



# Enhancement of adsorption inside of single-walled nanotubes: opening the entry ports

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## Abstract

Opening the ends of the single-walled carbon nanotube by thermal activation increases both the kinetic rate and the saturation capacity of the nanotubes for Xe adsorption at 95 K. Infrared studies show the existence of carboxylic acid and quinone groups on the nanotube surface prior to heating above 623 K. These groups decompose during heat treatment of nanotube sample from 623 to 1073 K producing CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. The removal of a large number of these groups opens the entry ports for adsorption on the inner surface of the nanotube and leads to dramatically enhanced Xe adsorption. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Single-walled carbon nanotubes (SWNT) were discovered by Ijima [1] in 1991. They are now envisioned as the fundamental molecular units for nanoelectronic devices, catalyst supports, sorbents and for drug delivery [2]. Access into the interior of the nanotubes is required for most of these applications. The interior surfaces of open-ended carbon single-walled nanotubes (o-SWNT) exhibit a stronger binding energy for adsorbate molecules compared to the planar carbon surface, as expected for a molecule in close proximity to the curved internal surface of the tube [3–6]. Nanotube synthesis produces closed-

end SWNTs, and chemical cutting is necessary in order to open the capped ends [2,7–9]. We report here that the chemically cut nanotubes contain functional groups which block adsorption, as observed by infrared (IR) spectroscopy. Thermal decomposition of the blocking functional groups leads to superior adsorption rates and adsorption capacity, since the kinetics of adsorption into the nanotubes will be governed by the fraction of the nanotube surface that contains open entry ports into the interior.

## 2. Experimental

The SWNTs employed in this work have a diameter distribution near that of a (10,10) tube [10]. They have been chemically cut using an H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixture followed by treatment with H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>,

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which is accompanied by sonication, and suspension in methanol or dimethyl formamide [7]. The most probable length of the open-ended tubes is 320 nm. Samples were deposited by the drop/dry technique for study.

The adsorption of Xe has been measured by temperature programmed desorption (TPD), a technique that permits measurement of the adsorption efficiency per gas molecule collision on the outer surface of the nanotubes, the absolute coverage, the kinetic order of desorption, and the activation energy of desorption.

Supporting the o-SWNT samples on the surface of CaF<sub>2</sub> powder pressed into a fine tungsten grid and held in a cell designed for transmission IR studies of opaque powders [11,12] allows us to witness the disappearance of the IR active functional groups present on the nanotubes as they are heated in vacuum.

### 3. Results

We have discovered that both the kinetics of Xe adsorption at 95 K and the Xe saturation capacity of o-SWNTs are strongly influenced by the temperature of activation used to prepare the deposited nanotubes in ultrahigh vacuum. As shown in Fig. 1, nanotube

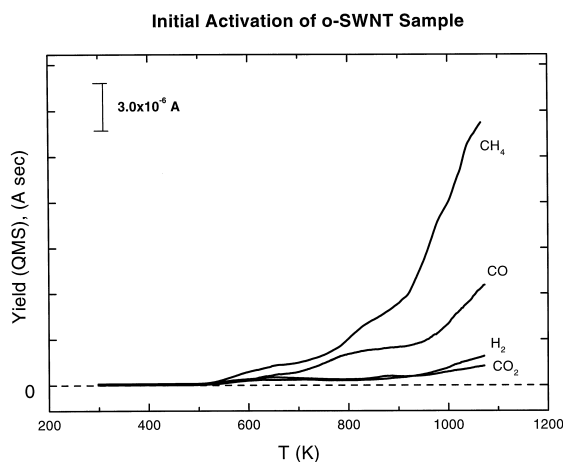


Fig. 1. Initial activation of o-SWNT sample. Gas evolution from a 46 μg sample of o-SWNTs upon being heated in ultrahigh vacuum at 1 K/s. The gases evolved originate from surface functionalities on the nanotubes.

