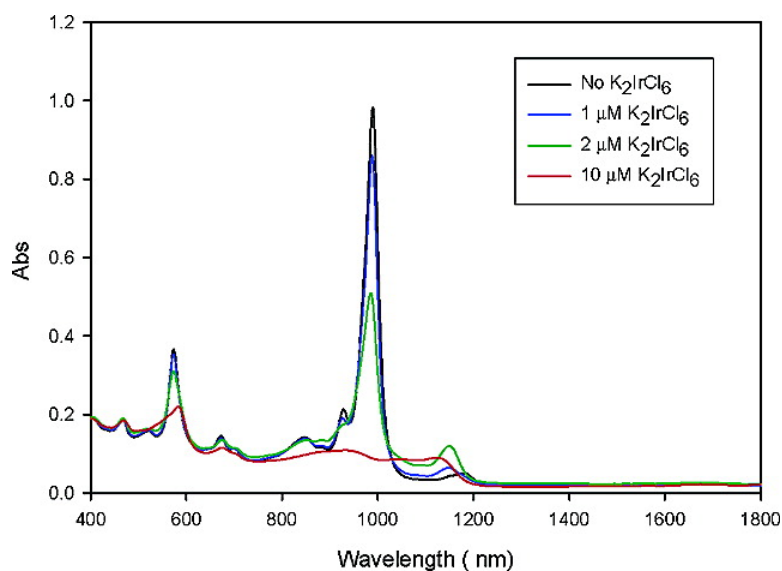


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Solution Redox Chemistry of Carbon Nanotubes

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Abstract: UV/vis/NIR absorbance spectra were used to monitor electron transfer between small-molecule redox reagents and carbon nanotubes (CNTs). The oxidation of (6, 5)-enriched nanotubes in water with $K_2Ir(Cl)_6$ reveals a valence electron density of 0.2–0.4 $e^-/100$ carbon atoms and a reduction potential of ~ 800 mV versus NHE. The reduction potential of CNTs is found to increase with increasing band gap and to decrease with the introduction of an anionic dispersant. In light of this newly revealed redox chemistry of CNTs, we propose that the previously observed bleaching of the CNT absorbance spectrum at low pH is most likely a consequence of the oxidation of the nanotubes by oxygen. These results demonstrate facile oxidation and reduction of CNTs, provide a way to quantify the population of valence electrons, and point to possible applications of CNT in the catalysis of redox reactions.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991,¹ research and application have been focused primarily on CNTs' unique physical properties arising from their one-dimensionality. The chemistry of CNTs, on the other hand, has suffered for a long time from inhomogeneity and impurity of the CNT materials and has been narrowly concentrated on surface modification reactions.^{2,3} Here, we report our investigation on the solution redox chemistry of highly purified CNTs and the exploration of CNTs as a unique chemical reagent. We have found that facile electron transfer occurs between small-molecule redox reagents and semiconducting nanotubes. We have identified a direct correlation between the band gap of a semiconducting nanotube and its reduction potential. In light of this newly observed CNT redox chemistry, we suggest that the previously reported pH effect on CNT optical properties is due to CNT oxidation at acidic pH by dissolved oxygen, and reduction of oxidized CNT at alkaline pH by water. These results reveal a fundamental chemical property of CNTs, provide a way to quantify populations of valence electrons, and point to possible applications of CNT in the catalysis of redox reactions.

2. Materials and Methods

Two sources of single-walled carbon nanotube materials were used in this study. CoMoCAT nanotubes were purchased from Southwest Nanotechnologies (Norman, OK). HiPco CNTs were from CNi (Houston, Texas). Single-stranded DNA sequences were custom-made by Integrated DNA Technologies, Inc. (Coralville, IA). All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO) unless otherwise specified. CNT dispersion and separation were conducted

