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High-resolution ^{13}C nuclear magnetic resonance evidence of phase transition of Rb,Cs-intercalated single-walled nanotubes

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We present ^{13}C high-resolution magic-angle-turning (MAT) and magic angle spinning nuclear magnetic resonance data of Cs and Rb intercalated single walled carbon nanotubes. We find two distinct phases at different intercalation levels. A simple charge transfer is applicable at low intercalation level. The new phase at high intercalation level is accompanied by a hybridization of alkali (s) orbitals with the carbon (sp^2) orbitals of the single walled nanotubes, which indicate bundle surface sites is the most probable alkali site. © 2011 American Institute of Physics. [doi:10.1063/1.3631052]

INTRODUCTION

The electronic of single-walled nanotubes (SWNTs) was shown to be drastically changed by alkali-metal intercalation.^{1,2} Electron transfer and the metallic character of intercalated SWNTs have also been probed by nuclear magnetic resonance (NMR).^{3,4} However, the existence of different stable phases was reported in intercalated SWNTs.^{1,5–10} Recent conductivity and Raman studies allow us to describe the different steps of intercalation and to identify two stable phases for Rb-intercalated SWNTs.^{9,10} Different models of the arrangement of the alkali atoms in intercalated single-walled carbon nanotubes (SWCNT) bundles have been proposed. In close-end SWCNTs, the dopants are expected to be inserted into the interstitial channel between the adjacent SWCNTs. Molecular dynamics calculations have predicted that, at low intercalation level, the alkali metals are inserted between the tubes and that at high intercalation level the sites of the alkali metals around the bundle.^{7,11}

In this systematic intercalation study we have applied ^{13}C magic-angle-turning (MAT) and MAS NMR to investigate Rb and seven Cs samples intercalated SWNTs Cs_xC ($x = 0\text{--}0.143$). We show that the intercalated SWNTs exhibit two distinct phases and the transition between these phases occurs around $x = 0.05$. At a low level of intercalation, the most favorable intercalation site is the interstitial channel between three tubes in a bundle of the SWNTs, therefore a simple charge transfer is applicable in this intercalation regime. At a higher doping level, the bundle surface sites are the most probable Rb, Cs sites. We present strong evidence that this new phase is accompanied by a hybridization of alkali (s) orbitals with the carbon (sp^2) orbitals of the SWNTs.

EXPERIMENTAL SECTION

Raw SWNTs samples were synthesized by arc-discharge using Pt and Rh as catalysts as described in Ref. 12 To lower measurement time and to increase signal to

noise ratio, the SWNTs were ^{13}C isotope enriched in a mass ratio of 10%. The SWNTs had an average diameter of 1.4 ± 0.2 nm and a bundle length of several micrometers.^{13,14} The preparation of Cs-intercalated SWNTs proceeded by saturating SWNTs by Cs vapor-transport onto degassed SWNT at 200 °C in a cycled process for 10 days. Theoretical and experimental studies have known that the intercalation of SWNTs saturates at a stoichiometry of approximately $\text{Cs}_{0.14}$.^{15–17} The saturated sample was then mixed in different ratios with the pure SWNTs sample to obtain a large spread in the stoichiometry. All samples were heated to 300 °C for two weeks and treated completely without contact with air or ambient atmosphere. The samples were controlled by NMR in Ref. 4 to estimate the stoichiometries Cs_xC ($x = 0.028\text{--}0.14$).

The preparation of Rb-intercalated SWNTs is very well described in Refs. 18 and 19. Thin films were prepared by spraying a homogeneous suspension of SWNTs in ethanol on a quartz substrate heated with hot air. The quartz plate supporting the SWNTs thin film was inserted in a quartz optical cell connected to a U-shaped glass tube where the second branch consists of an ampoule containing neutral molecules in solution in pure tetrahydrofuran (THF) and a piece of rubidium. The whole apparatus was then sealed under high vacuum. Electron transfer from rubidium to organic molecules results in the radical-anion form of the molecule with Rb^+ as the counter ion. Once the doping was achieved, the excess of doping solution was removed, the sample rinsed by internal distillation of the solvent and then dried by cooling the ampoule at -70 °C.

