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Interfacial interaction of gas molecules and single-walled carbon nanotubes

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The interfacial interaction between single-walled carbon nanotubes (SWNTs) and various gas molecules (H_2 , He, and N_2) at different pressures has been probed by *in situ* x-ray absorption near-edge structure (XANES) spectroscopy. Experimental results reveal the different strength of interfacial interaction (involving external and internal collisions) between SWNTs and various gas molecules under different pressures. At gas pressures higher than 5 Torr, the unoccupied states of SWNTs show some features corresponding to the structure deformation with a reversible behavior when cycling under vacuum and gas conditions. The XANES study for different gases (H_2 , He, and N_2) shows a strong dependence of gas molecular weight, which provides experimental evidence to the gas scattering mechanism. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4718421>]

Carbon nanotubes (CNTs) have attracted extensive interests owing to their unique properties and potential applications.¹ Many engineering methods have been used to modify the electronic structure to tailor the properties of CNTs for various applications. For example, the band gap of CNTs can be modulated by encapsulated metallofullerenes, or dividing a semiconductor nanotube into multiple quantum dots with lengths of about 10 nm;² also doping of different elements and decoration of different nanoparticles have been effective methods to tailor the electronic structure of CNTs.^{3–7} Thus, interfacial interaction between CNTs and different materials has been an essential issue to understand the electronic structure for designed applications.^{4,5} So far, CNTs have shown the sensitivity to various gases in gas sensing devices with obvious response in the electrical resistance or capacitance.^{8–10} Different interpretation of the mechanism for changes of the electrical resistance or capacitance in a gas sensing device have been reported, such as models of charge transfer between gas and CNTs,¹¹ the effect of defects and/or oxidation sites,¹² residual contaminants or contacting points in the devices,¹³ etc. However, the electronic structure changes of CNTs under gas sensing processes and the interfacial interaction between CNTs and gas molecules are less investigated and still the open question. In this work by using *in situ* x-ray absorption near-edge structure (XANES) spectroscopy, we directly probe the electronic structure changes of single-walled carbon nanotubes (SWNTs) upon exposure to different gases (H_2 , He, and N_2) and the experimental findings suggest that the gas collision resulting tube wall deformation is the main effect for the interfacial interaction of SWNTs and gas molecules.

XANES is an element-specific technique involving the excitation of electrons from a core level to local and partial empty states of a defined character, which is particularly useful to characterize complex systems.^{14,15} Working in the electron yield mode XANES is also a surface-sensitive technique that is particularly useful for probing the gas-solid interface electronic structure.¹⁶ In a previous report, we performed *in-situ* XANES experiments of SWNTs exposed to N_2 and the spectra showed evidence of the collision-induced tube wall deformation.¹⁶ In this work, we have performed the XANES study of SWNTs exposed to various pressures of H_2 and He gases in comparison with N_2 gas. A molecular weight dependence of the collision effect for H_2 , He, and N_2 has been observed. Experimental results clearly reveal the different strength of interfacial interaction between SWNTs and various gas molecules under different pressures.

In-situ XANES experiments were performed on beamline 7.0.1 at the advanced light source (ALS) of Lawrence Berkeley National Laboratory.¹⁷ The beamline is equipped with a spherical grating monochromator and the XANES experiments were performed at an energy resolution of 0.2 eV at the C K-edge with an incident photon beam normal to the sample surface. The sample of SWNTs was located inside a gas cell with gas flow in and out, and a 100 nm thick Si_3N_4 window was used to separate the ambient pressure cell and ultra-high vacuum (UHV) chamber and to allow a transmission of 50% at the C K-edge for the XANES experiments. XANES spectra were recorded with the total electron yield (TEY) detection mode. The experimental setup can be seen in Ref. 16. SWNTs were purchased from Carbon Nanotechnologies Incorporated (CNI). SWNTs have been synthesized by a gas-phase chemical-vapor-deposition process with high-pressure (30–50 atm) and high-temperature (900–1100 °C) flowing CO on catalytic clusters of iron (HiPco). Raw SWNTs have been purified and the purity of

