Electronic Supplementary Information for the Article:

A novel fluorescent aptasensor based on single-walled carbon nanohorns

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Experimental Section

Professor S. Iijima generously offered SWCNHs that were prepared at room temperature by CO_2 laser ablation. Dye-TA was synthesized by Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). DNA sequence of dye-TA was 5′-TCTCTCAGTCCGTGGTAGGGCAGGTTGGGGTGACT-FAM-3′). Thrombin was bought from Sigma (U.S.A.). Bovine serum albumin (BSA) and human IgG antibody were from Dingguo Biotech. (Beijing, China). Other regents were purchased from Aladin Ltd. (Shanghai, China) and used as received without further purification. Double distilled water was used throughout the experiments.

HRTEM measurements were performed on a FEI TECNAI G2 F20 microscope operated at an accelerating voltage of 200 KV. Zeta potential measurements were performed on a Zetasizer Nano-ZS 90 (Malver Instruments Ltd., U.K.). Fourier transform infrared (FTIR) spectroscopy experiment was operated using BRUKER Vertex 70 FTIR (Germany). Raman spectra were recorded using a Renishaw system 2000 Raman spectrometer operating with an Ar^+ ion laser (514.5 nm).

The preparation of oxSWCNHs was carried out in a microwave oven (DMS-7, SINEO Microwave Chemistry Technology Co. Ltd., Shanghai, China) with 100 mL reaction chamber. In a typical reaction, about 10 mg pristine SWCNHs were loaded in a reaction vessel, along with 15 mL of 30% HNO_3. The microwave power was 500 W. The procedures were as follows: 100 ºC for 5 min, 130 ºC for 5 min and 160 ºC for 30 min. After being cooled at room temperature, the reacted mixture was centrifugated, washed and dried.

Fluorescence measurements were done with Perkin Elmer LS55 Luminescence Spectrometer (Perkin Elmer Instruments. U.K.). In a typical measurement, a different concentration of thrombin was added to 50 nM dye-TA in 20 mM Tris-HCl buffer (pH 7.42, containing 100 mM NaCl, 5 mM KCl, and 5 mM Mg^{2+}) to incubate for 10 min. Then an aliquot of the freshly made oxSWCNH suspension was added to Tris-HCl buffer containing dye-TA or dye-TA-thrombin complex. After 1 min incubation, fluorescence measurements were performed. The time dependent experiments were conducted by monitoring fluorescence at different incubation time. In specificity studies, the aptasensor was incubated with 100 nM BSA, 100 nM IgG and 100 nM thrombin in Tris-HCl buffer for the same incubation time, respectively. The fluorescence was monitored at 522 nm with the excitation of 480 nm at room temperature.

Characteristics of oxSWCNHs.

Fig.S1 shows the HRTEM image of oxSWCNHs. Morphological changes of oxSWCNHs are not notable in comparison with as-grown SWCNHs[1] and oxSWCNHs still remains *dahlia*-like. Fig.S2 shows Raman spectra of the as-grown SWCNHs and oxSWCNHs. Both of them have two bands: G-band and D-band. The G-band is related to the vibration mode in graphite-like carbon, whereas the D-band is attributed to the disordered sp^2 carbon caused by the defects in graphite sheets. The Raman spectrum of the as-grown SWCNHs show two broad peaks centered at 1333 cm^{-1} (D-band) and 1577 cm^{-1} (G-band) with a similar intensity, which is characteristic of *dahlia*-SWCNHs.[2] For oxSWCNHs, the intensities of D-band increase with the respect to that of the G-band, which should be attributed to an increase in defect concentration on the nanohorn walls during oxidation process. In addition, the D- and G-bands of the oxSWCNHs are up-shifted significantly by about 15 and 26 cm^{-1}, compared with those of as-grown SWCNHs. The result should be related to charge transfer between SWCNHs and the electron acceptor (NO_2^+).[2,3] The FTIR spectra of both as-grown SWCNHs and oxSWCNHs are shown in Fig.S3. The peak at ~1559 cm^{-1} seen in both spectra was assigned to C=C stretching mode associated with SWCNH sidewall defects. The line at 1712 cm^{-1} was clearly assigned to the C=O stretching mode in the oxSWCNHs and indicated the generation of –COOH groups.[4] Thus, TEM, Raman and FTIR results suggest that HNO_3 treatment under microwave radiation leads to the formation of defects and –COOH groups on SWCNHs without destruction of structure. The zeta potential of oxSWCNHs is measured to be about -56 mV, indicating oxSWCNHs have a negatively charged surface which may be due to the presence of –COOH groups. So, there are electrostatic repulsion interactions between negatively charged oxSWCNHs, which contribute to the good dispersibility of oxSWCNHs in water.

