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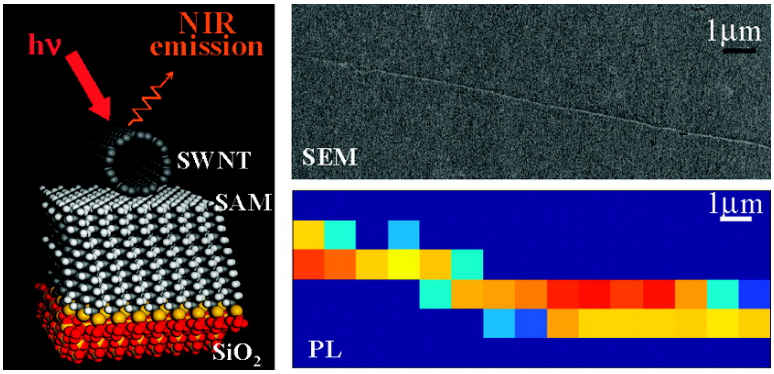

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Photoluminescence Recovery from Single-Walled Carbon Nanotubes on Substrates

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Single-walled carbon nanotubes (SWNTs) can give photoluminescence[1−3] (PL) and electroluminescence[4−6] (EL) in near-infrared (NIR) region, which makes it promising for future photonics and optoelectronics. In these applications, SWNTs on gate oxide (SiO_2 is commonly used) is a basic structure to build devices. However, SWNTs are non-photoluminescent on SiO_2[3] and EL efficiency from SWNT field effect transistors (FETs) is low (10^{-6} to 10^{-7} for ambipolar SWNT FETs[7] and $\sim 10^{-3}$ for partially suspended SWNT FETs[4]). This suggests significant substrate-induced nonradiative decay of excitons in SWNTs which may be caused by interactions between SWNTs and SiO_2, such as van der Waals forces[8] and chemical bonding.[9] Additionally, electron transfer between SWNTs and defect states in SiO_2 may quench excitons in SWNTs too. Herein we report an approach to block substrate-induced nonradiative decay of excitons by transferring SWNTs on self-assembly monolayers (SAMs) functionized SiO_2, and thus PL from SWNTs was recovered (Figure 1a).

Individual long SWNTs were prepared by Fe-assisted ethanol chemical vapor deposition (CVD).[10] Parallel SWNT arrays were grown on a sapphire ($11\bar{2}0$) plane (see Supporting Information). The SWNTs transfer was achieved by a polymer-mediated transfer method.[11] Briefly, a polymer film was formed on a SWNTs-contained substrate by spin-coating. The film was then peeled off together with nanotubes and put on a target substrate. Finally, the polymer film was removed by solvent washing. *N*-Octadecyltrimethoxysilane (Aldrich), hexyltrimethoxysilane (Tokyo Kasei Kogyo Co. Ltd), and ethyltriethoxysilane (Acros organics) were used as silanes to prepare C_{18}, C_6, and C_2 SAM functionized SiO_2/Si substrates (C_{18}/SiO_2/Si, C_6/SiO_2/Si, and C_2/SiO_2/Si, respectively). PL experiments were performed with a confocal Raman spectrometer (HORIBA Jobin Yvon, LabRam HR800). In a typical PL experiment, a 100× objective was used to focus excitation laser and collect NIR emission, a 633 nm laser at about 2 mW power was used as excitation source, and a 512-element InGaAs detector was used to record spectra.

Figure 1b shows SEM image of an individual SWNT transferred on C_{18}/SiO_2/Si. PL mapping image, shown in Figure 1c, indicates that the NIR emission of an individual SWNT was recovered compared with the nanotubes on SiO_2 substrates.[3] The emission wavelengths are similar along the tube, and the typical emission spectrum is presented in Figure 1d. This suggests a successful blocking of nonradiative decay of excitons in SWNTs. Since surface van der Waals force induced radial deformation can only change the bandgaps of SWNTs[12] but cannot induce energy levels to quench excitons, chemical bonding and electron transfer between SWNTs and SiO_2 may be two main contributions to PL quenching of