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the sample is higher than 95 wt. %. The sample has a diameter distribution of 0.8–1.2 nm measured from the transmission electron microscope (TEM) with the mean diameter of about 1.0 nm. The morphology of the sample is dry powder of nanotubes bundled in ropes, with individual SWNT length of 100–1000 nm. According to the TEM image, the SWNTs are partly open. SWNT powders were annealed under UHV at 500 °C for 12 h and then pressed on the sample holder inside a glove box under He environment before experiments.

Fig. 1 shows the C *K*-edge XANES spectra of SWNTs under the various pressures of gas H₂ (a), He (b), and N₂ (c). Fig. 1(a) shows the C *K*-edge XANES spectra of SWNTs at 2×10^{-6} Torr and different pressures of H₂. The spectrum of SWNTs at 2×10^{-6} Torr (black curve) is characterized by three main features at about 285.5, 288.4, and 292.9 eV labeled as A, B, and D, respectively.^{18,19} The A feature is assigned to the π^* excitation of C=C bonds, and the B feature is typically related to transitions to sp^3 hybridized states due to oxygenated surface groups or surface contaminations.^{15,18} The D feature to the σ^* excitation with a sharp core-exciton feature at about 291.9 eV which can be attributed to the intrinsic C 1s core-exciton resonance which is related to the crystalline structure (long range order) of CNTs.^{20–22}

Upon exposure to H₂, the XANES spectral shape changes dramatically. At a H₂ pressure of 5 Torr, peak A decreases and the D feature broadens. The weakening and broadening of the excitonic feature have been seen as the broken of long-range order in small nanoparticles due to the quantum confinement effect.²³ When the pressure increases up to 450 Torr, peak A decreases significantly and the spectral shape of D feature is strongly modified with the disappearance of the excitonic feature and also a shift towards low energies. Moreover, two additional peaks around the π^* excitation can be resolved at 284.6 eV (A') and 286.6 eV (A'') (the peak fitting is shown in Fig. 2(a)). According to the calculations based on external gas collisions,¹⁶ the A' peak can be simulated only when carbon atoms around the collision center have been taken into account, while the A'' peak is obtained when considering an area far away from the center of collision. The spectral behaviors suggest that the A' peak is mainly associated to the center of the collision area, while the A'' peak is related to a relaxation at an extended distance away from the center of collision along the tube. The calculations based on external gas collisions suggest that the A' peak is directly related to the tube wall deformation around the collision center while the A'' peak to a relaxation with delocalized nature along the whole tube. However, the TEM images show that the SWNTs we studied are partly open and the internal gas collisions may need to be taken into account. Recent report showed that argon gas could fill in SWNTs even at low pressure and tube collapse had been observed at various pressures of several GPa depending on the fillings.^{24,25} The gas molecules inside SWNTs may also contribute to the changes of XANES spectra.

External gas collisions can be related to the A' peak in agreement with existing calculations, while the A'' peak may be related to the internal gas collisions. When increasing the gas pressure, the A' peak becomes prominent in Fig. 1(a) due

