

Molecular photodesorption from single-walled carbon nanotubes

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Probing the photoelectrical properties of single-walled carbon nanotubes (SWNTs) led to the discovery of photoinduced molecular desorption phenomena in nanotube molecular wires. These phenomena were found to be generic to various molecule–nanotube systems. Photodesorption strongly depends on the wavelength of light, the details of which lead to a fundamental understanding of how light stimulates molecular desorption from nanotubes. The results have important implications to nanotube-based molecular electronics, miniature chemical sensors, and optoelectronic devices. © 2001 American Institute of Physics. [DOI: 10.1063/1.1408274]

Photophysical and -chemical properties of matter are of great fundamental and practical significance. Elucidation of photoinduced physical and chemical processes on solid surfaces has been actively pursued in recent years.^{1–3} Single-walled carbon nanotubes (SWNTs) are one-dimensional wires consisting of only surface atoms. Therefore, surface effects can strongly affect the physical properties of SWNTs, as revealed by a number of recent investigations.^{4–8} Nevertheless, photoinduced processes on nanotube surfaces remain unexplored thus far. In this letter, we reveal photoinduced molecular desorption from SWNTs. This phenomenon, initially observed by accident during our electrical transport measurements of SWNTs, is found to be generic for various types of chemisorbed and physisorbed molecules on nanotubes. Wavelength-dependent studies suggest that photons induce molecular detachment from SWNTs via electron plasmon excitations in the nanotubes.

We first carried out photoelectrical measurements with an individual semiconducting SWNT sample under ambient conditions, using an ultraviolet (UV) light source with a wavelength of $\lambda = 254$ nm for illumination (intensity = 2 mW/cm², photon flux $F = 2.5 \times 10^{15}$ /cm² s). Preparation of the sample involved chemical-vapor-deposition (CVD) growth on a catalytically patterned SiO₂/Si substrate, followed by controlled contacting of the nanotube via electron-beam lithography.^{4,5} The Si substrate underneath the surface SiO₂ layer was used to apply gate voltages. The conductance (G) of the nanotube decreased dramatically upon UV illumination, and then slowly recovered after the light was turned off [Fig. 1(a)]. This conductance decrease under illumination rules out photocurrent generation in the nanotube. When carrying out similar measurements in a 1×10^{-8} Torr vacuum, we observed that the conductance of the nanotube sample decreased by three orders of magnitude under UV, and exhibited no appreciable recovery when the light was switched off [Fig. 1(b)]. These results are consistent with UV light inducing desorption of molecular oxygen from the SWNT. It has been shown previously that under ambient conditions, oxygen adsorbs onto SWNTs with a binding energy of ~ 0.25 eV = 5.7 kcal/mol and oxidizes nanotubes by with-

drawing one tenth of an electron per oxygen molecule.^{6,7} As a result, semiconducting SWNTs appear hole doped in air. Under UV illumination, oxygen photodesorption causes a reduction of the hole carriers in the SWNT, thus lowering the conductance of the sample. In air, gradual oxygen reabsorption onto the nanotube upon turning off the light leads to the recovery of sample conductance. But in high vacuum, the conductance of the nanotube exhibits no appreciable recovery since there is a negligible amount of oxygen in the environment for reabsorption.

We find that molecular photodesorption can drastically alter the electrical characteristics of single semiconducting SWNTs. In air, prior to UV illumination, the nanotube exhibits typical p -type field-effect transistor (FET) behavior,^{5,9} showing finite conductance at zero gate voltage (V_g) and diminished conductance at large positive gate voltages due to electrostatic hole depletion [Fig. 1(c)]. In vacuum, after UV desorption of oxygen, the nanotube approaches an intrinsic semiconductor showing ambipolar FET behavior [Fig. 1(d)]. The system becomes insulating at zero gate voltage, and electrical transport through the valence band (p -type behavior) and conduction band (n type) of the nanotube occur at high negative and positive gate voltages, respectively. The zero-current region spans $\Delta V_g \sim 12$ V, and the band gap of the SWNT is estimated to be $E_g \sim \alpha \Delta V_g \sim 0.6$ eV (consistent with the tube diameter ~ 1.5 nm), where $\alpha \sim 0.05$ is the typical gate efficiency factor for the sample.¹⁰ These results prove that the adsorbed oxygen is indeed responsible for p -type behavior of semiconducting SWNTs in air, and reveal that the characteristics of nanotube FETs are sensitive to light-induced photochemical effects.