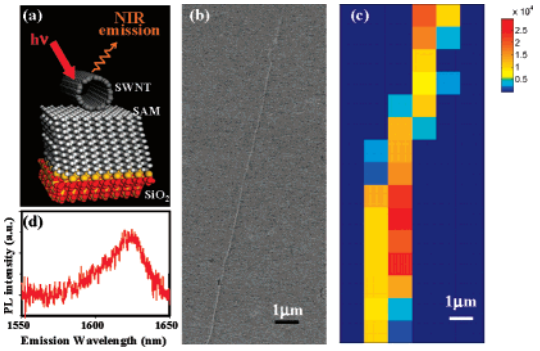

Figure 1. (a) Schematic illustration of PL from SWNTs on C_{18}/SiO_2/Si. (b) SEM image of an individual SWNT on C_{18}/SiO_2/Si. (c) PL mapping image of the same area in shown in panel b. The intensity was integrated from 1580 to 1630 nm. (d) Emission spectrum from SWNT in panel b.

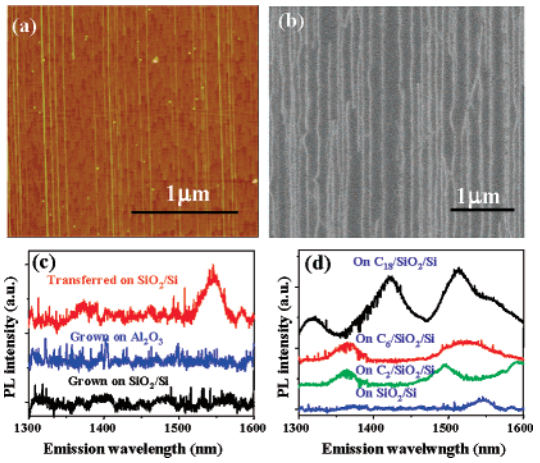

Figure 2. (a) AFM image of parallel SWNT array grown on Al_2O_3; (b) typical SEM image of transferred SWNT array; (This image was taken from SWNTs on C_6/SiO_2/Si.) (c) typical PL spectra from pristine SWNTs grown on SiO_2/Si, Al_2O_3 and transferred SWNTs on SiO_2/Si; (d) typical PL spectra from SWNTs transferred on SiO_2/Si, C_2/SiO_2/Si, C_6/SiO_2/Si, and C_{18}/SiO_2/Si.

SWNTs. Further PL experiment of larger numbers of SWNTs was carried out to investigate the effect of the two interactions on PL from SWNTs.

High-density parallel SWNT arrays on a sapphire ($11\bar{2}0$) plane was shown in Figure 2a. After transfer, SWNTs kept its original alignment: high density and parallel (Figure 2b). PL measurement shows that no NIR emission was observed from pristine SWNTs grown on Al_2O_3 and SiO_2/Si (Figure 2c). Interestingly, weak NIR emission was observed from transferred SWNTs on SiO_2/Si (Figure

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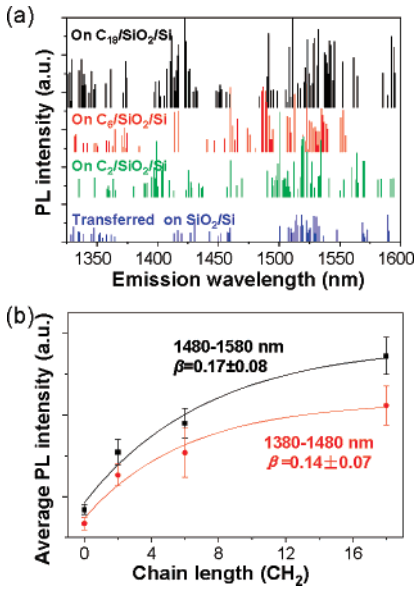

Figure 3. (a) Plot of PL intensity to emission position from SWNTs transferred on SiO_2/Si, $C2/SiO_2/Si$, $C_6/SiO_2/Si$, and $C_{18}/SiO_2/Si$. (b) Dependence of PL intensity on chain length of silanes. The solid lines are fits using $y = y_0 - A\exp(-\beta x)$.

2c). Further, stronger PL emission was observed from SWNTs on SAMs (Figure 2d).

