Optically Sensing Additional Sonication Effects on Dispersed HiPco Nanotubes in Aerated Water

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Ultrasonication is a necessary process to make single-walled carbon nanotubes (SWNTs) soluble in aqueous solution with surfactants such as sodium dodecyl sulfate (SDS). However, an understanding of the sonication effects on the electronic and optical properties of SWNTs in aqueous solution is still lacking. Here, we have observed that sonication-induced pH changes suppress the optical transitions of the first interband transition pair (S_{11}) in the density of states of semiconducting SWNTs while other possible intermediates induced by sonication contribute less significantly to the observed spectral changes without the involvement of sonication-induced pH decrease. The suppressed S_{11} peaks can be restored by adding basic solution, suggesting that the lattice structure of SWNTs is undisrupted by the sonication used here. The absorbance of S_{11} peaks shows a nearly linear relationship with sonication-induced pH changes in the narrow pH range of 5.2 and 6.1. The results indicate that SDS-encased SWNTs may be used as an indicator for sonolysis-related applications.

Introduction

Single-walled carbon nanotubes (SWNTs) have attracted a lot of scientific interest because of their promising applications as nanoscale probes and sensors in biological electronics and optical devices.[1–16] These applications are based on the extreme sensitivity of the electronic and optical properties of SWNTs to their surrounding environments.[1–16] Because current techniques produce SWNTs in a mixture form with about one-third of metallic nanotubes and two-thirds of semiconducting nanotubes,[17] separations of semiconducting SWNTs from metallic SWNTs are required for practical applications.[18,19] The study of SWNT separations is a subject of intense exploration.[20–23] The discovery of surfactant-assisted dissolution of SWNTs in aqueous sodium dodecyl sulfate (SDS) solution[16] has greatly stimulated the progress in this exciting area.[20–23] Vigorous ultrasonication is often employed to enhance the dissolution of SWNTs in SDS aqueous solution, by encasing individual nanotubes in SDS molecules. Such isolated nanotubes are crucial for separating metallic and semiconducting nanotubes.[20] However, the sonication of aerated water is a quite complex process which generates various reactive intermediates (Scheme 1S, Supporting Information).[24–29] It is unclear if or how these intermediates affect the electronic and optical properties of SWNTs in aqueous solution. In this report, we have studied the effects of sonication on the optical properties of SWNTs. We have observed that sonication decreases the solution pH and that the interband intensity of the first pair (S_{11}) of semiconducting SWNTs shows a nearly linear relationship with sonication-induced pH changes. The results suggest that SDS-encased SWNTs may be used as an indicator for sonolysis related applications.

Experimental Section

Raw HiPco SWNTs (purity ∼95 atm%), with tube diameters between 0.7 and 1.1 nm and an average length of several hundred nanometers, were purchased from Carbon Nanotechnology, Inc.[16] SDS was purchased from Sigma-Aldrich with purity >99%. A method similar to ref 16 was employed to prepare HiPco solutions in 1 wt % SDS in H_2O. Briefly, ∼2.4 mg pristine HiPco SWNTs were weighed on a microgram-scaled balance in a TGA and placed in a 10-mL test tube with 5-mL of 1 wt % SDS aqueous solution. An ultrasonic bath (Branson Model 1510R-MT, 42 kHz with rated power output of 70 W) was used to disperse HiPco SWNTs in SDS solutions. The starting ultrasonic bath temperature was room temperature but it may increase up to 40 °C under prolonged sonication. The mixture in the test tube was sonicated for about 4 min and then was centrifuged (Sargent-Welch Scientific Co.), ∼1300 g for 15 min. Approximately 2 mL of the top portion of the centrifuged sample was decanted and diluted with 6 mL of SDS solution. Two SWNT solution samples with volumes of 0.5 and 5 mL were transferred into two 10-mL test tubes for further sonication studies. One-half milliliter is the minimum volume we could use for optical absorption measurements and 5 mL is suitable for pH measurements. We observed that the effects of sonication on SWNT solutions were related to the solution volume. The 0.5-mL solution required much longer sonication time (up to 65.5 min) to exhibit optical property changes similar to those in the 5-mL solution (0–5 min). For the sake of clarity, we therefore report the results here mainly for the 5-mL SWNT solution. Some results from the 0.5-mL SWNT solutions were included in the Supporting Information. UV–vis–near-IR absorption spectra were measured using a Perkin-Elmer UV/Vis/NIR spectrometer. A quartz cell of 1-mm path length was used for holding solutions. The absorption spectra of the samples after different sonication times were recorded and the SDS solution was used as a reference for background subtraction. An Orion Model 420 pH meter with a Ag/AgCl referenced Orion pH glass electrode was used to measure the pH of 5-mL samples of SDS solution after sonication for various times. All measurements were conducted at room temperature.