^{13}C NMR experiments were carried out on a Bruker ASX200 spectrometer at a magnetic field of 4.7 T and a Larmor frequency of 50.3 MHz. High-resolution ^{13}C NMR at magic angle spinning (MAS) was performed at room temperature with spinning frequencies from 4 up to 10 kHz. ^{13}C MAT NMR experiment was carried out using the 5-pulse sequence. Data acquisition was performed directly after the last $\pi/2$ pulse. The MAT rotor frequency was 150 Hz and τ varied from 0.1 s to 6 s within 40 steps. The free induction decay (FID) acquisition during the acquisition included 1024

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points with a dwell time of 4 μ s. A two-dimensional Fourier transform technique represents the isotropic chemical shift projection in one frequency dimension (F1) and the static anisotropic powder pattern along the other frequency axis (F2).^{20–22} ^{13}C NMR line shift are referred to as TMS.

RESULTS AND DISCUSSION

Two-dimensional Fourier transformation as a function of τ and t_a results in the 2D-MAT spectrum of $\text{Cs}_{0.05}$ and Rb intercalated SWNTs in Fig. 1(a) and 2(a), respectively. It is important to note that projections of the 2D-spectrum onto the two axes of the contour plot do not directly represent the isotropic and chemical shift anisotropy (CSA) patterns, since data acquisition is already started after the last $\pi/2$ -pulse of the MAT pulse sequence. Therefore, the scalings of the axis in Figs. 1(a) and 2(a) is displayed in arbitrary units. Projecting the spectrum onto the acquisition dimension axis at an angle $\arctan(\zeta_2/3\zeta_1)$ will result in the isotropic-shift spectrum, while projection on a perpendicular axis will result in the CSA powder pattern. $\zeta_{1/2}$ are defined by the number of acquisition points and dwell times given by τ and t_a .²¹

In the 2D-spectrum two main peaks (A) and (B) are clearly visible. Projecting the spectrum onto the acquisition dimension axis yields the isotropic ^{13}C NMR spectrum in Figs. 1(b) and 2(b) for Cs and Rb intercalated SWNTs, respectively. Contrary to the isotropic spectrum of pristine SWNT that consists of only one main peak around 119

ppm,^{13,14} two sp^2 peaks are observed. Due to the broad spectrum, the line positions can only be roughly estimated to be around 100 ppm and 124 ppm. The sp^2 -line splitting suggests the existence of two inequivalent carbon sites in the intercalated samples. In order to allow further interpretations of the observed shifts and line splittings, ^{13}C MAS high resolution NMR measurements were carried out for all CsC_x samples shown in Fig. 3. For the pristine SWNTs, the MAS spectrum is in agreement with earlier studies by Goze Bac *et al.*^{13,14} with a NMR line at 119 ppm. At low intercalation level, this isotropic line δ_{iso} exhibits a clear paramagnetic shift of about 10 ppm when comparing the pristine SWNTs to the samples with $x = 0.028$ – 0.038 , indicating a transition into an metallic sample. A comparable paramagnetic shift was also observed on lithium intercalated SWNTs.³ At the highest intercalation level, the MAS spectra indicate some difference between the samples. Starting at $x = 0.05$, a distinct split of the sp^2 carbon line is observed; with one component at 111 ppm and another at 128 ppm (corresponding to the line position of the low intercalated level). Increased intercalation level at both lines remain but the intensity of the former increases progressively at the cost of the 128 ppm line. We assign this evolution of the NMR profile to a phase transition between two different types of intercalated stable phases. We assign spectrum with $x = 0.028$ to $x = 0.038$ to an intrinsic stable phase I of the alkali metal intercalated SWNTs and the spectrum of the second stable alkali metal intercalated phase II to that of the high intercalated SWNTs with $x = 0.143$. The two

FIG. 1. (Color online) (a) Room temperature ^{13}C MAT NMR spectrum of $\text{Cs}_{0.05}\text{C}$, (A) and (B) can be assigned to ^{13}C nuclei of intercalated SWNT. The scaling of the axis is displayed in arbitrary units. (b) Isotropic ^{13}C NMR spectrum. The spectrum was extracted from the corresponding 2D-MAT experiment.

