J|A|C|S
COMMUNICATIONS

Published on Web 05/26/2006

Photoinduced Charge Transfer Mediated by DNA-Wrapped Carbon Nanotubes

Ming Zheng* and Vsevolod V. Rostovtsev

DuPont Central Research and Development, Wilmington, Delaware 19880

Received March 2, 2006; E-mail: ming.zheng@usa.dupont.com

DNA-wrapped single-walled carbon nanotubes (DNA−CNT) form well-dispersed solution in water.[1,2] The purified and structurally separated DNA−CNTs through liquid chromatography should enable more quantitative examination of the solution chemistry of the CNT. An example in place is the CNT redox chemistry, which has recently become an area of active research.[3−7] We have previously employed separated DNA−CNTs to quantify CNT's redox potential and valence electron density.[4] As an extension of our earlier work, we have been particularly interested in identifying donor−acceptor complexes that are formed between soft Lewis acids and aromatic side walls of CNTs. Here, we choose to describe one of such complexes formed by Ag^+ and DNA−CNT. We report our observation of a charge-transfer (CT) band from the complex and photoinduced redox reactions related to the CT band. These results demonstrate a new use of CNTs as photocatalysts.

Although the donor−acceptor complex formation can be observed in both mixed and separated DNA−CNT solutions, and in some surfactant-dispersed CNT solutions, we present results obtained from the separated DNA−CNT solution for more quantitative analysis. A (6,5) enriched DNA−CNT (average length ∼ 400 nm) solution is obtained by a two-step purification involving size-exclusion and ion-exchange chromatography. The optical spectrum of the solution (Figure 1, dashed line) is devoid of the so-called "π-plasmon band" in the UV region, which we have shown earlier is due to graphitic impurities.[8] As will become evident, the purity of the solution is critical for the observation made in this work. Figure 1 (solid line) shows spectroscopic changes upon addition of 1 mM $AgNO_3$ to the (6,5) enriched DNA−CNT solution (∼1 μg/mL): a slight red shift of the E_{11} (990 → 1000 nm) and E_{22} (574 → 577 nm) transitions and appearance of a very strong optical absorption band in the UV region. Difference spectrum ([(6,5) + $AgNO_3$] spectrum − (6,5) spectrum − $AgNO_3$ spectrum) reveals that the putative CT band has two overlapping transitions centered at 239 and 285 nm, respectively, and extends into the visible region. Figure 1 inset plots the intensity of the 285 nm peak as a function of the Ag^+ concentration. The CT peak is detectable at a Ag^+ concentration as low as 10 μM and reaches saturation level at $[Ag^+] = 300$ μM. The observed spectroscopic change is presumably due to Ag^+ binding to DNA−CNT, via Ag^+ interacting directly with the CNT π-electrons[9] and with the wrapping DNA.[10] We find that addition of 100-fold more (30 mM) Na^+ ions partially replaces Ag^+, as indicated by a ∼20% intensity decrease in the CT band. This implies that electrostatic interaction also contributes to the binding affinity of Ag^+ to DNA−CNTs.

Our assignment of the enhanced UV absorption to a CT band is supported by a photochemical reaction of the Ag^+/DNA−CNT complex. Illumination of the Ag^+/DNA−CNT complex with either UV or visible light results in reduction of Ag^+ to Ag^0. Figure 2a shows spectroscopic changes in a typical photochemical reaction with 200 μM Ag^+ and 5 μg/mL (or 2 μM reducing equivalent[4]) of (6,5) tubes in water. Brief exposure to a source of visible light

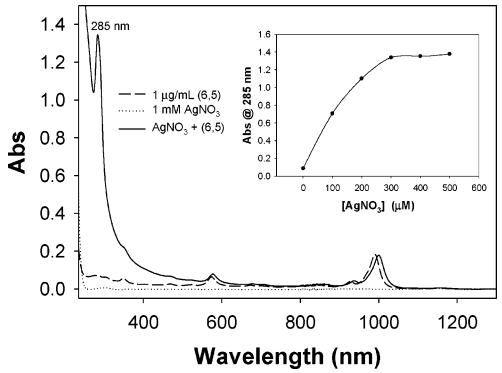


Figure 1. Absorption spectra of (6,5) DNA−CNT (1 μg/mL), $AgNO_3$ (1 mM), and the Ag^+/ DNA−CNT complex. The inset plots the intensity of the 285 nm CT peak as a function of added Ag^+ concentration.