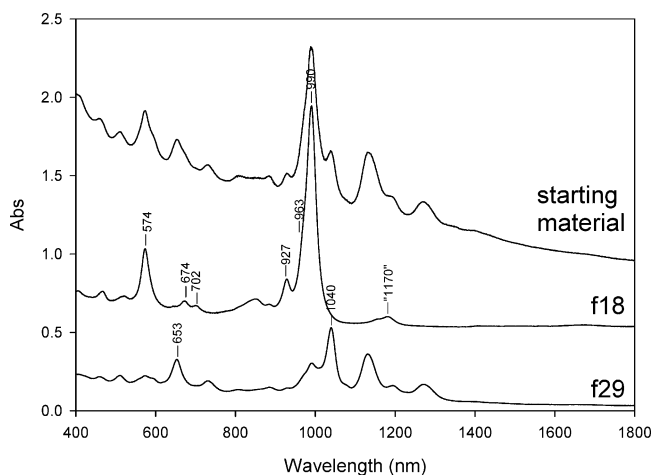


Figure 1. Purification of (6, 5)-enriched CNT solution from the CoMoCAT CNT material. Single-stranded DNA d(GT)30 was used to disperse as-produced CoMoCAT tubes, and anion exchange chromatography was used for the separation, following procedures described before.⁵ The trace labeled as “starting material” is from the unfractionated starting CNT solution. Traces labeled as “f18” and “f29” are from fractions 18 and 29, respectively, of a typical separation run.

according to procedures described previously.^{4,5} Buffer exchange of DNA-CNT solutions was carried out using a Microcon centrifugal filter YM-100 (Millipore, Bedford, MA).

To estimate the concentration and extinction coefficient of DNA-CNT solution, we scaled up the previously described CNT dispersion procedure^{4,5} to process ~ 15 mg of raw CNT materials for each run. The obtained DNA-CNT solution in 15 mL volume was centrifuged at 410 000g for 2 h to bring down carbon nanotubes individually wrapped with DNA. The pellet was weighed after being baked at 65

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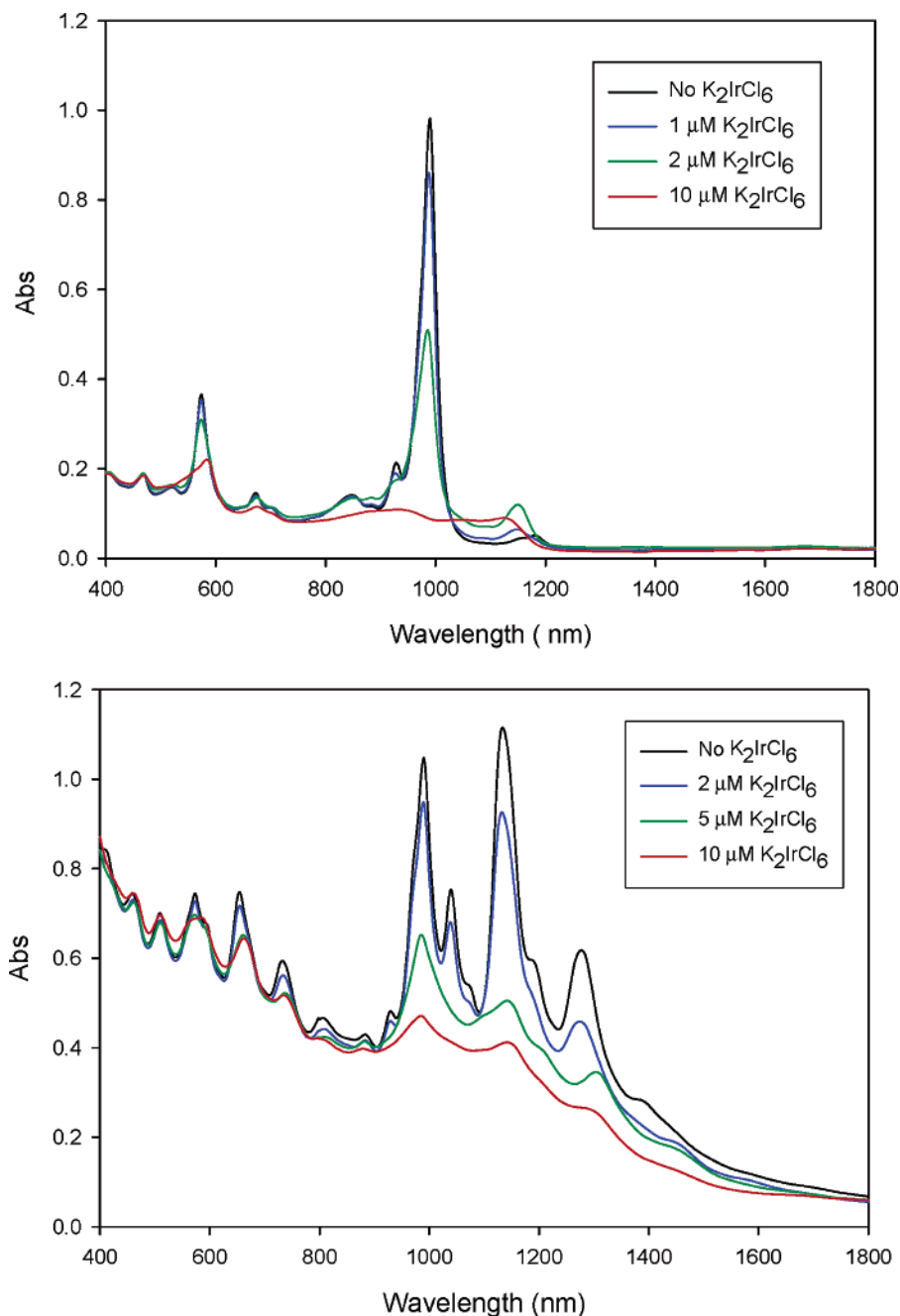