Photodesorption phenomena are also observed with SWNT film samples consisting of large numbers of mixed metallic and semiconducting nanotubes. Preparation for a SWNT film sample involves catalyst spin cast, followed by growth of a thin film of nanotubes on a quartz substrate by chemical-vapor deposition.⁵ 20 nm of Ti and 60 nm of Au are then evaporated onto the SWNT film with a 0.5 mm metal wire placed across the substrate as a shadow mask, which leads to SWNTs in a 0.5 mm gap contacted by two electrodes. Figure 2(a) shows the electrical responses of such a film sample to cycles of UV desorption of oxygen recorded

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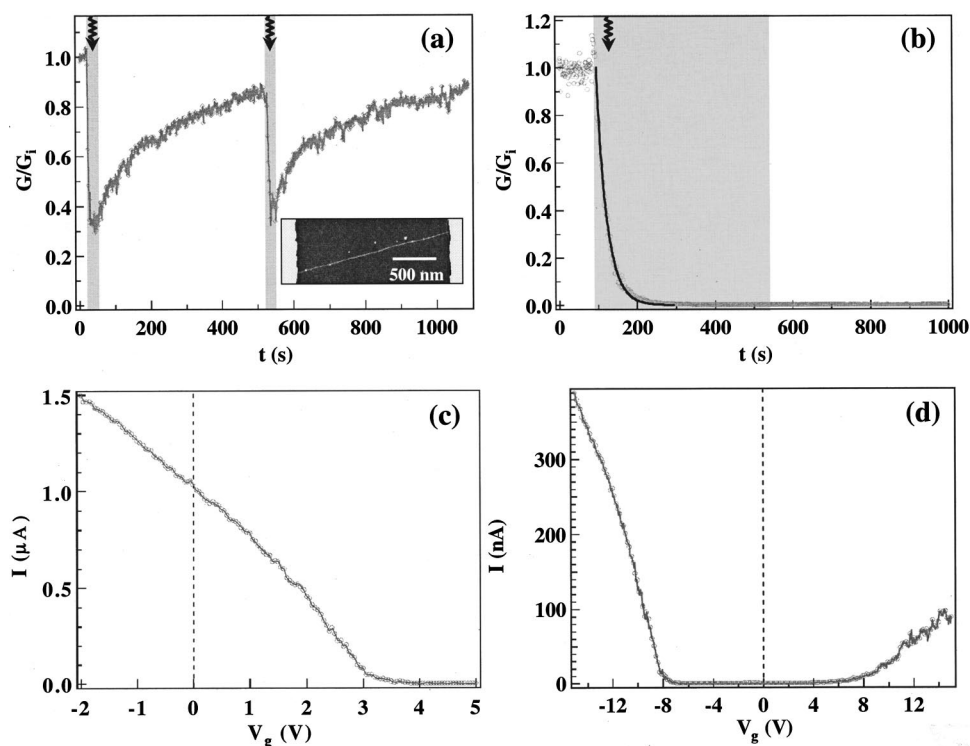


FIG. 1. (a) Normalized conductance [initial conductance $G_i = (1.0 \text{ M}\Omega)^{-1}$] of an individual semiconducting SWNT vs time (t) during UV illumination cycles in air. Shaded and unshaded regions mark the UV-on and -off periods, respectively. The nanotube diameter is ~ 1.5 nm measured from atomic-force microscopy topography (inset). (b) Conductance response to UV illumination in a 10^{-8} Torr vacuum. Solid line: curve fitting of $G \sim \exp(-\sigma Ft)$. (c) Current (I) vs gate voltage (V_g) recorded under a bias voltage of 100 mV in air prior to any UV illumination. (d) I vs V_g of the sample recorded in vacuum after UV illumination.