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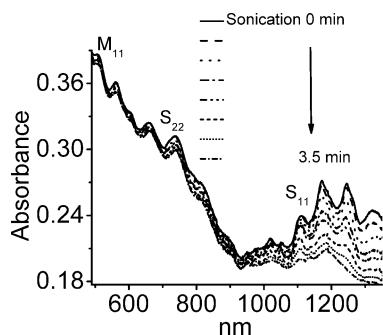Sonication Effects on Dispersed HiPco Nanotubes

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Figure 1. Absorption spectra of a 5-mL HiPco solution after different sonication times.
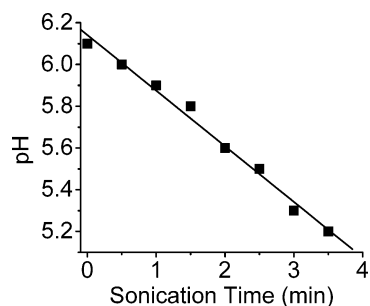
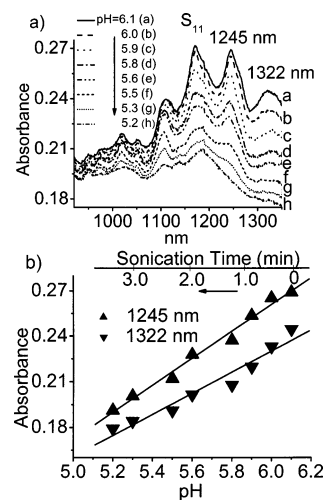**Figure 2.** Changes in pH of an SDS solution as a function of sonication time.

Figure 3. (a) Enlarged absorption spectra showing the details in the S_{11} region with corresponding pH changes induced by sonication. (b) Absorbance dependence of two S_{11} peaks of the HiPco solution on different pHs induced by sonication. The top x axis shows the corresponding sonication time increasing from right to left.
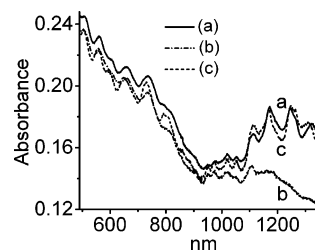

Figure 4. Absorption spectra of a 0.5-mL HiPco SWNT solution sonicated for (a) 0.5 min, (b) 65.5 min, and (c) showing the recovery of the S_{11} peaks after addition of 0.1 M NaOH to pH ~10.

Results and Discussion

Figure 1 shows the absorption spectra of the 5-mL SWNT solution after sonication for times ranging from 0 to 3.5 min, with 0.5-min increments. The absorption bands at >830 nm come from the S_{11} transitions of semiconducting SWNTs with different diameters while the bands at <830 nm belong to the interband transitions of the first pair (M_{11}) of metallic nanotubes and the second pair (S_{22}) of semiconducting nanotubes.[12-16,21,30,31] The intensity of the S_{11} bands decreases with sonication time while sonication has less impact on the M_{11} and S_{22} bands. The observed changes in the spectra after the sonication are very similar to pH induced spectral changes observed in refs 12, 15, and 23, an indication that the pH of the SWNT solution may drift into a more acidic range with sonication because of the formation of nitric and nitrous acids.[24-29]

To confirm that sonication induces changes in pH of the SWNT solution, a control experiment was conducted for direct pH measurements under the same sonication conditions used for the SWNT solution in Figure 1. The measured pH values are shown in Figure 2, where a linear relationship is observed between sonication-induced pH and sonication time. On the basis of the result in Figure 2, the S_{11} region in Figure 1 is enlarged as shown in Figure 3a, with corresponding sonication-induced pH changes. The sonication reduces the pH by only about 1 unit while significant spectral changes in the S_{11} bands simultaneously occur, suggesting that SDS-encased SWNTs may be used as a sensor for detection of sonolysis-induced pH changes with high sensitivity.[5,12] To further check the sonication-induced pH decrease, pure water and SDS solutions in 1, 3, 5, 7, and 9 wt % were also examined with 5-min sonication. A pH decrease in all solution samples was observed, indicating that it is a general phenomenon for aerated water.[24-29] In addition, after mixing a SWNT solution (the top portion of the centrifuged SWNT sample with well-preserved S_{11} band intensities) with a 1 wt % SDS solution whose pH decreased to 5.0 after sonication, a decrease in S_{11} band intensities was also observed. This result further indicates that the sonication-induced pH changes in the solution may cause the spectral changes.

