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Enhanced chemical shift of carbon nanotube from laser assisted gas incorporation

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We investigate the position-selected electronic structure of laser modified carbon nanotubes (CNTs) by scanning photoelectron microscopy. After laser pruning removed the top layer of CNTs in air and N₂ environment, the modified region shows enhanced chemical shifts of 0.9 and 0.6 eV in carbon 1s state, respectively. The modification of electronic structure is shown to be strongly dependent on the gaseous environment. We demonstrate an effective postgrowth process to modify the electronic structure of CNTs for further applications. © 2007 American Institute of Physics.
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Since multi-walled carbon nanotube (MWCNT) was discovered by Iijima,¹ carbon nanotubes (CNTs) have become promising candidates for chemical sensors,² nanoelectronic devices,³ and field-emission devices.⁴ The character of single-walled CNTs is either metallic or semiconducting depending on the chirality and the tube diameter.⁵ Recently, a focused laser system has been developed to prune the CNT arrays to form three-dimensional structure.^{6,7} After pruning the CNTs by focused laser, the turn-on electric field decreased and its emission current density increased in a field emission experiment.⁸ However, the correlation between laser modification and electronic structure of CNTs has not been explored. In this letter, the precise information on electronic structure is investigated by x-ray photoelectron spectroscopy and converted to a two-dimensional mapping image for the space-resolved chemical state analysis by scanning photoelectron microscopy (SPEM).^{9,10} After the laser beam irradiates on the pristine CNTs in air, N₂, and O₂ environments, the modified electronic structure presents a maximal chemical shift of C 1s up to 0.9 eV, which is identified as the gas-doped effect assisted by laser energy.

The MWCNTs were grown on the Si substrate by plasma-enhanced chemical vapor deposition using iron nanoparticles as catalyst.¹¹ The CNTs were then transferred into a chamber under optical microscope for further laser modifi-

cation. By controlling the pressure and gas flow rate, the laser system can be operated with the sample housed in different gaseous environments. The detail of laser focusing system was reported elsewhere.^{6,7} The laser-modified CNTs were transferred to SPEM at National Synchrotron Radiation Research Center (NSRRC) in Taiwan. SPEM is located at the U5-SGM undulator beamline and equipped with a combination of Fresnel zone plate and order sorting aperture to focus the monochromatic x-ray beam. With the present setup, the beam spot at the focal point is smaller than 100 nm.¹⁰ By raster scanning the sample relative to the x-ray beam, the multichannel detector enables a simultaneous acquisition of 16 images at different binding energies (BEs).^{9,10}

As-grown CNTs were pruned off repeatedly by focused laser in various gaseous environments (air, vacuum, N₂, and O₂). The modified morphology resembles the edge of sawtooth because the laser beam passed the focusing lens obliquely, as illustrated in Fig. 1(a). The as-grown and laser-

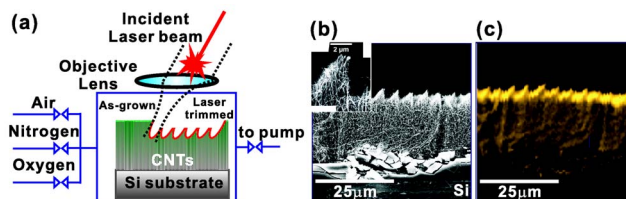


FIG. 1. (Color online) (a) The schematic diagram of oblique focused laser beam to prune CNTs in the selected gaseous environment. [(b) and (c)] Cross-sectional SEM image and corresponding SPEM image. The inset of (b) shows magnified SEM image.

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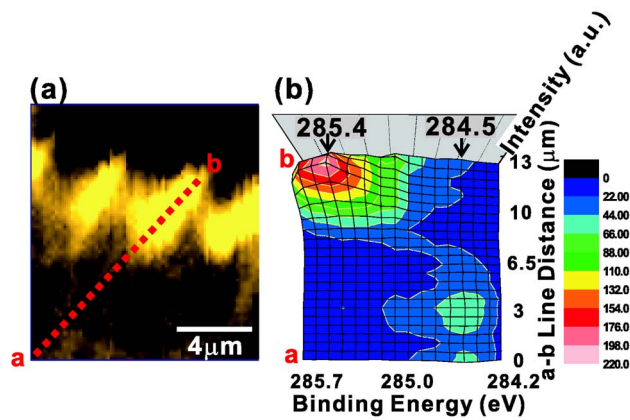