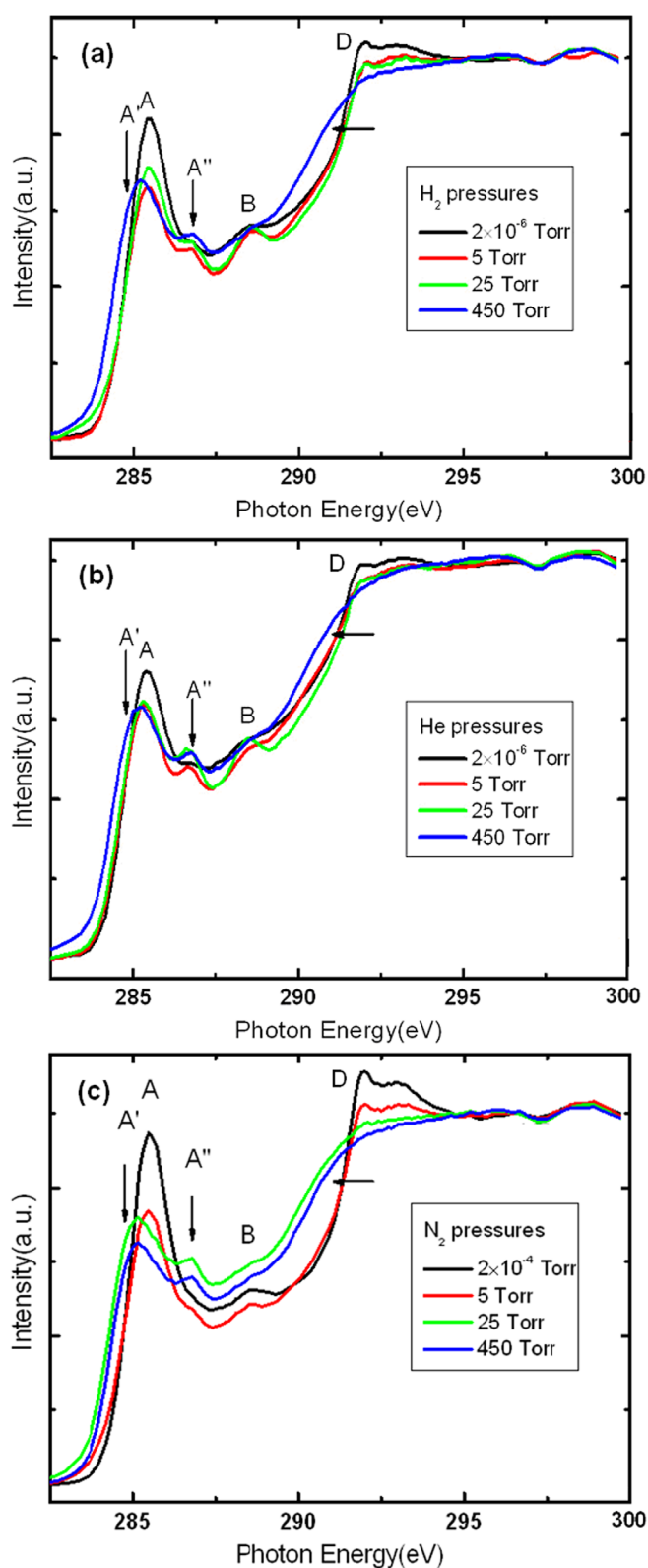


FIG. 1. C *K*-edge XANES spectra of SWNTs at high vacuum and different pressures of H₂ (a), He (b), and N₂ (c). The XANES spectra of SWNTs exposed to all three kinds of gases show an evolution under increased pressures with a decreased peak A, increased peaks A' and A'', and a broaden feature D.

to the stronger external gas collisions. At the meantime, as more gas molecules fill in SWNTs with the increased pressure, there may be internal collisions that weaken the impact of the external collisions at the opposite direction. Thus, at a

