

Optical gas sensing with dip-coated carbon nanotubes through the modulation of photoluminescence and optical absorption

Konstantin Iakoubovskii, Nobutsugu Minami* and Annamalai Karthigeyan

Received 18th October 2011, Accepted 21st December 2011

DOI: 10.1039/c2jm15284c

Photoluminescence (PL) and optical absorption (OA) of single-wall carbon nanotube (CNT) thin films are shown to substantially change after exposure to NO₂ or NH₃ gas. These films prepared by dip-coating in surfactant-aided CNT dispersions consist of unbundled and well-exposed tubes; the former property enables the detection of PL, a task difficult for bundled CNTs, while the latter enlarges the effective surface area available for gas adsorption. The observed changes correspond well to those in electrical resistance, which are consistently explained by charge transfer between the CNTs and the gas molecules. Highly resolved spectral peaks in two-dimensional PL excitation contour maps and their changes induced by the gas exposure revealed that wider tubes are more sensitive to gas adsorption.

Introduction

The single-wall carbon nanotube (CNT) is one of the most promising gas sensing materials because of its unique nano-structures and properties;^{1,2} specific surface areas are extremely high, all the constituent atoms are located at the tube surface, and its electronic structure can be tuned by the donation or acceptance of electrons. These features make various properties of CNTs extremely sensitive to gas adsorption.

In our previous work, we proposed a simple and very low-cost fabrication procedure of CNT gas sensors capable of detecting NO₂ concentrations as low as 10 ppb at room temperature;^{3,4} a change in electric current was used for gas detection, similar to many previous studies of CNT gas sensors. Because this change essentially derives from an alteration of electronic states of CNTs, it appears relevant and intriguing to study how gas adsorption influences other electronic properties, in particular, the optical properties. Probing such different aspects of the gas–CNT interaction should clarify the gas detection process, identify important factors involved, and yield essential information for developing practical CNT gas sensors.

In the present work, we have studied changes in the photoluminescence (PL) and optical absorption (OA) of CNTs induced by exposure to electron accepting (NO₂) or donating (NH₃) gases and compared them with variations in the electric current. We used CNT network thin films prepared by dip-coating from surfactant-assisted CNT dispersions, as such films allow us to perform a combination of PL, OA and electrical measurements. The advantages of optical gas sensing include strong signals originating from resonant near infrared light absorption and

emission that enable sensitive detection, non-perturbing, contact-less (electrode-free) measurements, and, above all, the capability of spectroscopically distinguishing signals from CNTs of different structures. The last advantage derives from the fact that peaks in OA and PL spectra systematically shift depending on chiralities and diameters of CNTs. While gas sensing using changes in OA of CNTs was reported before,^{5,6} relatively small changes in OA intensity and broad peaks deriving from the heavy bundling of CNTs hampered detailed spectral analysis. Here by devising a novel preparation technique of well-unbundled CNT network thin films and by measuring highly resolved PL excitation contour maps, we have revealed strong and chirality-dependent changes in PL spectra induced by gas exposure. In particular, longer-wavelength PL peaks showed larger changes. As PL peaks are generally red-shifted with an increase in tube diameter, this observation established that wider tubes are more sensitive than narrower ones. We stress that this result should have been unachievable by conventional electrical gas sensing, because electric measurements on CNT ensembles cannot distinguish the diameter and chirality of CNTs and their distribution.

Experimental

CNT powder produced by the HiPco method was used as the starting material. Observation of PL from CNTs requires their isolation because bundling quenches PL through intertube electronic interactions. This was performed following a widely adopted routine:⁷ the powder was dispersed for 15 min in a 1% D₂O solution of sodium dodecylbenzene sulfonate (SDBS) using a tip sonifier (20 kHz, ~100 W). After centrifugation of the solution for 5 h at 45 000 rpm (150 000g), the upper part (80%) of the supernatant was collected, yielding well-isolated tubes. To study the effect of gas adsorption, one needs to deposit clean

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, 305-8565, Japan. E-mail: n.minami@aist.go.jp

CNT films on an appropriate substrate without allowing the re-bundling of the tubes that would quench PL. Here a simple and novel routine has been implemented for this purpose using an SDI Nano Dip Coater ND-0407: silica substrates were dipped into SDBS/CNT dispersions, slowly pulled out ($\sim 50 \text{ nm s}^{-1}$), and dried. The substrates were cleaned in a KOH/ethanol solution, thoroughly rinsed in deionized water and then dried with nitrogen jet before use.