changes the color of the solution from light gray to yellow. Illumination causes the disappearance of the CT band and the appearance of the characteristic Ag nanoparticle surface plasmon band at ∼400 nm (Figure 2a, solid line). On the basis of the reported extinction coefficient for the Ag plasmon band,[11] we conclude that nearly all Ag^+ ions are converted to Ag^0 in nanoparticle form. TEM analysis confirms that the product is indeed silver nanoparticles, with an average size of ∼20 nm (Figure 2b). Control experiment shows that Ag particles form only in the presence of CNT. Direct involvement of the CNTs is demonstrated by the changes in the CNT spectrum during the reaction; the E_{11} transition intensity drops gradually as the reaction proceeds, indicating oxidation of the CNTs. Figure 2a (solid line) shows the extent of oxidation (∼60%) at the end of the reaction. The oxidized CNTs return to the fully reduced state in ∼15 min after the light is turned off. If the reaction is carried out in a pH neutral (20 mM MES, 4-morpholineethanesulfonic acid, pH 7) buffer or at basic pH by addition of NaOH, the E_{11} peak retains its intensity throughout the reaction. Conversely, at acidic pH, illumination results in full oxidation of the CNTs and very low level of Ag particle formation. The photosynthesized Ag nanoparticles can be removed from the solution by centrifugation. The supernatant DNA−CNT solution is found to maintain full photocatalytic activity.

What is the source of electrons for the reduction of 0.2 mM Ag^+ in the above reaction? DNA−CNT is unlikely to be the source, as there is no detectable change in its oxidation state at the end of the reaction at pHs ≥ 7. Neither does it have enough valence electrons available (2 μM reducing equivalents from CNT, ∼10 μM nucleotides from the wrapping DNA). We conclude that water is the only possible source of electrons for Ag^+ reduction. Scheme 1 presents a working model for how the observed reaction proceeds: (1) formation of a charge-transfer complex, $Ag^+ \cdot CNT_{red}$; (2) photoinduced charge separation leading to Ag^0 and oxidized CNT (CNT_{ox}); (3) reduction of CNT_{ox} by water to complete the cycle. The last reaction step has been implicated in our previous study.[4] Efforts to identify the water oxidation products are ongoing in our

10.1021/ja061464l CCC: $33.50

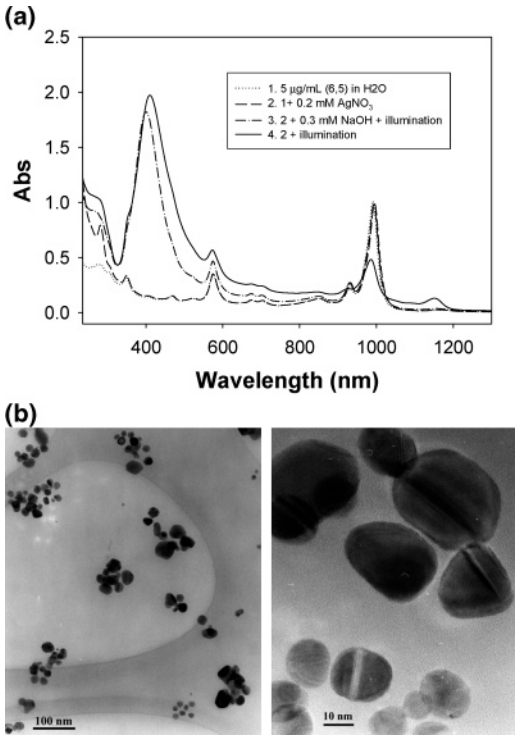
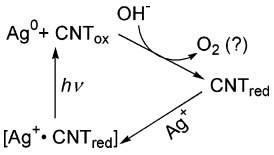


Figure 2. (a) Spectroscopic changes detected during the DNA−CNT catalyzed photosynthesis of Ag nanoparticles. The concentration of the DNA−CNT catalyst is 5 μg/mL or 2 μM reducing equivalents in water, and the added $AgNO_3$ is at 0.2 mM. Illuminating 0.1 mL of Ag^+/DNA−CNT mixture in an Eppendorf tube for 3 min (40 K foot candles from a broadband visible light source, 150 W, Cole-Parmer, Vernon Hills, IL) yields the solid trace, with the Ag nanoparticle surface plasmon band centered at 400 nm. The dash−dotted line is obtained when the photochemical reaction mixture contains 0.3 mM NaOH. A water bath is used to keep the sample temperature at 25 °C during illumination. (b) TEM image of the Ag nanoparticles synthesized by the CNT catalyzed photochemical reaction.