Comparing of photoluminescent property of transferred SWNTs on SiO_2/Si and pristine SWNTs grown on SiO_2/Si or Al_2O_3 indicates that a quenching path might be introduced in a CVD process. This quench path may be provided by midgap energy levels introduced by chemical bonds between SWNTs and SiO_2. Theoretical calculation shows that carbon−oxygen (C−O) bonds can be formed between SWNTs and SiO_2[9]. A high-temperature CVD process may activate this chemical reaction. The forming of C−O bonds introduces sp^3 C atoms on the sidewall of SWNTs. The sp^3 C atoms introduce unoccupied energy levels near the Fermi level of SWNTs.[13] Excitons can be deactivated to these midgap energy levels, and hence PL is quenched. For pristine SWNTs grown on Al_2O_3, both chemical bonding and surface states (see Supporting Information) may contribute to PL quenching.

By analyzing PL intensity from transferred SWNTs on SiO_2/Si, $C_2/SiO_2/Si$, $C_6/SiO_2/Si$, and $C_{18}/SiO_2/Si$, dependence of PL intensity on chain length of silanes was found: SWNTs on SAMs with a longer chain give a stronger PL emission (Figure 3a). Several possibilities can lead to this distance-dependent PL intensity on the chain length of silanes, including laser-induced heating, energy transfer, and electron transfer. Although heating can induce NIR emission from SWNTs,[6] Raman experiment shows that there is no laser-induced heating in our PL measurement (see Supporting Information). Additionally, energy transfer from SWNTs to SiO_2 is not possible because the lowest electronic transition energy of defects in SiO_2 (ca. 1.9 eV)[14] is larger than the bandgaps of SWNTs (0.5−0.9 eV). Finally, an electron-transfer mechanism is proposed. Electrons can transfer from excited states of SWNTs to defect states in SiO_2, because lowest unoccupied orbits of defects in SiO_2, such as silicon danging bonds (≡Si•, $\equiv Si^+$), peroxyl radical (≡Si−O−O•), and nonbridging oxygen (≡Si−O•), lie below the conducting band of SWNTs (see Supporting Information).

The rate of electron transfer (k_{et}) can be expressed as[15]

$$k_{et} = k_0 \exp(-\beta d_{DA})$$

where k_0 and β are constants, d_{DA} is the distance between electron donor and acceptor. The key constant β determines the rate of falloff of k_{et} with distance. PL efficiency decreases linearly with the rate of electron transfer. Therefore, theoretically, we can get an exponential dependence of PL intensity on distance between SWNTs and SiO_2. Optical field amplitude in the vicinity of different SAMs is approximately equal because the thickness of SAMs is much smaller than the excitation wavelength. Additionally, by assuming no distortion of SAMs when SWNTs contact with SAM/SiO_2/Si, the distance from SWNTs to SiO_2 can be approximately calculated from the chain length of silanes and the tilt angle of SAMs (10° is used[16]). The average PL intensity from two frequently appeared emission regions was plotted against the chain length of silanes for exponential fitting (Figure 3b). The fitting result gives a β value of 0.14 ± 0.07 per CH_2 (0.11 ± 0.06 $Å^{-1}$) and 0.17 ± 0.08 per CH_2 (0.14 ± 0.06 $Å^{-1}$) for emission regions in 1380−1480 and 1480−1580 nm, respectively (Figure 3b). This shows that β is smaller for SWNTs with shorter emission wavelength.

In summary, we have observed strong PL from SWNTs on methyl-terminated SAM functionized SiO_2/Si. PL recovery is attributed to breaking the chemical bonding between SWNTs and SiO_2 and blocking the electron transfer from SWNTs to defect states in SiO_2. Electron-transfer parameter β obtained in our experiment is a fundamental parameter for designing SWNT-based tunneling devices and SWNT-involved charge-transfer systems, the latter which has potential application in light harvesting.[17,18]

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Supporting Information Available: Complete ref 15, experimental details for preparation of SAMs, growth of parallel SWNT arrays on sapphire, energy level diagram of SWNTs and SiO_2, and examination of laser-induced heating. This material is available free of charge via the Internet at http://pubs.acs.org.

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