The effect of gas exposure on the electrical conductivity was measured *in situ* using a sealed gas-flow chamber.³ To prepare electrical contacts, two interdigitated gold electrodes with 0.1 mm wide fingers and gaps were thermally evaporated onto the nanotube network. All conductivity results were reproduced on several samples. OA and PL measurements were performed *ex situ*; the samples were exposed to the gases, taken out of the chamber and quickly transferred to the optical systems. The optical measurements were started within 1 min after the interruption of the gas exposure and lasted less than 1 min. We checked that the relaxation of the electrical and optical signals was sufficiently slow and no significant change occurred during this time.

OA measurements were performed with a Shimadzu UV 3100PC spectrometer. PL excitation contour maps were recorded with a home-built system, utilizing a tunable Ti-sapphire laser for excitation, a 0.3 m single-grating monochromator for dispersion, and an InGaAs diode array for detection. Atomic force microscopy (AFM) images were obtained with a Seiko SPA400/SPI3800 system operated in the non-contact mode.

Results and discussion

Dip-coating was performed at various pulling speeds, and the film quality was assessed by AFM, OA, and PL. As shown in Fig. 1, the intensity of the OA and PL signals, monitored at the dominant 1.3 μm peak, increased linearly with the inverse pulling speed. AFM revealed that, at pulling speeds faster than $2 \mu\text{m s}^{-1}$, SDBS severely contaminated the film and few CNTs could be observed (Fig. 2(a)). The contamination was much less pronounced at lower pulling speeds, in spite of the excessive concentration of SDBS in the dispersion. At a pulling speed of $0.5\text{--}1 \mu\text{m s}^{-1}$ a relatively clean CNT network was formed

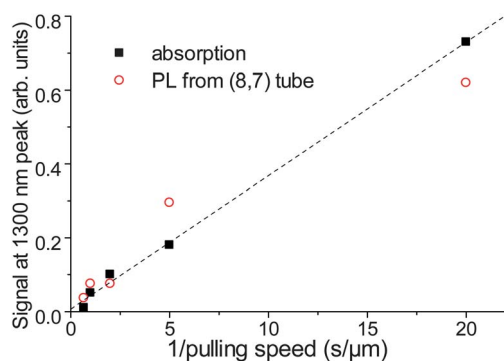


Fig. 1 Intensity of absorption and PL signals at the 1.3 μm peak from a CNT film prepared by dip coating. The signals are plotted vs. the inverse pulling speed of the silica substrate from the SDBS/CNT dispersion.

(Fig. 2(b)) and at 50 nm s^{-1} a dense aggregate of CNTs (Fig. 2(c)) that nevertheless showed a sizable PL signal was obtained; the latter result indicates that a significant number of CNTs remained unbundled. Since the PL signal was stronger for the pulling speed of 50 nm s^{-1} than that for $0.5 \mu\text{m s}^{-1}$, the density of unbundled CNTs is considered to be higher for the former than for the latter.

While the detailed mechanism remains unknown, this observation could be a result of the different rates of the attachment of CNT and SDBS onto the silica surface that change with the pulling speed. This finding has enabled the preparation of luminescent films consisting of exposed and mostly unbundled CNTs, a prerequisite for gas sensing using PL. For most gas-sensing experiments, films prepared at a pulling speed of 50 nm s^{-1} were used.

Fig. 3 presents changes in the electrical resistance of a dip-coated CNT film induced by NH_3 or NO_2 exposure (30 ppm for 5 min). Note that in either case the baseline of the resistance was established by flushing the chamber with purified air. Moderate positive and strong negative changes were observed as expected for the moderate donor (NH_3) and strong acceptor (NO_2), reproducing previous results by us and other groups.¹⁻⁴ The relaxation after the gas removal was sufficiently slow, thus justifying the *ex situ* optical measurements described below.