### Decomposition of Oxygen Related Functionalities on o-SWNTs

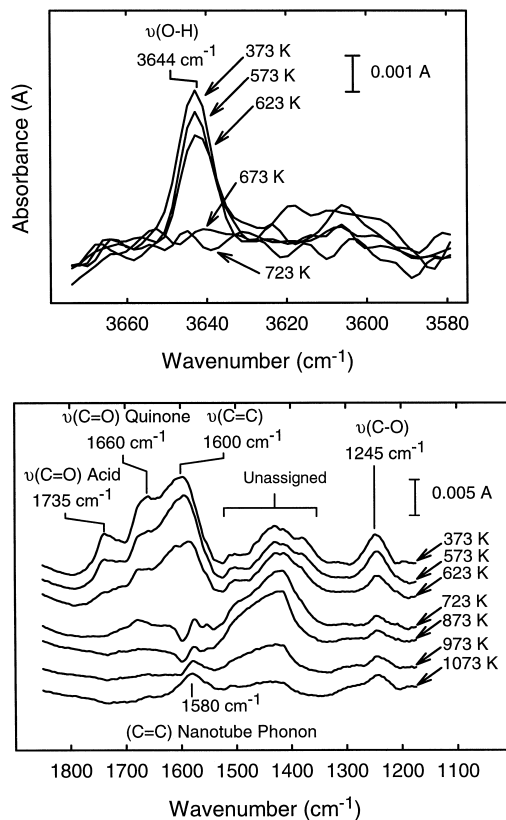


Fig. 2. Decomposition of oxygen related functionalities on o-SWNTs. Transmission IR spectra of o-SWNTs following heating in vacuum to the indicated temperatures. The spectra indicate that carboxylic acid and quinone groups are thermally destroyed in vacuum above about 600 K. Other unassigned surface functionalities are also observed to disappear upon heating. Removal of these functionalities reveals the IR transition associated with a 1580 cm<sup>-1</sup> phonon mode of nanotubes.

activation above about 600 K leads to the evolution of the gases CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub> as determined by mass spectrometric studies. Careful control experiments on the blank Au-coated Ta foil support surface indicate that the gas evolution originates entirely from the o-SWNT sample. The fact that products containing carbon, hydrogen and oxygen are evolved indicates that a carbon removal process occurs above about 600 K [13].

A sequence of transmission IR spectra is shown in Fig. 2. Vibrational modes characteristic of quinone

## Xe Adsorption/Desorption on o-SWNT Sample

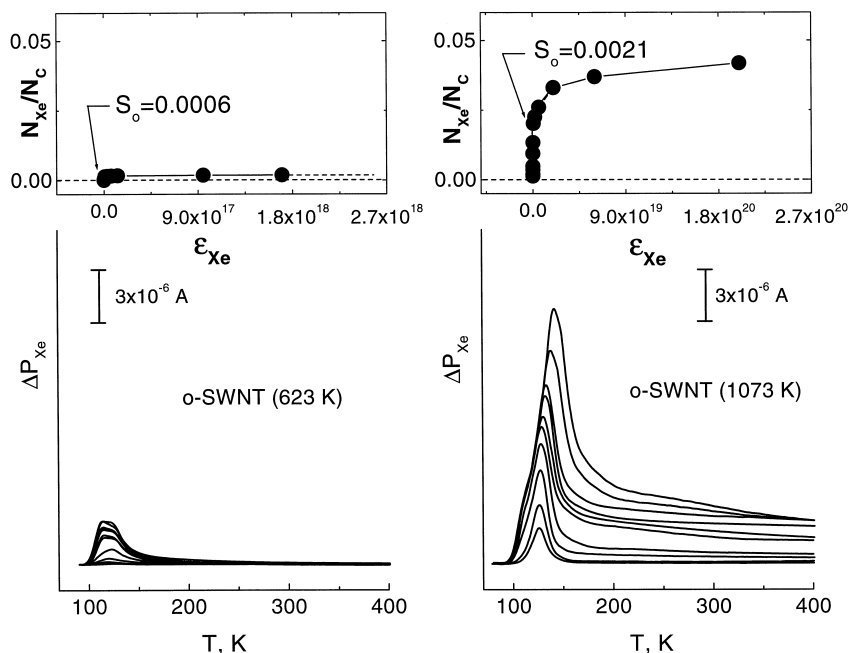


Fig. 3. Temperature programmed desorption spectra of Xe from o-SWNTs following adsorption at various Xe exposures at 95 K. The upper panels show the measured Xe coverage for increasing exposure. For the 1073 K annealed sample, the overlap of the leading edges of the desorption spectra indicate that desorption occurs by zero-order kinetics in the high coverage range. Xe exposures for o-SWNT (623 K) =  $1.8 \times 10^{14}$ – $1.7 \times 10^{18}$  Xe/cm<sup>2</sup>; for o-SWNT (1073 K) =  $2.7 \times 10^{15}$ – $2.0 \times 10^{20}$  Xe/cm<sup>2</sup>.

and carboxylic acid groups [14] present on the nanotube surface are observed, consistent with recent XPS measurements [15]. The vibrations due to carbonyl groups detected at 1735 and 1660 cm<sup>-1</sup>, hydroxyl groups at 3644 cm<sup>-1</sup>, and C–O groups at 1245 cm<sup>-1</sup> are observed to disappear upon heating. Upon activation to 1073 K, only an IR band at 1580 cm<sup>-1</sup>, assigned to nanotube phonon modes [16,17] and small residual bands in the 1430 and 1245 cm<sup>-1</sup> regions remain.