in air. The SWNT film sample contains both metallic and semiconducting SWNTs, and only the semiconducting nanotubes exhibit electrical conductance change upon molecular doping and de-doping.^{5,8,10}

We have shown previously that electron withdrawing NO_2 and donating NH_3 molecules chemisorb and physisorb, respectively, onto SWNTs and affect their electrical properties.^{4,5} Here, we observe NO_2 and NH_3 photodesorption from SWNTs. As a pulse of NO_2 (20 ppm) was introduced [wide arrow in Fig. 2(b)] to a SWNT film sample placed in a chamber under constant Ar flow, the conductance of the sample rapidly increased [Fig. 2(b)] due to increased hole carriers in the nanotubes caused by electron transfer from SWNTs to adsorbed NO_2 .^{4,5} Upon UV illumination, the conductance of the sample quickly recovered, signaling photoinduced desorption of NO_2 .

A vacuum system was used to investigate photodesorption of NH_3 from SWNTs. Oxygen was first removed from a nanotube film sample by UV illumination, followed by filling the sample chamber with about 1 Torr of NH_3 . The conductance of the sample increased during NH_3 adsorption (response slower than that of NO_2 due to weaker NH_3 -SWNT interaction), and immediately decreased upon UV illumination [Fig. 2(c)]. In repeated UV illumination-on and -off cycles, NH_3 photodesorption and re-adsorption were reproducibly detected [Fig. 2(c)]. Since oxygen was fully removed from SWNTs prior to introducing NH_3 into the system, adsorption of the weakly donating NH_3 molecules doped the sample into n type, causing the increase in the sample conductance. Notably, a minute amount of oxygen impurity present in the NH_3 gas (< 50 ppm) also coadsorbed onto the nanotubes, causing the incomplete recovery of the sample conductance when UV was turned off, and the downward drift [marked by the dashed line in Fig. 2(c)] during the measurement. At the end of the experiment, we intentionally leaked air into the vacuum chamber, and observed an n - to

p -type transition of the sample as oxygen adsorbed onto the nanotubes [Fig. 2(c), inset]. These results reveal that photodesorption is a generic phenomenon for various chemisorbed and physisorbed molecules on SWNTs.

To understand the observed photodesorption phenomena in SWNTs, we investigated their dependence on the wavelength and intensity of light. As the wavelength of light increased from UV to near-infrared (IR) the photodesorption effect became less pronounced (Fig. 3). A substantial photodesorption signal was detectable for 254 nm (5.1 eV) UV light under an intensity of 0.2 mW/cm^2 . In contrast, only weak photodesorption effects were observed for 780 nm (1.6 eV) near-IR light even under 1.3 W/cm^2 .

Previously, photoinduced molecular desorption has been studied on surfaces of various solids including metals and metal oxides.^{1-3,11-13} Thermal and nonthermal processes are the two general mechanisms for photodesorption.¹⁻³ We can rule out direct thermal heating as the mechanism for photodesorption from nanotubes, based on the low light intensities (down to $20 \mu\text{W/cm}^2$) involved. Direct molecular excitation is also ruled out since no molecular transitions are expected in the range of wavelength studied.

We suggest that photodesorption in nanotubes is a non-thermal process and is mediated by electronic transitions in the nanotube "substrate." The wavelength-dependent photodesorption data (Fig. 3) exhibit a profile similar to the optical absorption spectrum of SWNT films [Fig. 3(c), inset]. Since the strong optical absorption of SWNTs around the broad 270 nm (~ 5 eV) peak is due to π -electron plasmon excitation,¹⁴ it is plausible that photoexcited plasmons in SWNTs are responsible for inducing molecular desorption. The collective electron oscillations in nanotubes de-excite on a time scale of $h/\Delta E \sim 1$ fs ($\Delta E \sim 2$ eV is the broad plasmon peak width) into single-particle hot-electron excitations.¹⁵ The hot electrons (or holes) may attach to adsorbed molecules and induce desorption. Part of the plasmon excitation