Figure 2. (A) Redox titration of (6, 5) tubes. A (6, 5)-enriched CNT solution was centrifuged using a Microcon spin filter YM100 (Millipore) and was resuspended in D₂O. Freshly made K₂IrCl₆ solution in D₂O was added to 100 μ L of the CNT solution to the indicated final concentration. The spectrum was recorded after 10 min of incubation. (B) Redox titration of unfractionated HiPco tubes. Conditions are similar to those described in Figure 2A.

$^{\circ}$ C overnight. The measured pellet weight and optical absorption for the starting solution were then used to calculate the solution concentration corresponding to one unit of optical absorption at 990 nm. Three independent experiments yielded $1 \text{ OD}_{990\text{nm}} = 26 \pm 2 \mu\text{g}$ (carbon nanotube + wrapping DNA)/mL for the CoMoCAT material, or $1 \text{ OD}_{990\text{nm}} = 13 \pm 1 \mu\text{g}$ carbon nanotube/mL, assuming a 1:1 mass ratio between DNA and CNT based on molecular modeling.⁴ Because of material limitation, a corresponding number for the (6,5)-enriched fraction could not be obtained according to the described procedure. Assuming an equivalent extinction coefficient for all nanotubes, then from the spectral intensity shown in the top trace of Figure 1, we estimated that (6,5) tubes account for $\sim 50\%$ of the total mass in the starting material, which implies that $1 \text{ OD}_{990\text{nm}}$ would correspond to $13 \times 50\% \mu\text{g/mL} = 6.5 \mu\text{g/mL}$ of (6, 5) tubes. On the basis of this

estimate, we used $1 \text{ OD}_{990\text{nm}} = 5\text{--}10 \mu\text{g}$ carbon nanotube/mL for the (6,5)-enriched fraction in our redox titration.

3. Results and Discussion

Separation of CNT. Our current study is enabled by the CNT purification and separation capability we have recently developed.^{4,5} In a report published earlier,⁵ we showed diameter as well as electronic property-based separation of HiPco carbon nanotubes dispersed by d(GT)_n sequences. Recently, a synthetic procedure called “CoMoCAT” was developed by Resasco and co-workers that produces narrow (*n*, *m*)-distribution single-walled carbon nanotubes.⁶ Using the CoMoCAT nanotubes as the starting material, and following our DNA-assisted separation procedure,⁵ we can now obtain fractions enriched with single

chirality tubes. The CoMoCAT tubes have two major types of semiconducting tubes, (6, 5) and (7, 5), as was characterized in the literature.⁶ In Figure 1, optical absorption profiles of two eluted fractions (f18 and f29) from a typical separation run are shown, along with that of the starting material. The absorption spectrum of f18 has two dominant peaks at 990 and 574 nm. These are close to the literature assignment of 975 nm (E_{11}) and 567 nm (E_{22}) for the (6, 5) tubes, but are red-shifted.^{6,7} Similarly, peaks at 927 and 702 nm can be assigned to (9, 1) tubes (same diameter as (6, 5)); peaks at 963 nm (overlapping with the 990 nm peak) and 674 nm can be assigned to (8, 3). By spectral fitting, the ratio of the E_{11} peak areas from (6, 5), (9, 1), and (8, 3) is determined to be 1:0.17:0.11. Note that (7, 5) tubes (E_{11} = 1040 nm, E_{22} = 653 nm), the second major species in the starting material, are almost completely excluded in f18 and become the dominant component in f29.