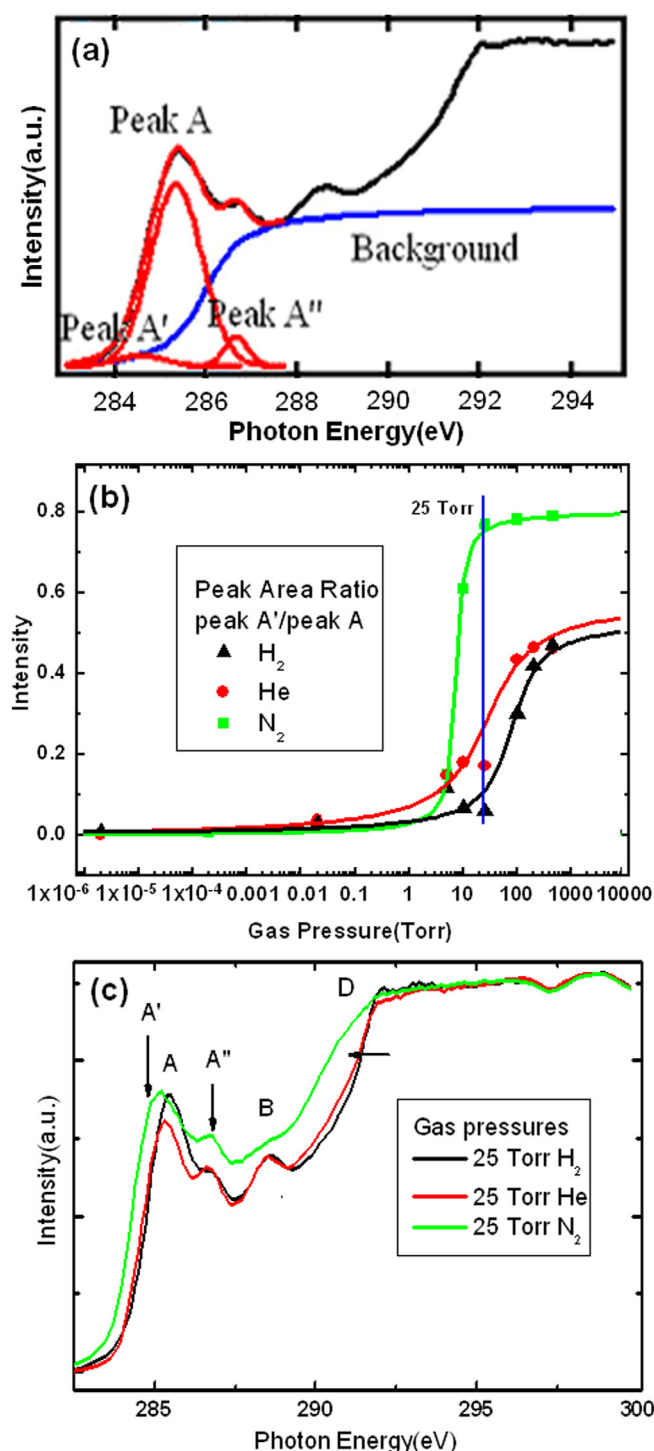


FIG. 2. (a) Peak fitting example in the region of the π^* excitation at a H_2 gas pressure of 5 Torr. (b) Peak area ratios of peak A'/peak A versus increasing pressures of H_2 , He, and N_2 . The blue vertical line indicates the ratios at 25 Torr for H_2 , He, and N_2 . (c) C K-edge XANES spectra of SWNTs exposed to 25 Torr H_2 , He, and N_2 .

high pressure such as 450 Torr, an equilibrium condition may be reached at a balance of the internal and external pressure which may result in a saturation in the XANES spectra, along with the overlap of the deformations from neighboring collision sites along the tube.

Hydrogen sensing has been widely investigated and reported to be sensitive to CNTs based films.^{6,7} Kong *et al.*

showed electrical response of H_2 for Pd-coated SWNTs,⁷ while Khalap *et al.*⁶ reported the important roles of Pd-decorated defects which would strongly amplify the chemoresistant response of SWNT devices to H_2 gas. Pristine CNTs showed nearly no intrinsic response to H_2 and only CNTs with modified surface chemistries showed prominent response.^{6,7} In Fig. 1(a), it is shown that by exposure to H_2 , the changes in electronic structure of SWNTs have been probed by XANES. Gas collisions and the corresponding tube wall deformation result in a different electron distribution of CNTs. The degree of structure deformation increases with gas pressure from 5 Torr to a saturation pressure of about 450 Torr. Moreover, the XANES spectra recorded during an evacuation process at the H_2 pressures from 450 Torr to 2×10^{-6} Torr (data not shown) exhibit a reversible behavior of x-ray absorption features under those collected increasing pressures. The reversible behavior of the XANES spectra indicates the occurrence of a reversible deformation. Moreover, when comparing the compression and evacuation process for H_2 , hysteresis has been observed suggesting the gas filling in tube and the internal gas collisions may contribute to the XANES spectra.

