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Controllable Redox Reaction of Chemically Purified DNA−Single Walled Carbon Nanotube Hybrids with Hydrogen Peroxide

Yang Xu,[†] Pehr E. Pehrsson,[‡] Liwei Chen,[§] and Wei Zhao*,[†]

Department of Chemistry, University of Arkansas, 2801 South University Avenue, Little Rock, Arkansas 72204, Chemistry Division, Naval Research Laboratory, Washington, D. C. 20375-5000, and Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701

Received April 15, 2008; E-mail: wxzhao@ualr.edu

The redox chemistry of noncovalently functionalized soluble single-walled carbon nanotubes (SWNTs) has received intense attention. For example, dispersion with polymers and surfactants[1−14] such as DNA and surfactant sodium dodecyl sulfate (SDS) results in excellent SWNT aqueous suspensions for redox chemistry studies. The understanding of their behaviors may lead to various applications, including SWNT chirality separation,[1,3,6,7] biosensors,[3,4,8,9] photocatalysts,[10] and hydrogen fuel cells.[11] Preliminary studies suggest that the redox properties of surface-modified SWNTs depend on the specific coating material used,[3a,4a,9,15] but the way in which these materials affect SWNT properties is still an open question. In particular, single stranded (ss) DNA encased SWNTs are stably dispersed in aqueous solution, which allows them to be purified according to their length and chirality by using liquid chromatographic methods.[1,6,14] In this work, we report that the redox chemistry of ssDNA-SWNTs with a biologically important oxidant, hydrogen peroxide,[16,17] is dramatically different before and after chromatographic separation. The chromatographically purified SWNT suspensions are less sensitive to hydrogen peroxide than the untreated suspensions.[4d] However, adding thiocyanate ions accelerates the reaction with H_2O_2 and also accelerates the regeneration of the suppressed spectral intensity over time at the later reaction stage.

Here we focus on suspensions of ssDNA-HiPco SWNTs separated by length using size-exclusion chromatography (SEC).[6a,14] The observed results reported here are reproducible for various fractions with different lengths. Similar results were also obtained from ssDNA-SWNTs enriched with a few (n,m) nanotube types by ion-exchange chromatography (IEC),[6] as will be reported elsewhere. The SEC-separated ssDNA-HiPco SWNT suspensions were prepared by the method described in refs 6a and 14. Figure 1 is an AFM image of fraction f23 deposited onto a mica substrate and shows the length at ~380 nm. The measured heights of the nanotubes confirm that they are individual tubes,[6a] which eliminates complications stemming from bundling. Detailed AFM and chromatographic characterizations of the fractions are described in the Supporting Information with Figures S1−S3.

A surprising result was observed when testing the reactivity of the chromatographically purified ssDNA-SWNTs with hydrogen peroxide. Figure 2 shows that the relative near-infrared (NIR) spectral intensity of the SWNT suspension reacting with H_2O_2 in the pH 7.3 MES buffer decreases only by 0.05 after 50 min of reaction, much smaller than the 0.25 decrease at the same reaction period for the tubes before separation (see Figure 4 in ref 4d). Regardless, when 50 mM thiocyanate SCN^- is added, the reaction

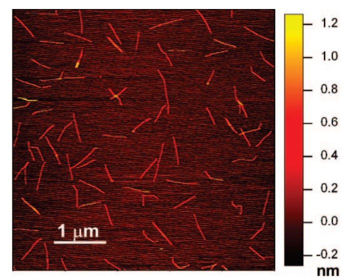

Figure 1. AFM image of an SEC-purified DNA-SWNT fraction f23.

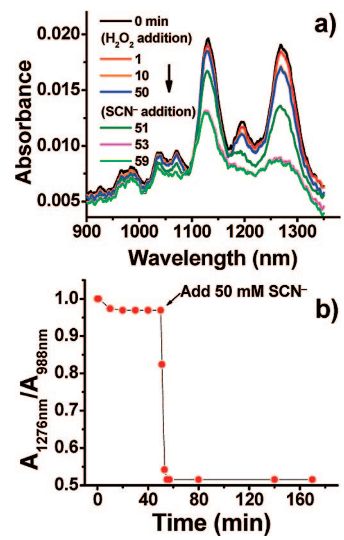

Figure 2. (a) Time-dependent NIR absorption spectra and (b) time-dependent, normalized $A_{1276\ nm}/A_{988nm}$ of a 100 ppm H_2O_2-reacting ssDNA-SWNT sample in 2-(4-morpholino)ethanesulfonic acid (MES) buffer before and after addition of 50 mM SCN^-.

is accelerated dramatically. It finishes within 3 min, which is a more than 10-fold increase in the reaction rate.