Fig. 4(a) summarizes changes in the PL excitation contour map for a dip-coated CNT film after exposure to NO_2 or NH_3 . The top panel shows the PL map from the initial sample; here each peak is defined by a PL emission and excitation wavelength and corresponds to a nanotube chiral index (n,m), the assignment of which was done according to the widely accepted data of Weisman and Bachilo.⁸ The middle panel presents the map after NO_2 exposure (100 ppm, 30 min), which reveals strong quenching of all PL signals. Those changes were reversible, but took 1–2 days to fully recover in air. After the recovery, the same sample was exposed to NH_3 (30 ppm, 45 min), and, remarkably, a significant increase in PL signals was observed (see the bottom panel). Here again, the PL intensity returned to the initial level within 2 days in air. Next, we studied the effect of tube diameter. Fig. 4(b) shows the relative gas-induced changes defined as $(I_{\text{gas}} - I_0)/I_0$ for individual (n,m) peaks plotted against the tube diameter calculated as $0.0794(n^2 + nm + m^2)^{1/2}$ in nanometre.⁸ Remarkably, it demonstrates that wider tubes are more sensitive to both NO_2 and NH_3 . We also checked the dependence of the PL quenching on the NO_2 concentration for the prominent (8,7) PL peak (Fig. 4(c)). A linear dependence was revealed for 3 min exposures at concentrations ranging from 3 to 100 ppm.

Fig. 5 shows OA spectra before and after 100 ppm NO_2 exposure for 3, 15, and 30 min. The peaks at $>1 \mu\text{m}$ originate from the S_{11} transitions across the first band gap of the semi-conducting CNTs of various chiralities: transitions occurring at shorter wavelengths involve higher-lying bands (S_{22} , S_{33} , etc.). Here again, diameter-dependent changes of the S_{11} transitions are observed in such a way that the signals from wider CNTs (those occurring at longer wavelengths) decrease faster than those from narrower CNTs, showing additional evidence for the higher sensitivity of wider tubes. Monitoring the gas-induced changes in OA, however, appeared less straightforward than in PL because of the background absorption, the less resolved peaks, and the instability of the instrumental baseline. Similar to

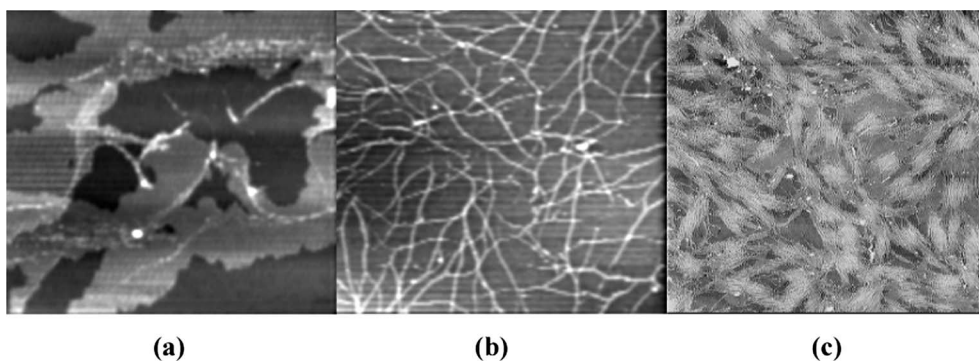


Fig. 2 AFM images ($20 \times 20 \mu\text{m}^2$) of CNT films dip-coated on silica prepared at pulling speeds of $2 \mu\text{m s}^{-1}$ (a), $0.5 \mu\text{m s}^{-1}$ (b), and 50 nm s^{-1} (c).

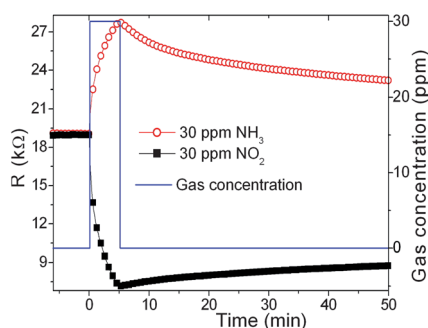


Fig. 3 Time dependence of the electrical resistance of a dip-coated CNT film during and after 5 min 30 ppm exposure to NO_2 or NH_3 gas.