FIG. 2. (Color online) (a) Cross-sectional SPEM image of laser modified CNTs. The image is the intensity summation over 16 channels around C 1s state. (b) C 1s spectra taken along the a-b line in (a). The distance along the a-b line is the ordinate and the binding energy of the 16 channel represents the abscissa. The chemical shift of 0.9 eV is observed between the laser-modified and sidewall region.

modified areas were manufactured together in one sample in order to study their respective electronic structure under the same experimental condition. Figure 1(b) shows the cross-sectional scanning electron microscope (SEM) images of modified CNTs. Figure 1(c) shows the carbon 1s (C 1s) SPEM image obtained by collecting photoelectrons from C 1s state. The cracks of the Si substrate in Figs. 1(b) and 1(c) clearly indicate that they were imaged from the same area.

Figure 2(a) shows a cross-sectional C 1s SPEM image of the laser-modified CNTs. The sample was treated in ambience with laser power of 19.3 mW. This image corresponds to the intensity summation of the 16 SPEM images in the C 1s BE range between 284.2 and 285.7 eV. The C 1s spectra extracted along the a-b line, as denoted in Fig. 2(a), were analyzed to reveal its position-dependent electronic structure. Figure 2(b) shows the result. The ordinate is the position along the a-b line; the abscissa is the BE of the 16 channels, the photoelectron intensity presents as different colors. These spectra are the intensity summation over $400 \times 400 \text{ nm}^2$ selected along the a-b line. With the aids of this representative method, we can easily visualize the quantities of the spatially distributed chemical shifts with their relative intensity. Near point a (around sidewalls region), the C 1s state shows the lowest BE with 284.5 eV, which is identical to the sidewalls of the as-grown CNTs.¹² Around point b (modified top region) the C 1s peak shifts to the highest BE with 285.4 eV. The shadow effect also results in the relatively high signal intensity. It is surprising that the chemical shift of C 1s state between sidewalls and tips is as large as 0.9 eV. In pristine CNTs, the C 1s peak in the top region is higher than that in the sidewalls region only by 0.2 eV.¹³

In order to understand how gas molecules and morphological changes affect the electronic structure, we treated CNTs in vacuum to clarify its difference. Figures 3(a) and 3(b) show the cross-sectional SPEM images, acquired around C 1s state with BE 282.5–288.5 eV, with and without laser treatment in vacuum (10^{-2} – 10^{-3} torr), respectively. Figure 3(c) shows the C 1s spectra of various locations, as denoted in Fig. 3(a). C 1s spectra obtained from the modified (A–C) and as-grown tip (1) areas show the same BE with the slight upshift of C 1s ($<0.1 \text{ eV}$), as compared to the spectrum measured at as-grown sidewall area (2). It means that

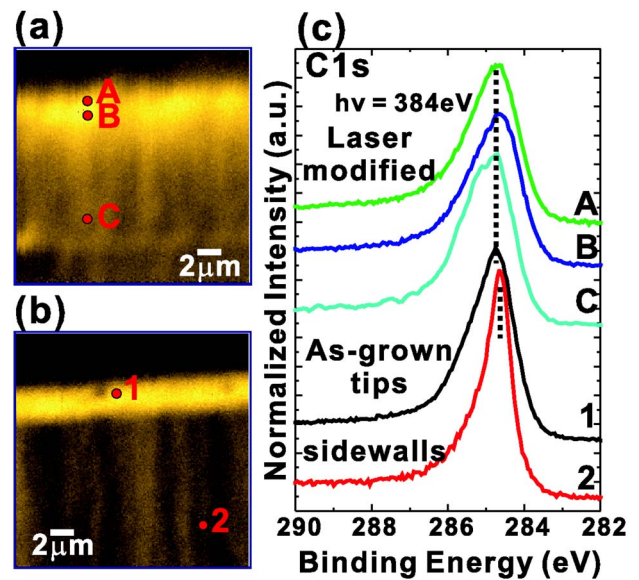


FIG. 3. (Color online) (a) Cross-sectional SPEM C 1s image of CNTs for laser modification in vacuum. (b) Cross-sectional C 1s mapping image of as-grown CNTs. (c) Photoelectron spectra of C 1s state from as-grown area (1 and 2) and the area modified in vacuum (A, B, and C).

the morphological change alone is not sufficient to induce the enhanced chemical shift of C 1s state.