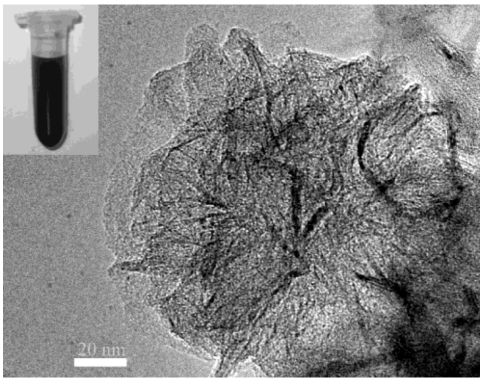

Fig.S1 HRTEM images for oxSWCNHs. Inset: photograph of 0.5 mg/mL oxSWCNHs aqueous solution.

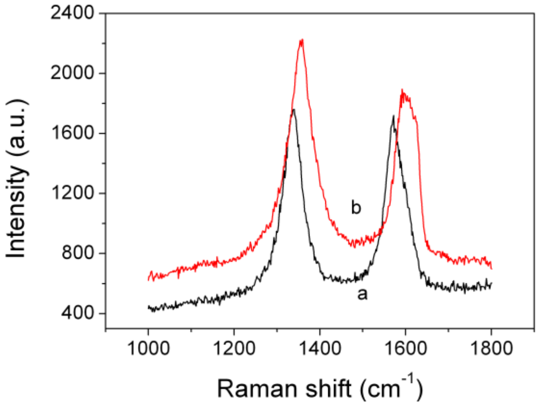

Fig.S2 Raman spectra for as-grown SWCNHs (a) and oxSWCNHs (b).

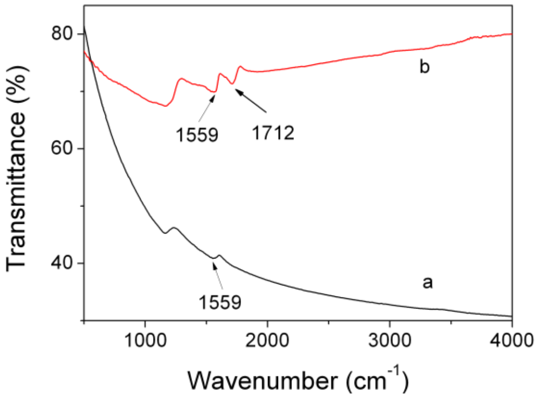

Fig.S3 FTIR spectra for as-grown SWCNHs (a) and oxSWCNHs (b).

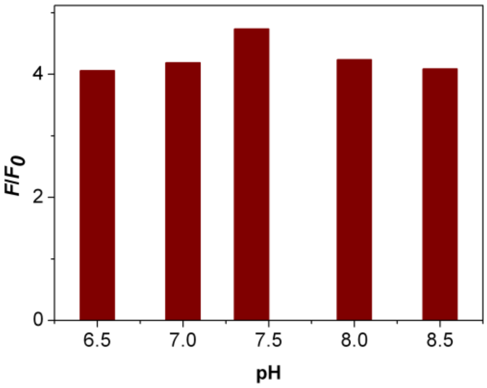

Fig.S4 Fluorescence intensity ratio of dye-TA after addition of oxSWCNHs as a function of pH, where F_0 and F are the fluorescence intensity of 50 nM dye-TA in the absence and presence of 100 nM thrombin, respectively. Excitation was at 480 nm, and the emission was monitored at 522 nm. All experiments were done in Tris-HCl buffer in the presence of 5 mM Mg^{2+} (pH: 7.42).

References

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