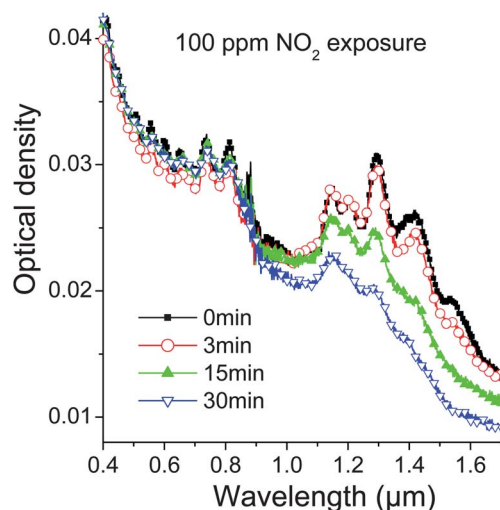


Fig. 5 Optical absorption spectra from a dip-coated CNT film before and after progressive exposure to 100 ppm NO_2 for 3, 15, and 30 min.

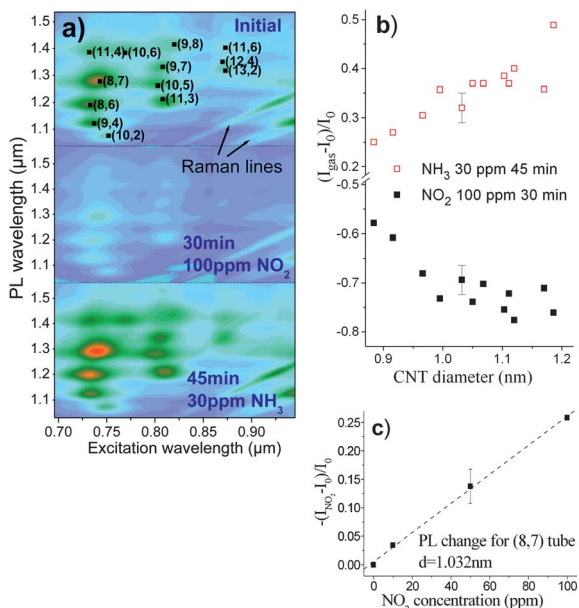


Fig. 4 (a) PL excitation contour maps from a dip-coated CNT film before (top panel) and after exposure to NO_2 (middle panel) or NH_3 gas (bottom panel). (b) Changes in intensities of individual PL peaks upon gas exposure plotted vs. the CNT diameter (data deduced from the PL maps). (c) Changes in the PL intensity from (8,7) tubes upon 3 min exposure to various concentrations of NO_2 . I_{gas} (or I_{NO_2}) and I_0 denote PL intensities immediately after and before the exposure, respectively.

the PL observations, the NO_2 -induced decrease of absorption recovered within 2 days. An additional exposure of the same sample to NH_3 revealed an increase in OA, but the changes were significantly weaker than those for PL.

We stress that the present results using PL from CNTs have demonstrated much higher sensitivities than those reported in previous optical gas sensing using OA (a 35% PL increase to 30 ppm NH_3 versus a 3% OA increase to 20 ppm or 100 ppm NH_3).^{5,6} We attribute this improvement to two effects. One is the unbundled state of the CNTs in the film achieved by dip coating: this increases the effective surface area of CNTs providing more gas adsorption sites and enhancing the gas–CNT interaction. Another effect is exciton migration through the π -conjugation of CNTs: this increases the chance of exciton's collision with doped charge carriers leading to the stronger PL quenching, an effect not expected for OA measurements.