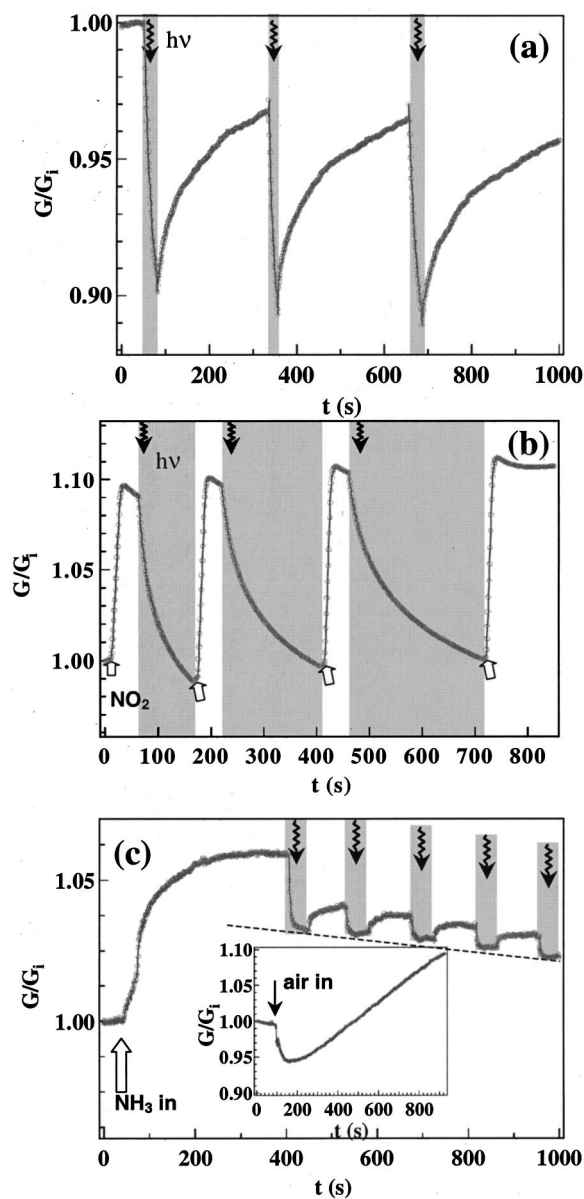


FIG. 2. (a) Normalized conductance [$G_i = (2.8 \text{ k}\Omega)^{-1}$] of a SWNT film sample to UV illumination cycles in air. (b) G/G_i of a SWNT film sample during cycles of NO_2 adsorption and photoinduced desorption. The sample was deoxygenated prior to the measurement by UV illumination in Ar. (c) G/G_i [$G_i = (610 \text{ k}\Omega)^{-1}$] of a sample during NH_3 adsorption and photodesorption cycles. Inset: evolution of the sample conductance as air was leaked into the system.

energy is dissipated through breaking molecule–nanotube binding. The high electric fields associated with plasmons¹⁶ may also be involved in enhancing hot-electron generation in nanotubes and causing molecular detachment. Notably, plasmon-induced photodesorption has been observed previously on metal surfaces.¹²

We can obtain an estimate of the molecular photodesorption cross-section σ based on the photoelectrical characteristics of individual SWNTs. The initial photodesorption follows $dn/dt = -\sigma F n$,^{1–3} where n is the number of adsorbed molecules and F is the photon flux. With the individual SWNT, fitting of the conductance response curve to $G(t) \sim \exp(-\sigma F t)$ yields $\sigma \sim 1.4 \times 10^{-17} \text{ cm}^2$ [solid line in Fig. 1(b)]. In comparison, the cross section found here is 1–2