The accelerated NIR spectral changes of the purified SWNTs upon addition of SCN^- are surprising because SCN^- is a reductant and should slow down the reaction by competing with SWNTs to react with hydrogen peroxide.[18,19]

To address this question, we changed the SCN^- concentration and observed that increasing the SCN^- concentration increased the reaction rate until a maximum at about 1 M (Figure 4S in the Supporting Information). The SWNT spectral intensity decreases during the initial reaction period (Figure 3a), in agreement with the results shown in Figure 2. However, the suppressed spectral intensity increases after about 35 min, and fully recovers after 265 min (Figure 3b). The recovery rate is faster at higher SCN^-

[†] University of Arkansas at Little Rock.
[‡] Naval Research Laboratory.
[§] Ohio University.

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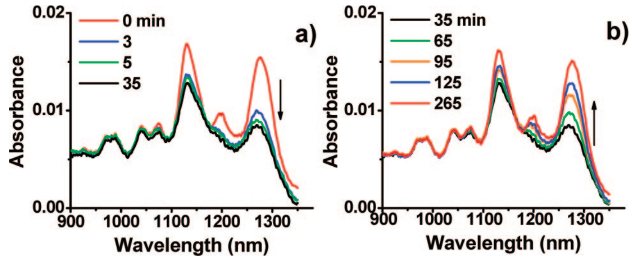

Figure 3. NIR absorption spectra of an ssDNA-SWNT sample in MES buffer containing 1 M SCN^- change as a function of time after addition of 100 ppm H_2O_2: (a) suppression and (b) recovery in spectral intensity.

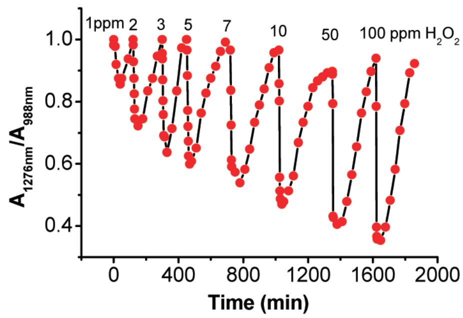

Figure 4. Recoverable spectral intensity changes of an ssDNA-SWNT sample in pH 7.3 MES buffer containing 1 M SCN^- after addition of different concentrations of H_2O_2.

concentration. The results suggest that SCN^- accelerates both the spectral suppression and recovery.

One of the unique features of ssDNA-SWNT hybrids exposed to SCN^- is that the spectral changes can be tuned by adding H_2O_2 of different concentrations into the same suspension. Figure 4 shows that the intensity of the 1276 nm band changes *reversibly* after adding H_2O_2 at each concentration. The magnitude of the change increases with H_2O_2 concentration. When H_2O_2 concentration >10 ppm, the magnitude recovered does not fully reach its initial value, possibly related to the produced acids in the reaction of H_2O_2 with SCN^- (see the reactions in the Supporting Information). The increased acids may decrease the suspension pH slightly, which will suppress SWNT NIR spectral intensity as observed previously.[4,15] The pH effect can be eliminated by exchanging the suspension with fresh buffer or adjusting the pH back to 7.3.[4a,d] On the basis of this unique controllable reaction property, one may be able to design a sensing system using SWNT-based materials to continuously monitor H_2O_2 concentration.[4,17]

SCN^- does not react with SWNTs alone. It is a reductant and is expected to react with H_2O_2 and restore the SWNT to their original state. However, the acceleration role observed here is surprising. The relative inertness of the purified ssDNA-SWNT hybrids to H_2O_2 may be related to the SEC purification process that may remove the impurities existing in the SWNT suspensions before separation such as metal catalyst particles (see the discussion in the Supporting Information).[12] These impurities may work as catalysts for hydrogen peroxide to initiate the reaction with SWNTs.[4d,12] The results observed here suggest that SCN^- or the intermediates produced in the reaction of SCN^- and H_2O_2 (see the reactions shown in the Supporting Information) may possibly work as a catalyst for hydrogen peroxide to react with SWNTs. Specifically, the intermediate hyperthiocyanite $OSCN^-$ may be involved in the reaction with SWNTs. This ion is an antimicrobial agent[18] and its existence has been confirmed by capillary electrophoresis.[19] From the IR spectra shown in Figure 5S in the Supporting Information, there is a transient band at 2183 cm^{-1} which could be assigned to $OSCN^-$. It disappears upon further reaction with H_2O_2, which might corroborate with the observed spectral suppression and recovery results.

In summary, we observe for the first time that the redox reaction of ssDNA-encased SWNTs with hydrogen peroxide is diminished by chromatographic purification but can be initiated and accelerated by adding thiocyanate ions which work as a mediator to control the reaction rate. This controllable redox reaction of SWNTs and H_2O_2 may offer a new sensing scheme for continuously monitoring H_2O_2 concentration.[4,17]

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Supporting Information Available: Figures 1S−3S, SEC details, Figure 4S, [SCN^-]-dependent spectral changes, Figure 5S, IR spectra, SCN^- and H_2O_2 reaction scheme, and more mechanism discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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