Figures 4(a) and 4(c) present the C 1s SPEM images which correspond to nitrogen-treated and oxygen-treated CNTs, respectively. The photoemission spectra of CNTs treated in nitrogen (300–500 torr) or oxygen (300–600 torr) environment were measured with photon energy of 649 eV, as shown in Figs. 4(b) and 4(d). In Fig. 4(b), C 1s spectrum obtained from point A shifts toward higher BE by 0.6 eV as compared to that of as-grown CNTs. Moreover, N 1s spectrum measured at the same point shows two nitrogen peaks located at BEs of 400.9 and 399.2 eV. The spectra have been smoothed without loss of energy resolution. The component at 400.9 eV is related to C–N bond; the other component at 399.2 eV is contributed from surface-absorbed nitrogen¹⁴ because both laser modified and as-grown areas have been immersed in nitrogen and ambience environments. The upshift of C 1s state and enhanced C–N bond (400.9 eV) can be

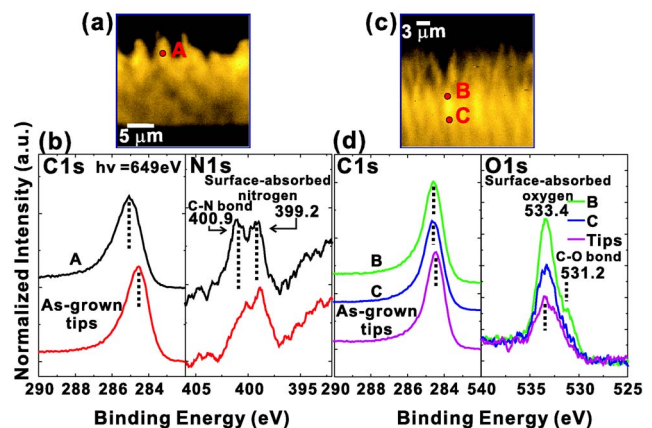


FIG. 4. (Color online) [(a) and (c)] C 1s mapping images of CNTs treated by laser irradiation in nitrogen and oxygen environments, respectively. (b) Position-related C 1s and N 1s spectra as denoted in (a). (d) The comparison of C 1s and O 1s spectra after laser modification.

explained by the substitutional N atoms in the graphite sheet.¹⁵

In the oxygen-treated CNTs, the C 1s peak (B and C) after laser modification also shifts toward higher BE, however, only by 0.2 eV as compared to the “tips” of as-grown CNTs, as shown in Fig. 4(d). O 1s spectrum measured from point B also exhibits two oxygen components located at BEs of 533.4 and 531.2 eV. The weak feature with lower BE is related to C–O bond, and the other feature is due to the absorbed oxygen linked to carbon.¹⁶ The amount of absorbed oxygen at the modified regions (B and C) is more than that of as-grown CNTs.

The dangling bonds and topological defects are supposed to be increased upon laser pruning.⁴ Naturally, laser pruning causes the breakage of the C–C bond in CNTs and the gas molecules nearby can bond with the C atoms with dangling bonds. The existence of stable C–N and C–O bonds on the surface of nanotubes was expected to become metallic, independent of the tubular diameter and chirality.^{2,17} Both N₂ and O₂ molecules can be bonded with CNTs assisted by laser and result in the different chemical shifts (0.6 and 0.2 eV). The highest chemical shift (0.9 eV) in the air-treated CNTs may be attributed to the mixing mechanism, which needs to be further studied. Furthermore, as shown above, the gas-treated CNTs show a larger C 1s chemical shift than those treated in vacuum. However, even after the gas treatment, a lot of defects are still expected to exist at the laser pruned surface of the gas-treated CNTs. These defects may also contribute to the observed C 1s chemical shift besides the gas interaction. The bonded gas molecules and the rest of defects are thus both available at the pruned surface, causing the modification of electronic structure.

In summary, we have compared the change of electronic structure of CNTs due to various gas dopant under laser treatment. The enhanced chemical shift of 0.9 eV in C 1s state was found for the air-treated CNTs. Laser pruning proved to be a viable technique in functionalizing CNTs with incorporation of N and O atoms onto the CNTs. By controlling the type of gas molecules used, we can change and tune the electronic character of CNTs for the development of electronic device.

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