For a comparison, we have also performed *in-situ* XANES experiments of SWNTs exposed to He gas. Due to intrinsic chemical nature of He without the donor/acceptor behavior, He gas becomes a choice to test the gas collision effect without the influence of charge-transfer interaction between SWNTs and gas. Fig. 1(b) shows the C K-edge XANES spectra of SWNTs at 2×10^{-6} Torr and different pressures of He. Again, the XANES spectra show decreased peak A, broaden D feature (disappearing of excitonic feature) and additional peaks A' and A'' under increased He gas pressures, similar to those behavior observed for H_2 and N_2 . Because of the chemical inert properties of He on SWNTs, the gas collisions of He on SWNTs could be the only interaction mechanism to induce the structure deformation. The XANES spectra recorded during an evacuation process for He also exhibit a reversible behavior and the comparison of the compression and evacuation process shows the hysteresis confirming the tube filling and internal gas collisions. The XANES results for H_2 , He, and N_2 gases with similar spectral responses indicate the interfacial interaction of gas/SWNTs a major effect in SWNT-based devices.

The fitting results with the peak area ratios of peak A'/peak A versus increasing pressures of H_2 , He, and N_2 have been shown in Fig. 2(b) (for clarity we have used more experimental pressure points than those shown in Fig. 1). The A' peak can be attributed to structure deformation by external gas collisions involving changes of the geometrical structure and bond lengths.¹⁶ We thus use the peak area ratios of peak A'/peak A as an indicator for the electronic structure change and show the results for different gases in Fig. 2(b).

The area ratios of peak A'/peak A for all gases show a dependence increasing along with the increased pressures, indicating enhanced changes to the tube wall deformation. At higher pressures above 450 Torr, the peak ratios become almost constant, which can be associated to the equilibration between internal and external pressure and the overlap of the deformations from neighboring collision sites along the tube.⁹ Moreover, the curves in Fig. 2(b) (arctangent

functions have been used in the fitting) show a dependence of molecular weight for the collision effect of gas H₂, He, and N₂ with a transition in a pressure region around 10 Torr (the gas collision effect is enhanced in this region). It is seen that the curve for H₂ shows lowest peak area ratios but curve for N₂ shows highest ratios. The molecular dynamics simulations in Ref. 9 have revealed that the deformation of the tube wall upon collision would exhibit a $M^{1/3}$ (M is the mass of the collision gas species) dependence. The structure deformation dependence on molecular weight for H₂, He, and N₂ also provides the experimental evidence for the collision effect in the scattering mechanism. To illustrate the differences of the area ratios of peak A'/peak A, Fig. 2(c) displays the XANES spectra for H₂, He, and N₂ measured at 25 Torr as an example (the pressure point has been indicated in Fig. 2(b)). It is obvious that at the same gas pressure the curve for N₂ shows the largest spectral changes (maximum area ratios of peak A'/peak A) and the curve for H₂ has the smallest changes.

In this work by using *in situ* XANES, the interfacial interaction of SWNTs and various gas molecules (H₂, He, and N₂) at different pressures has been probed. When exposed to H₂, He, and N₂ gases under increased pressures, the XANES spectra show decreased absorption A feature, broaden D feature, and the appearance of additional A' and A'' features. The spectral changes can be attributed to the external and internal interfacial interactions (gas collisions) between SWNTs and gas molecules which results in tube wall deformations. The XANES study for different gases (H₂, He, and N₂) shows also a strong dependence of gas molecular weight, which provides experimental evidence to the gas scattering mechanism.

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