Redox Titration of (6, 5)-Enriched Carbon Nanotubes. We have found that the purified CNT can be readily oxidized by strong oxidants such as KMnO_4 and K_2IrCl_6 , and fully reduced back by reductants such as NaBH_4 and $\text{Na}_2\text{S}_2\text{O}_4$, as indicated by the disappearance and reappearance of the E_{11} transition. Previous studies have demonstrated the use of E_{11} transitions to monitor electron transfer.^{8,9} Figure 2A shows a typical redox titration in D_2O of the (6, 5)-enriched fraction by the one-electron oxidant, K_2IrCl_6 . Redox titration in H_2O exhibited a similar trend with half CNT oxidation occurring at 1 μM of K_2IrCl_6 . Because the reduction potential of K_2IrCl_6 in H_2O is known (867 mV)¹⁰ and its total concentration in a titration can be controlled, the titration experiment offers a simple way to quantify the number and reduction potential of the electrons in the first valence (v_1) band. Analysis of data from three independent titrations in H_2O using the Nernst equation yielded a reduction potential of 800 ± 10 mV (vs NHE) for the (6, 5) tube, and $2 \pm 0.2 \mu\text{M}$ v_1 band electrons per optical absorption unit at 990 nm ($\text{OD}_{990\text{nm}}$, 10 mm optical path). We estimate that 1 $\text{OD}_{990\text{nm}}$ is equivalent to 5–10 μg CNT/mL for the (6, 5)-enriched fraction. This gives an electron density of 0.2–0.4 electrons per 100 carbon atoms residing in the v_1 band of the (6, 5) tubes, or 250–500 carbon atoms per valence electron or chromophore. Valence electron density is a fundamental parameter in transport phenomena. Profiles of CNT electronic density of states have been measured by scanning tunneling spectroscopy.^{11,12} However, this approach has not yielded a direct measure of the valence electron density. A nanotube unit equal to ~ 250 –500 carbons is far smaller than the number of carbon atoms in a complete nanotube of several hundred nanometers in length. This means that the chromophore responsible for the electronic transition is a much smaller region within a nanotube and that there are many per nanotube. Such a unit also defines the density of the chemical reaction site along a CNT.

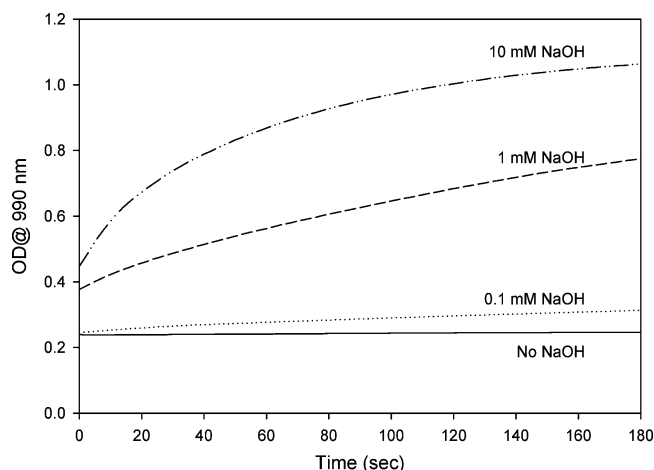


Figure 3. Reduction kinetics as a function of pH. A (6, 5)-enriched CNT solution at 5–10 $\mu\text{g/mL}$ was first oxidized by 10 μM K_2IrCl_6 . After 10 min of incubation, the reaction mixture was centrifuged using a Microcon spin filter YM100 (Millipore) and was resuspended in H_2O . Sodium hydroxide was added to the indicated concentration at $t = 0$, and the recovery of the 990 nm optical transition was recorded.

The redox titration experiment also provides some insight into the origin of the weak and broad absorption feature around 1170 nm observed in the (6, 5)-enriched solution (Figure 2A). Because the intensity of the “1170 nm” feature grows upon oxidation, reaching a maximum and then decreasing, it is unlikely that the “1170 nm” feature comes from the E_{11} transitions of different tubes (see next paragraph).

