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A practical approach for adsorption modeling of heterogeneity of single-walled carbon nanotube (SWNT) bundles has been developed. The method integrates experimental analysis with grand canonical Monte Carlo (GCMC) simulation of a small probe molecule, such as nitrogen at 77 K. Using this method, it is possible for one to separately estimate adsorption inside the nanotubes, adsorption on the external surface of the bundles, and adsorptive contributions from the impurities present in samples. By introducing a scaling parameter for adsorption in the internal porous volume of the bundles, the predicted adsorption isotherm results in a near replication of the experimental N₂ adsorption isotherm. We refer to this parameter as the volume fraction of open-ended nanotubes. Our GCMC-assisted experimental characterization method has been applied successfully to several commercial samples obtained from different suppliers, such as MER Corp., Carbon Nanotechnologies Inc., Carbon Solutions Inc., Carbolex Inc., and BuckyyUSA. It was found that the volume fraction of open-ended SWNTs in these samples ranged between 0 and 55%. The majority of the samples were subjected to some purification treatment by the manufacturer and exhibited an already high BET surface area of hundreds of square meters per gram. The near-perfect reproduction of the experimental N₂ (77 K) adsorption isotherm for each of the tested samples shows that our characterization method is not specific to a particular sample and can be extended to most SWNTs successfully. The fraction of open-ended SWNTs cannot otherwise be estimated by visual characterization of the samples because of the large aspect ratio of nanotubes and the spaghetti-like arrangement of the bundles. Our method has the potential to become a standard technique to quantify this structural property of SWNT samples.

1. Introduction

In recent years, considerable interest has centered on adsorption in nanotubes. The hollow nanoscaled structure of single-walled carbon nanotubes (SWNTs) is especially attractive for their potential use as adsorbents, catalyst supports and related materials, and hydrogen storage. It has been reported that the adsorptive surface area and porosity of nanotubes can evolve for several months after their manufacture, nanotubes can be used as nanoscaled cylinders, and adsorption of small polar molecules can alter the electrical properties of nanotubes, which can be used for developing sensors. Interaction between organic molecules and nanotubes has also been explored. Theoretical studies have modeled interactions of organic molecules, such as CH₄ with nanotubes, and have reported mechanisms for the separation of binary mixtures of simple alkanes by diffusive flow. Some experimental studies have reported adsorption isotherms for benzene and methanol, high affinity of nanotubes for ppb levels of dioxins, adsorption kinetics of ethanol, isopropanol, cyclohexane, benzene and hexane on SWNT samples, potential use of nanotubes as adsorbent traps for VOCs, and adsorption of various organics on SWNTs by temperature-programmed desorption and gravimetric analysis.

The depiction of bundle heterogeneity is a known problem in developing a better understanding of adsorption in SWNTs. Heterogeneity refers to the nonuniform geometry of the cross section of a nanotube bundle. It arises as a result of a range of nanotube sizes that are generated during synthesis and high van der Waals interaction between individual nanotubes. It is specific to each sample. Several attempts have been made to understand the effect of heterogeneity on adsorption in nanotubes. Recently, Striolo et al. used grand canonical Monte Carlo (GCMC) simulation in a bundle of three armchair nanotubes to study adsorption and transport of water. Zhao et al. explored exohedral and endohedral N₂ adsorption on the side walls of homogeneous SWNTs. Kuzmany et al. functionality of single-walled nanotubes. Of most significance is the work of Shi and Johnson, who simulated a heterogeneous bundle of SWNTs comprising several armchair tubes of varying chiralities. These authors showed that adsorption in the interstitial channels between adjacent nanotubes can occur for a wide diameter distribution. However, practical modeling of heterogeneous SWNT bundles with the same distribution and positional arrangement as that in an actual sample is not computationally tractable at present. Theoretical modeling of heterogeneity, therefore, could become sample-
The tube-diameter distribution for a given SWNT sample can be obtained from the radial breathing mode (RBM) region of the spectrum at a given excitation energy, \( \lambda \). Adsorption for a particular diameter, \( D \), is thus corrected by a weighting parameter, \( w_{D,i} \), which is taken to be proportional to the peak intensity at the corresponding RBM frequency, \( \nu_{RBM} \).