The corresponding changes in resistance and OA upon gas exposure (Fig. 3 and 5) can be understood following the previously developed model.^{5,6} NO_2 injects holes into the valence band of CNTs, increasing the conductivity and bleaching OA by depleting electrons participating in the optical transitions. For the effect of NH_3 , we note that the valence band is already p-doped to some extent with oxygen from air. By injecting electrons, NH_3 compensates the p-doping effect, thus decreasing

conductivity and restoring OA. The PL quenching by p-doping should derive from interactions between excitons and dopants (or charge carriers), as explained by non-radiative Auger processes⁹ or exciton trapping.¹⁰

The result that wider tubes are more sensitive in gas detection is important for the development of CNT gas sensors; the finding could not be made in previous studies using only electrical conductance, but has been obtained here by using unbundled and luminescent CNT networks in combination with the measurements of the well-resolved PL excitation contour maps.

The higher sensitivities of wider tubes can be explained by the way the top of the valence band shifts with the tube diameter. As reported by O'Connell *et al.*, wider tubes undergo faster electron transfer to oxidizing agents in solutions, which was explained by the rise of the valence-band top with increasing diameter.¹¹ More recently, by the measurement of OA or PL while electrochemically tuning the electrode potential, it was shown that the oxidation potentials of CNTs shift upward with increasing diameter.^{12,13} In addition, for a solution-phase glucose sensor employing solubilized CNTs, a similar dependence of the sensitivity on the tube diameter was reported, although different behavior between OA and PL leads to a partially different mechanistic interpretation.¹⁰ The present study has established that a similar trend holds true for interactions between gases and solid-state CNTs, where solution effects such as solvation and reorganization energy are not involved. We also note that the sensing experiment based on the wide-range PL excitation mapping (excitation: 700–1000 nm, emission: 1000–1600 nm) allowed to individually probe CNT groups with a wide range of (*n,m*) indices.

Conclusions

We have performed optical gas sensing using dip-coated thin films of well unbundled and exposed CNTs. The observed changes in PL, OA, and electrical resistance are consistently

explained by reversible electron or hole doping. The spectral dependence of the PL and OA changes revealed that wider CNTs are more sensitive to gas exposure. Gas sensing through PL changes, in particular, showed its advantages in terms of sensitivity and spectrally well-resolved changes. This approach should complement conventional electrical sensing and thus help to elucidate the gas sensing process, eventually proving useful in realizing industrial CNT gas sensors.

Acknowledgements

This research was supported by the Ministry of the Environment.

References

- 1 J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dai, *Science*, 2000, **287**, 622.
- 2 D. Kauffman and A. Star, *Angew. Chem., Int. Ed.*, 2008, **47**, 6550.
- 3 A. Karthigeyan, N. Minami and K. Iakoubovskii, *Jpn. J. Appl. Phys.*, 2008, **47**, 7440.
- 4 I. Sasaki, N. Minami, A. Karthigeyan and K. Iakoubovskii, *Analyst*, 2009, **134**, 325.
- 5 E. Bekyarova, I. Kalinina, M. E. Itkis, L. Beer, N. Cabrera and R. C. Haddon, *J. Am. Chem. Soc.*, 2007, **129**, 10700.
- 6 D. Kauffman and A. Star, *J. Phys. Chem. C*, 2008, **112**, 4430.
- 7 M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. P. Ma, R. H. Hauge, R. B. Weisman and R. E. Smalley, *Science*, 2002, **297**, 593.
- 8 R. B. Weisman and S. M. Bachilo, *Nano Lett.*, 2003, **3**, 1235.
- 9 L. Cognet, D. A. Tsybolski, J. R. Rocha, C. D. Doyle, J. M. Tour and R. B. Weisman, *Science*, 2007, **316**, 1465.
- 10 P. W. Barone, S. Baik, D. A. Heller and M. S. Strano, *Nat. Mater.*, 2005, **4**, 86.
- 11 M. J. O'Connell, E. E. Eibergen and S. K. Doorn, *Nat. Mater.*, 2005, **4**, 412.
- 12 D. Paolucci, M. M. Franco, M. Iurlo, M. Marcaccio, M. Prato, F. Zerbetto, A. Penicaud and F. Paolucci, *J. Am. Chem. Soc.*, 2008, **130**, 7393.
- 13 Y. Tanaka, Y. Hirana, Y. Niidome, K. Kato, S. Saito and N. Nakashima, *Angew. Chem., Int. Ed.*, 2009, **48**, 7655.