Redox Titration of HiPco Carbon Nanotubes. We have also found that the reduction potential of a semiconducting CNT depends on its band gap and therefore its diameter. When a redox titration was conducted with purified but nonfractionated HiPco tubes (Figure 2B), we observed that peaks at longer wavelengths (1270 nm or 0.98 eV, 1130 nm or 1.10 eV) arising from larger diameter tubes disappeared first at lower concentrations (1 and 2 μM) of K_2IrCl_6 . Peaks at shorter wavelengths (1040 nm or 1.19 eV, 990 nm or 1.25 eV) from smaller diameter tubes disappear at higher concentrations (5 and 10 μM) of K_2IrCl_6 . These data suggest that the larger the band gap, the higher the reduction potential, and therefore the lower the v_1 band position. A similar conclusion was arrived at by Okazaki et al. based on their electrochemical study of CNT.¹³ We estimate that the reduction potential increases by ~ 50 mV from a 0.98 eV band gap tube to a 1.25 eV band gap tube. Because the energy level of a valence electron dictates its chemical reactivity, the systematic change of nanotube valence energy levels as a function of their band gaps may manifest itself in many other chemical reactions.

Reaction with $\text{O}_2/\text{H}_2\text{O}$ Redox Couple. The redox stability of small molecules in aqueous solution is known to be affected by water that can act as a reducing agent and by dissolved oxygen that can act as an oxidizing agent. We have found that this is also true for carbon nanotubes. In water, oxidized CNTs are gradually reduced over 1–3 days in the absence of any exogenous reductant, suggesting that water itself serves as the electron donor. The reduction kinetics are also found to be band gap-dependent: the smaller the band gap, the slower the reduction rate. This is consistent with the previously observed trend of CNT reduction potential increasing with increasing band

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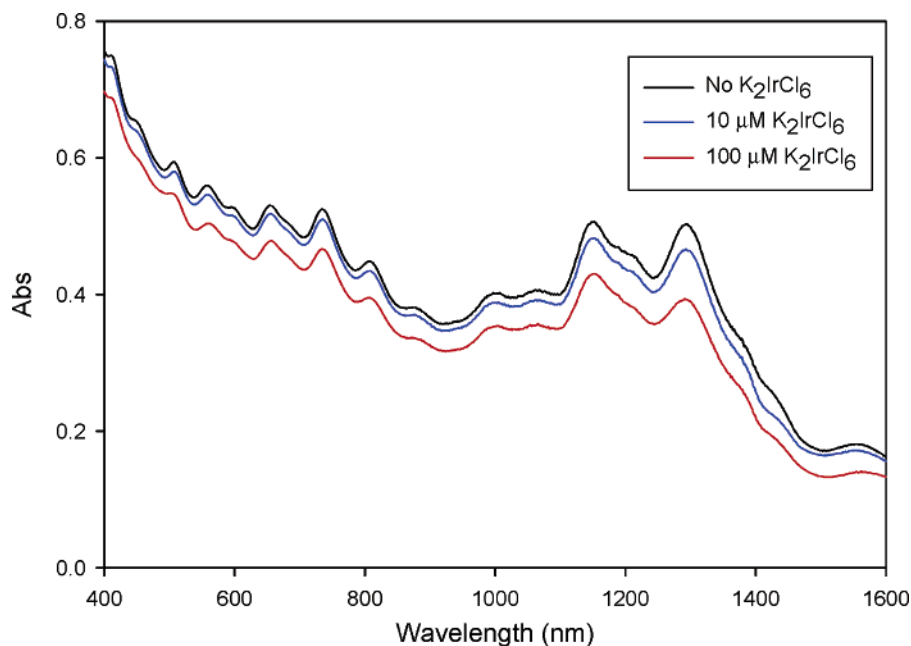
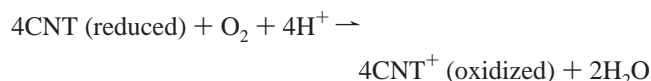


Figure 4. Redox titration of HiPco tubes dispersed in 1% Triton X-405. Spectra were recorded before and after the addition of 10 μM and 100 μM K_2IrCl_6 .

gap. As the $\text{O}_2/2\text{H}_2\text{O}$ redox couple becomes more reducing at higher pH, it is predicted that the kinetics of reduction should be accelerated under alkaline conditions due to an increase in the free energy difference for the reduction. Such a prediction can be made because we are comparing reactions between the same reductant (water) and oxidants of similar structure (carbon nanotubes of different kinds). To examine this phenomenon more quantitatively, we again employed the (6, 5)-enriched fractions. Indeed, we observed that the higher the pH, the faster the reduction kinetics of the (6, 5) tubes. At pH 12, the reduction process shortens to a few minutes (Figure 3).