FIG. 2. (Color online) (a) Room temperature ^{13}C MAT NMR spectrum of Rb intercalated SWNT, (b) isotropic ^{13}C NMR spectrum. A splitting of the isotropic sp^2 line is clearly visible.

FIG. 3. ^{13}C MAS NMR spectra of Cs_xC . Stars represent spinning sidebands. Spinning rate $\omega = 10$ kHz for pristine SWNT and $\omega = 4$ kHz for doped SWNT with a repetition time of $\tau = 30$ s.

phase intercalation model is also supported by ^{133}Cs experiments in Ref. 4 shows that at low intercalation level, only one single quadrupolar broadened line located at 0 ppm is present. However at higher intercalation level, a second line strong paramagnetically shifted located around 2700 ppm appears and is assigned to a different type of Cs ions, which increases consistently with Cs concentration. The two lines at high Cs concentration may be explained by the existence of two nonequivalent Cs adsorption sites in the SWNTs bundle as proposed by Bendiab *et al.*⁶ and Bantignies *et al.*⁷

A two phase model for intercalated SWNTs has been discussed in several reports and our results are in excellent agreement with *in situ* conductivity and Raman studies of Rb intercalated SWNTs.^{9,10} At a low level of intercalation, the most favorable intercalation site is the interstitial channel between three tubes in a bundle, relatively far from the carbon atoms of the SWNTs that exhibit a very weak hyperfine coupling and are fully ionized and therefore a simple charge transfer is applicable in this intercalation regime. At a higher doping level, as the alkali content increases, this site becomes however unfavorable and is replaced by bundle surface sites as the most probable alkali site. This implies a strong hyperfine coupling between alkali nuclei and conduction electrons of the carbon nanotubes arising from the strong s-character of the involved alkali (s)-orbitals, which cause a Fermi contact like electrons-nuclear interaction. This suggests a limited charge transfer from alkali to SWNTs explained by alkali (s) – carbon (sp²) hybridization. The results are compatible with results of Lu *et al.*¹ who theoretically found a charge transfer limitation in potassium intercalated nanotubes. Above a stoichiometry of $\text{K}_{0.037}\text{C}$, the

FIG. 4. (Color online) Simulation of the structural configuration of Cs-SWNT $x = 0.143$. For clarity only four SWNT forming the triangular nanotube bundle lattice as well as a few alkali ions are shown. The Cs ions cover the nanotubes completely.

authors claim a preferential hybridization between K (4s) orbital and nearly free electrons (NFE) states of the nanotube leading to limitation of the charge transfer.

In order to draw a simple picture for the Cs arrangement upon intercalation, structural simulations were performed. The carbon nanotube bundle was treated as a fixed triangular lattice of charged cylinders and van-der-Waals and electrostatic interactions were taken into account. For high levels of intercalation, the Cs ions appear in a dense packed matter enwrapping the individual nanotubes as illustrated in Fig. 4. Probably this structure reflects best the Cs ion arrangement attributed to high doping level.

CONCLUSION

We have shown by using ^{13}C MAT and MAS NMR that Rb and Cs intercalated SWNTs have a phase transition between two different types of intercalated stable phases, which is tunable by the alkali content. The MAT shows the line splitting that suggests the existence of two inequivalent carbon sites in the intercalated samples. The MAS measurements are in an accordance that shows at low intercalation levels a transition into a metallic sample, therefore a simple charge transfer is applicable, indicating that the most favorable intercalation site is the interstitial channel between three tubes in a bundle. But at a high intercalation level, the spectra give support of two-phase intercalation level indicating bundle surface sites are the most probable alkali sites, this shows that some alkali atoms do not give full charge transfer explained by a alkali (s) – Carbon (sp²) hybridization.

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