Supplementary Material (ESI) for Chemical Communications  
This journal is (c) The Royal Society of Chemistry 2009

Supporting information

Materials

The as grown SWNTs (HiPCo) were purchased from Carbon Nanotechnologies, Inc., Houston, TX). Thrombin and bovine serum albumin (BSA) were purchased from Aldrich. All PAGE-purified DNA synthesis reagents were from Sangon Corp. Shanghai. Different concentrations of DNA, thrombin and BSA were all prepared in 10 mM Tris-HCl buffer (pH=7.4) and the aptamer/protein interaction was completed in 10 mM Tris-Mg buffer (10 mM Tris-HCl, pH=7.4, containing 100 mM NaCl, 10mM KCl and 10mM MgCl₂). Milli-Q water (18.2 MΩ-cm) was used throughout the experiments.

General Procedure

The as-grown SWNTs (HiPCo) (1.0 mg) were mixed with DNA aptamer (0.5 mg) in Tris-HCl buffer under sonication for 2h (the temperature was controlled lower than 30 degree.) to get a homogeneous black solution and then centrifuged at 12000 rpm for 2h. The pellet comprising of impurities, aggregates, and bundles of nanotubes at the bottom of the centrifuge tube was discarded, and the supernatant was collected and underwent an additional centrifugation round. The free DNA was removed by centrifuging for 30min at 12000 rpm with a 30K molecular weight cut-off (MWCO) membrane and then the buffer solution was added to re-suspend the SWNT/DNA material.

Detection methods

The absorption spectrums of SWNT solutions were recorded in a Shimadzu UV-3150 UV-vis-NIR spectrophotometer using the quartz microcuvette with the optical path 1cm.

A typical sample on mica for AFM imaging was prepared by first treating the freshly cleaved mica surface with 1 M MgCl₂ aqueous solution for 1 min, rinsing with water, and then spotting 5μL of sample solution onto the mica surface. The liquid drop was blown away in one minute by compressed air followed by washing the surface twice with water. The sample was then imaged with Nanoscope IV (Veeco) atomic force microscope operated in tapping mode.

Raman spectroscopy measurements were performed using a Jobin Yvon LabRam Model 1B equipped with an Ar-ion excitation laser (λ = 633 nm).

The photoluminescence of the SWNT solution was illuminated with the 650nm laser and the fluorescence signal was collected with a BTC261E- 512-element InGaAs spectrometer.

All CD spectra were recorded on a Jasco-715 spectropolarimeter equipped with a programmable temperature controlled water bath. The optical chamber of CD spectrometer was deoxygenated with dry purified nitrogen (99.99%) for 45 min before use and kept the nitrogen atmosphere during experiments. Three scans were accumulated and automatically averaged. SWNTs alone did not contribute to the CD signal between 220 nm and 320 nm in our experimental conditions.
Figure S1

Figure S1 The AFM height image of SWNT/DNA at 800nm × 800nm scale. Most of the individual SWNTs can be seen. The height of individual SWNT is about 4 nm, which is larger than the diameter of bare SWNTs (0.7 to 1.1 nm) due to the DNA absorption on the SWNTs sidewall.

Figure S2
Figure S2 (a) Plots of changes in the absorption over 30min after the addition of thrombin; (b) The dependence of absorption on the concentration of thrombin.

Figure S3
Figure S3 (a) The CD spectrum of AP28 DNA, SWNT/DNA and SWNT/DNA at room temperature. Note that the positions of positive and negative peaks are almost the same at about 265nm and 240nm. The different intensity of peaks is resulted from the different DNA concentrations of AP28 and SWNT/DNA (SWNT/DNA/TMB) solutions. (b),(c),(d): The temperature dependence of CD spectrum for Ap28, SWNT/DNA and SWNT/DNA/TMB respectively from 25°C to 95 ºC.
Figure S4  
(a)  

(b)  

Figure S4  Raman spectra of the radial breathing mode region (a) and the tangential G-band (b) of SWNTs after the addition of thrombin with different concentrations. The inset in (b) shows the linear relationship between the G-peak intensity at 1592 cm\(^{-1}\) and the thrombin concentration.
Raman spectroscopy is particularly useful in characterizing SWNTs, since it gives finger-printing information about the chemical structures and electronic properties of SWNTs. The Raman spectrum profiles in Figure S4 (a) show the radial breathing mode (RBM) with two peaks at 258 and 286 cm\(^{-1}\) and the strong tangential G-band of SWNTs at about 1592 cm\(^{-1}\), which represents the semiconductive properties of the SWNTs.\(^1\) After the thrombin protein was added into SWNT/Aptamer solution, the intensity of G peak increased greatly. Moreover, there is also a linear relationship between the intensity of G peak and the thrombin concentration from 3 nM to 20 nM, with a detection limit of 0.5 nM. It is hypothesized that the enhancement of G peak intensity after the protein addition was due to the release of DNA molecules on the SWNTs sidewall and the resulting increase of freedom of tangential G-band of SWNTs intrigued by the DNA aptamer-protein interaction. The G peak intensity of SWNTs is affected by the aggregation and dissolution states and this correlation can be applied in bioassay area.