Scheme 1. Proposed Outline of the CNT-Catalyzed Ag^+ Reduction



laboratories. To account for the observed photocatalytic rate at pH $\geq$ 7, CNT_{ox} reduction has to be as fast as the observed rate of Ag^0 formation. This gives a rate of $\sim$ 2 μM/s at neutral pH, which is almost 100 times faster than what we observed earlier for chemically oxidized CNT.[4] We propose one possible mechanism that may contribute to the higher rate of reduction of the photogenerated CNT_{ox}: it preserves nuclear coordinates of the CNT_{red}, thereby minimizing the reorganization energy for its reduction.

The charge-transfer band we report here represents a clear spectroscopic signature of electronic interactions between CNTs and small molecule species. The corresponding photochemical reaction has implications in solar energy conversion. It is worth noting that the photoreduction of Ag^+ catalyzed by CNT solutions bears striking similarity to that catalyzed by TiO_2,[12] the latter reaction also prefers basic pH and involves concomitant water oxidation and oxygen evolution. However, there are potential advantages of using DNA−CNTs over heterogeneous catalysts. The molecular nature and spectroscopic signature of CNTs may allow better control and characterization of the reaction mechanism; the wrapping DNA may serve as tunable substrate binding sites, as has been demonstrated for the formation of several metallic and semiconducting nanoparticles.[13−16]

Acknowledgment. We thank Drs. Bruce Diner and Salah Boussaad for discussion, Dr. Shekhar Subramoney for TEM analysis, and Ms. Ellen Semke for technical support. Management support from Dr. T. D. Gierke is greatly appreciated.

References

(1) Zheng, M.; Jagota, A.; Semke, E. D.; Diner, B. A.; McLean, R. S.; Lustig, S. R.; Richardson, R. E.; Tassi, N. G. *Nat Mater.* **2003**, *2*, 338−342.
(2) Zheng, M.; Jagota, A.; Strano, M. S.; Santos, A. P.; Barone, P.; Chou, S. G.; Diner, B. A.; Dresselhaus, M. S.; McLean, R. S.; Onoa, G. B.; Samsonidze, G. G.; Semke, E. D.; Usrey, M.; Walls, D. J. *Science* **2003**, *302*, 1545−1548.
(3) Dukovic, G.; White, B. E.; Zhou, Z.; Wang, F.; Jockusch, S.; Steigerwald, M. L.; Heinz, T. F.; Friesner, R. A.; Turro, N. J.; Brus, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 15269−15276.
(4) Zheng, M.; Diner, B. A. *J. Am. Chem. Soc.* **2004**, *126*, 15490−15494.
(5) O'Connell, M. J.; Eibegen, E. E.; Doorn, S. K. *Nat Mater.* **2005**, *4*, 412−418.
(6) Napier, M. E.; Hull, D. O.; Thorp, H. H. *J. Am. Chem. Soc.* **2005**, *127*, 11952−11953.
(7) Song, C.; Pehrsson, P. E.; Zhao, W. *J. Phys. Chem. B.* **2005**, *109*, 21634−21639.
(8) Huang, X.; Mclean, R. S.; Zheng, M. *Anal. Chem.* **2005**, *77*, 6225−6228.
(9) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1949**, *71*, 3644−3647.
(10) Jensen, R. H.; Davidson, N. *Biopolymers* **1966**, *4*, 17−32.
(11) Mulvaney, P.; Giersig, M.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 7061−7064.
(12) Ohtani, B.; Okugawa, Y.; Nishimoto, S.; Kagiya, T. *J. Phys. Chem.* **1987**, *91*, 3550−3555.
(13) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature* **1998**, *391*, 775−777.
(14) Coffer, J. L.; Bigham, S. R.; Li, X.; Pinizzotto, R. F.; Rho, Y. G.; Pirtle, R. M.; Pirtle, I. L. *Appl. Phys. Lett.* **1996**, *69*, 3851−3853.
(15) Dittmer, W. U.; Simmel, F. C. *Appl. Phys. Lett.* **2004**, *85*, 633−635.
(16) Hinds, S.; Taft, B. J.; Levina, L.; Sukhovatkin, V.; Dooley, C. J.; Roy, M. D.; MacNeil, D. D.; Sargent, E. H.; Kelley, S. O. *J. Am. Chem. Soc.* **2006**, *128*, 64−65.

JA061464L