Strano and co-workers have observed that, in the presence of oxygen, the E_{11} transitions diminish beginning with the small and ending with the large band gap CNTs as the pH drops.¹⁴ The chemical origin of the pH effect is not well understood. In light of the redox chemistry we describe here, we propose that the reported pH effect arises from nanotube oxidation by dissolved oxygen:



Thermodynamically the above reaction is possible, because the potential of the half reaction $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ is 820 mV at pH 7 and is higher than that of the smallest tubes. Because the reduction potential of oxygen increases with $[\text{H}^+]$ (-60 mV/pH unit), and the reduction potential of CNT increases with increasing band gap, it is expected that a gradual oxidation by oxygen from smaller to larger band gap tubes takes place as the pH drops. This explains the observed trend of the pH effect. Oxidation may also be the cause for the observed sensitivity of the electronic properties to oxygen.¹⁵ That the $\text{O}_2/2\text{H}_2\text{O}$ couple can oxidize nanotubes upon lowering the pH, reversing the

oxidation at high pH implies that unlike the $\text{O}_2/2\text{H}_2\text{O}$ redox couple which has a pH dependence of -60 mV/pH unit ($1 \text{H}^+/\text{e}^-$), the carbon nanotube oxidation and reduction involves $<1 \text{H}^+/\text{e}^-$. In other words, for each electron withdrawn from the nanotube through oxidation, there is a δ positive charge generated on the nanotube, where $0 < \delta < 1$.

Effect of Dispersing Agents. To elucidate the effect of dispersing agents on the CNT redox chemistry, we conducted redox and pH titration experiments on aqueous solution of HiPco tubes dispersed by the nonionic surfactant Triton X-405. In comparison with the same amount of DNA-wrapped HiPco tubes, Triton X-405 dispersed HiPco tubes require at least 10 times more K_2IrCl_6 for the same degree of oxidation (Figure 4). At the same time, pH-induced changes in the E_{11} transitions occur more than 2 pH units lower than those observed in solutions of CNT dispersed by anionic surfactants, such as DNA, RNA, and sodium dodecyl sulfate (SDS) (not shown). Zhao et al. has also observed low sensitivity of the absorbance spectrum to pH in Triton X-100 dispersed HiPco tubes.¹⁶ These results are consistent with the notion that pH-induced E_{11} changes arise from CNT oxidation and reduction. They also suggest that the negative charge of DNA and SDS lowers the reduction potential of CNT, as compared to that observed with a nonionic surfactant, presumably through polyanionic stabilization of the oxidized form of CNT.

Conclusions

In this work, we have used UV/vis/NIR absorbance spectra to monitor electron transfer between small-molecule redox reagents and carbon nanotubes (CNTs). The oxidation of (6,5)-enriched nanotubes in water with $\text{K}_2\text{Ir}(\text{Cl})_6$ reveals a valence electron density of $0.2\text{--}0.4 \text{e}^-/100$ carbon atoms and a reduction potential of ~ 800 mV versus NHE. We find that the reduction potential of carbon nanotubes increases with increasing band gap and decreases with the introduction of an anionic dispersant.

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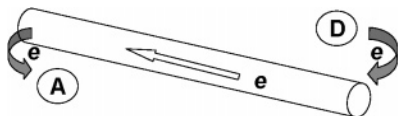


Figure 5. Schematic illustrating the concept of CNT-mediated distant electron transfer between a donor and an acceptor molecule.

On the basis of this newly revealed redox property of CNT, we propose that the previously reported bleaching of the CNT absorbance spectrum upon lowering the pH is most likely a consequence of the oxidation of the nanotubes by oxygen. These results demonstrate facile oxidation and reduction of CNTs, provide a way to quantify the population of valence electrons, and point to possible applications of CNT in the catalysis of

redox reactions. As a molecular wire with a large surface area and delocalized valence electrons and holes, CNTs may facilitate electron transfer between a donor and an acceptor by increasing the reaction cross-section. Oxidizing equivalents generated by a molecule at one location along a nanotube may be used to oxidize another molecule at a distance (Figure 5). These applications are currently under investigation in our laboratory.

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