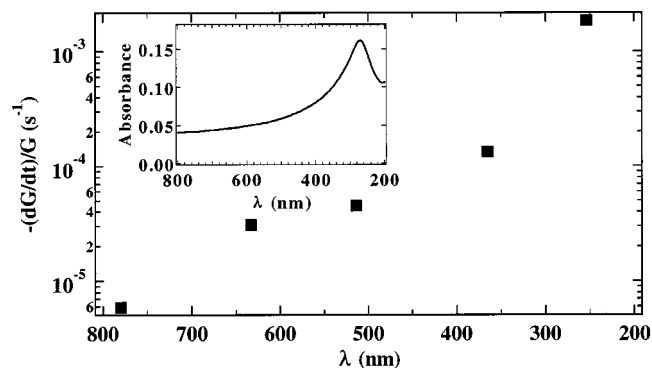


FIG. 3. Rate of conductance change $-(dG/dt)/G$ (in log scale) due to photodesorption of oxygen vs wavelength of light. For the UV ($\lambda = 254, 365 \text{ nm}$) and green (514 nm) light, the light intensities were 2 mW/cm^2 . For red ($\lambda = 633 \text{ nm}$) and near-IR (780 nm) light, the light intensities were 20 and 1300 mW/cm^2 , respectively, as photodesorption effects were negligibly small at 2 mW/cm^2 for these wavelengths. Inset: optical absorbance spectrum of a SWNT film grown on a quartz substrate.

orders of magnitude larger than that of UV-induced oxygen desorption from Pt surfaces,^{2,3} and is comparable to that of oxygen photodesorption from TiO_2 surfaces.¹¹

The molecular photodesorption effects revealed here have significant implications to basic science and applications of nanowires. Our results point to electron plasmon excitation as a pathway to nanotube–substrate-mediated molecular desorption. Elucidating photochemical effects as a function of wavelength at high resolution should allow the measurement of plasmon frequency in a single tube. Photoelectrical and chemical studies could, therefore, be used to probe the optical and electronic properties of individual nanotube “molecules.” On the practical side, molecular photodesorption can be utilized to “clean” nanotubes and enable rapid reversibility of nanotube chemical sensors.^{4–6} Nanophotodetectors and optoelectronic devices based on molecular scale wires are also envisioned.

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- ¹X. L. Zhou, X. Y. Zhu, and J. M. White, *Surf. Sci. Rep.* **13**, 73 (1991).
- ²H.-L. Dai and W. Ho, in *Advanced Series in Physical Chemistry 5* (World Scientific, Singapore, 1995).
- ³R. Franchy, *Rep. Prog. Phys.* **61**, 691 (1998).
- ⁴H. Dai, *Phys. World* **13**, 43 (2000).
- ⁵J. Kong, N. Franklin, C. Zhou, M. Chapline, S. Peng, K. Cho, and H. Dai, *Science* **287**, 622 (2000).
- ⁶P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, *Science* **287**, 1801 (2000).
- ⁷S. H. Jhi, S. G. Louie, and M. L. Cohen, *Phys. Rev. Lett.* **85**, 1710 (2000).
- ⁸J. Kong and H. Dai, *J. Phys. Chem.* **105**, 2890 (2001).
- ⁹S. Tans, A. Verschueren, and C. Dekker, *Nature (London)* **393**, 49 (1998).
- ¹⁰J. Kong, C. Zhou, E. Yenilmez, and H. Dai, *Appl. Phys. Lett.* **77**, 3977 (2000).
- ¹¹C. N. Rusc and J. J. T. Yates, *Langmuir* **13**, 4311 (1997).
- ¹²W. Hoheisel, K. Jungmann, M. Vollmer, R. Weidenauer, and F. Trager, *Phys. Rev. Lett.* **60**, 1649 (1988).
- ¹³R. T. Kidd, D. Lennon, and S. R. Meech, *J. Chem. Phys.* **13**, 8276 (2000).
- ¹⁴S. Kazaoui, N. Minami, H. Yamawaki, K. Aoki, H. Kataura, and Y. Achiba, *Phys. Rev. B* **62**, 1643 (2000).
- ¹⁵C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
- ¹⁶C. F. Bohren and D. R. Hoffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).