To further elucidate the relationship between the sonication-induced pH changes and the interband intensity of S_{11} bands, we select two representative S_{11} bands at 1245 and 1322 nm corresponding to semiconducting nanotubes (8, 7) and (9, 7) with diameters 1.03 and 1.1 nm, respectively.[30] The 1245-nm band may also overlap with bands from (9, 5), (10, 3), and (10, 5) nanotubes, and the 1322-nm band overlaps with bands from (12, 4) and (13, 2) nanotubes.[30,31] The intensity of the two bands is plotted as a function of sonication-induced pH changes (Figure 3b). There are nearly linear relationships between the S_{11} band intensity and sonication-induced pH changes.

It has been observed that the S_{11} bands reversibly respond to pH changes.[12,15,23,31,32] It was therefore unsurprising that increasing the pH recovered S_{11} bands which were suppressed by sonication. As shown in Figure 4 for a 0.5-mL solution sample, addition of NaOH fully restores the S_{11} bands. Lowering the solution pH to 5.0 by adding 0.1 M HCl suppresses the S_{11} bands again, similar to other observations of SDS-encased SWNTs in ref 15.

The sonication of aerated water is a complex process involving various reactive intermediates.[24-29] The above results suggest that the acids generated by sonication may be responsible for the observed spectral changes. There is also a consideration that degassing CO_2 during sonication and redissolution of CO_2 after sonication may cause the observed pH changes. We did a pH calculation on water in equilibrium with CO_2 (assuming a maximum CO_2 concentration of 400 ppm) and found that the lowest pH attributable to atmospheric CO_2
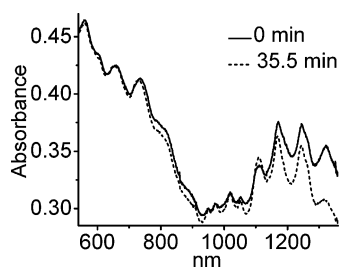
Figure 5. Absorption spectra of a 0.5-mL SDS-encased HiPco solution in a pH 6.0 phosphate buffer (0.05 M) before and after an extensive sonication.

was about 5.65.[33] Therefore, atmospheric CO_2 cannot bring the pH down to 5.2 as shown in Figure 2. The observed decrease in pH by sonication is mainly due to nitric acid and nitrous acid produced from the sonolysis of O_2, N_2, and H_2O (Scheme 1 in Supporting Information) as well documented in refs 24–29 and the references therein. The protonation of SDS-encased SWNTs induced by these acids depletes the valence band electrons of semiconducting SWNTs and so decreases the S_{11} band intensity.[12,13] However, the observed full restoration of the S_{11} bands by addition of NaOH also indicates that the actual lattice structure of the SWNTs is undisrupted after sonication.

To further examine whether the pH changes are the dominant factor in the optical changes of SWNTs, we also sonicate SDS-encased SWNTs in a 50 mM phosphate buffer of pH 6.0. The pH changes in a buffer should be small so we should expect only subtle changes in optical absorption of sonicated SWNTs under these conditions. The results are shown in Figure 5. Prolonged sonication causes no significant spectral changes for most absorption bands except the 1322-nm band. The intensity of the 1245-nm band also decreases slightly. The result is significantly different from nonbuffered solutions (Figure 1 and Figure 1S of Supporting Information), suggesting that the spectral changes of SWNTs under sonication are mainly caused by a pH-related process. Other possible intermediates such as oxidizing species NO and H_2O_2[26–29] may contribute to the spectral suppression through electron withdrawal from SWNTs. However, as shown in Figure 5, their contribution is more distinct for the larger-diameter nanotubes such as the (9, 7) nanotubes at 1322 nm and is less significant for the smaller-diameter nanotubes with bands <1170 nm without the involvement of the sonication-induced pH decease. Further work regarding these oxidative intermediates' contributions to the observed spectral changes is underway to elucidate the detailed mechanisms.

Conclusions

Our results suggest that to avoid sonication-induced optical changes of SWNTs, sonication can be done in a buffer with pH > 6.0 or by making the SDS solution more basic, as is usually done in sonication-related HiPco research.[15,16,31] The results further indicate that the negatively charged groups on the coating materials are necessary for SWNT-based pH sensing.[5,12,32] The pH range for observation of the optical changes of SWNTs might differ depending on the encasing material used and its isoelectric point or equilibrium constants, which changes the pH range for protonation and deprotonation. Furthermore, our results suggest that SDS-encased SWNTs could be used for sensors for sonolysis-related applications. Further fine-tuning of the SWNT surface by selective functionalization may greatly improve the sensing ability for the applications.

Supporting Information Available: Figure 1S, absorption spectra of a 0.5-mL HiPco solution after different sonication times. Scheme 1S, formation of nitrous acid and nitric acid in aerated water under sonication. This material is available free of charge via the Internet at http://pubs.acs.org.

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