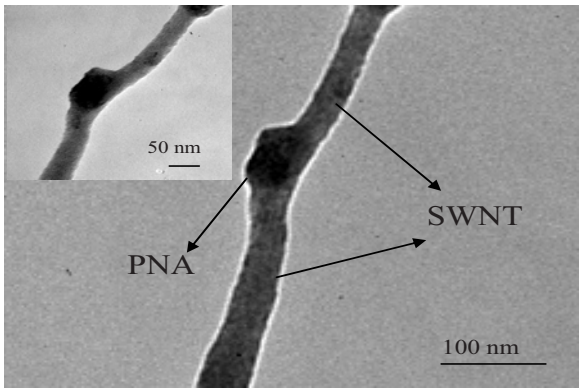

Figure 2. TEM micrograph of a SWNT-PNA bioconjugate. SWNTs are joined by PNA molecules (dark cluster). The high resolution image (inset) of the same component clearly shows that the dark cluster of PNA molecule is more in contrast than SWNTs and joins them.

To support the observations of Raman spectroscopy and confirm the conjugation of PNA molecules with SWNTs, these nanocomponents were visualized under TEM. TEM image (Fig. 1b) clearly shows the joining of two SWNTs ropes with a PNA cluster, which appears as dark spot in the image. PNA molecules form clusters as they aggregate because of their neutral backbone and functionalization with glutamate on both the ends.

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