Heating o-SWNTs to 1073 K produces both enhanced capacity for Xe adsorption and enhanced rates of Xe adsorption. This has been determined by comparing Xe adsorption experiments on an o-SWNT sample which has been activated only to 623 K to remove solvents with identical experiments after activation in vacuum at 1073 K.

Fig. 3 shows a sequence of Xe TPD spectra obtained for increasing Xe exposure at 95 K on the same sample annealed to 623 K or to 1073 K. The

absolute coverage of Xe in the nanotubes at various exposures was measured from the area of the Xe desorption traces compared to desorption from a Au standard surface containing a monolayer of Xe at 95 K, and the Xe coverage in the nanotubes is expressed as the atom ratio,  $N_{\text{Xe}}/N_{\text{C}}$ . In Fig. 3, the approach to saturation is shown as the Xe exposure is increased.

#### 4. Discussion

From the saturation coverage measured for the o-SWNT sample (1073 K activation), it is found that the density of Xe atoms inside the 13.6 Å diameter nanotubes at saturation is about three times that of a chain of single Xe atoms aligned at their van der Waals spacing down the SWNT axis. Therefore, the saturation condition at 95 K represents almost complete filling of the o-SWNTs' interior. The saturation capacity for Xe adsorption is found to be about 20

### Schematic of Blocking Terminal Groups - o-SWNT

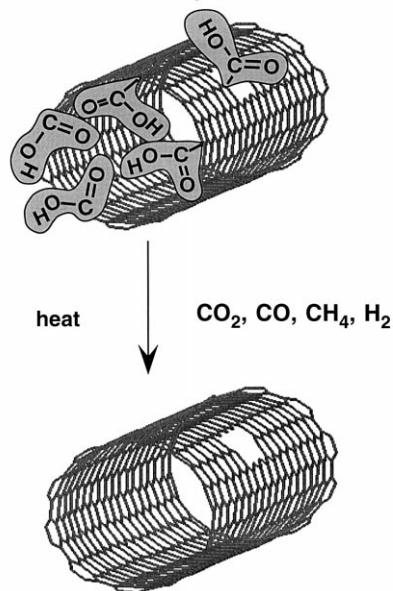


Fig. 4. Schematic drawing of an o-SWNT containing carboxylic acid groups at entry ports to the nanotube. Both the end ports and defect ports in the walls are blocked. IR studies indicate that quinone and other surface functionalities are also present on the nanotube surface. These blocking groups are removed by heating in vacuum to temperatures above about 600 K, leading to enhanced adsorption rates and increased saturation coverage of adsorbates inside the nanotubes.

times higher for the o-SWNT (1073 K) sample compared to the o-SWNT (623 K) sample as a result of the blocking functionalities at the entry ports. The o-SWNT (1073 K) sample adsorbs 280 times as much Xe as a closed SWNT sample heated to 623 K. Interestingly, the initial efficiency of Xe adsorption at low coverages ( $S_0$ , expressed as a ratio of the adsorption rate to the collision rate with the outer surface) also increases, from  $S_0 = 0.0006$  to  $S_0 = 0.0021$  Xe/collision at 95 K comparing the 623 K to the 1073 K o-SWNT samples [13].

The activation energy for zero-order desorption kinetics from the dense Xe deposit inside the nanotubes has been measured from the initial rate of desorption in the TPD measurements (Fig. 3), and is found to be  $26.8 \pm 0.6$  kJ/mol [13], in good agreement with theoretical estimates of the binding energy of internally bound Xe (22.6 kJ/mol) [5]. This en-

ergy is far above the enthalpy of sublimation of Xe(s) (14.2 kJ/mol) and the theoretically calculated Xe binding energy on the nanotube exterior (8.7 kJ/mol) [5]. The observation of zero-order desorption kinetics indicates that a phase transition involving the internal Xe phase is involved in controlling the desorption kinetics.

These results show that the thermal activation of o-SWNTs involves the destruction of oxygen- and hydrogen-containing carbonaceous functional groups, including carboxylic acid and quinone groups, which generate the gases observed. These groups, when present on the nanotubes, block adsorption, causing the kinetics of adsorption to be retarded and also causing the capacity for adsorption at saturation exposure to be severely diminished. Thermal destruction of these blocking groups opens entry ports for adsorption, allowing the nanotubes to become filled by adsorption to their saturation capacity. It is likely that the blocking groups are present at the ends of the o-SWNTs and also at vacancy defect sites [18] on the walls of the nanotubes. A schematic diagram of blocked and open entry ports on a o-SWNT is shown in Fig. 4.

## 5. Conclusion

In conclusion, these studies indicate that o-SWNTs, when used for adsorption purposes, will require the removal of blocking functional groups from the entry ports of the nanotubes. Thermal activation at moderate temperatures is effective for this purpose, decomposing the end groups and leaving the molecular structure of the tube walls unchanged.

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