Figure 1. (a) Depiction of a typical heterogeneous SWNT bundle; the presence of impurities is approximated by an equivalent amount of planar nonporous carbon (\( q_{i}^{\text{sim}} \)). (b) Deconvolution of the heterogeneous bundle into several homogeneous bundles; the tube diameter, \( D \), for each homogeneous bundle is determined from Raman-scattering experiments. (c) GCMC simulation of adsorption on the external grooves and external surfaces (\( q_{i}^{\text{sim}} \)) and in the internal accessible volume (\( q_{s}^{\text{sim}} \)) of each homogeneous bundle. Total adsorption for the heterogeneous bundle is determined by weighted averaging of the individual contributions over the tube-diameter distribution obtained at each excitation energy, \( \lambda \). Adsorption for a particular diameter, \( D \), is thus corrected by a weighting parameter, \( w_{D,i} \), which is taken to be proportional to the peak intensity at the corresponding RBM frequency, \( \nu_{RBM} \).

Specific; it may or may not be extended to the variety of samples that are now being synthesized worldwide.

2. Methodology

We have developed a practical approach for modeling the heterogeneity of SWNT bundles for adsorption applications. The method integrates sample morphology, especially tube-diameter distribution and sample purity, into GCMC simulation of a small probe molecule, such as nitrogen at 77 K, for comparison with commonly used standard experimental adsorption measurements. The methodology has been developed only recently and tested successfully for compatibility with other nanotube–sorbate combinations besides nitrogen. Here we are presenting a broader application of our method to several new commercially available samples, incorporating sample characterization by Raman scattering with multiple laser energies, and corroborate the need to take into account sample purity into GCMC modeling of experimental samples. Following is a brief description of the integrated experimental-simulation strategy for the modeling of heterogeneous SWNT bundles.

i. Simulation Procedure. GCMC calculations are carried out in three steps. First, a heterogeneous bundle (Figure 1a) is deconvoluted into several homogeneous bundles (Figure 1b). The tube-diameter distribution for a given SWNT sample can be obtained from the radial breathing mode (RBM) region of the spectrum at a given excitation energy, \( \lambda \), for example, \( \nu_{RBM} = 12.5 + 223.5/D \) (nm) for \( \lambda = 785 \) nm, where \( D \) is the tube diameter and \( \nu_{RBM} \) is the corresponding RBM frequency in the 100–300 cm\(^{-1} \) region.

Second, each homogeneous bundle is deconvoluted further into two parts: the endohedral volume and the exohedral surface of the outermost SWNTs in the bundle (Figure 1c). The former comprises adsorption inside the nanotubes and in the interstitial channels, whereas the latter represents adsorption in external groove sites and external surfaces, including the void space between the bundles. For each of these configurations, GCMC simulations of a small probe molecule are then carried out for comparison with experimental adsorption at same temperature and pressure conditions. For N\(_2\) adsorption at 77 K, each nanotube can be approximated as a smooth structureless nanocylinder. The intertube distance for all simulations is kept fixed at 3.4 Å to mimic SWNTs adhering to each other via van der Waals forces forming bundles. Nitrogen is treated as a structureless spherical particle that interacts via dispersive forces only. The interaction between adsorbate molecules is modeled by a 12−6 Lennard-Jones (LJ) potential, \( u_{ij} = 4\epsilon_{ij}(a_{ij}/r)^{12} - (a_{ij}/r)^{6} \) (\( r \) is the intermolecular distance), as is the interaction between the carbon atoms of a nanotube and each adsorbate site. The well depths, \( \epsilon_{N2}/k_{B} \) and \( \epsilon_{N2}/k_{B} \) (\( k_{B} \) is Boltzmann constant), used in the calculations are 28.0 K and 100.4 K, respectively, and the collision diameters, \( a_{C} \) and \( a_{N2} \), are 3.4 and 3.69 Å, respectively; the cross terms are obtained using standard Lorentz–Berthelot combination rules: \( \epsilon_{ij} = (\epsilon_{i}\epsilon_{j})^{1/2} \) and \( a_{ij} = (a_{i} + a_{j})/2 \). The potential parameters for N\(_2\) were obtained by fitting the simulated vapor–liquid coexistence curve to experimental data. Using these interaction parameters, we have obtained very good agreement between the simulated N\(_2\) adsorption isotherm and experimental data for nonporous carbon, which indicates that these parameters are a good first approximation to the adsorbate–nanotube interaction potential at the temperature of interest. The carbonaceous impurities are modeled as stacked graphene layers, with platelet spacing of 3.4 Å, using Steele’s 10–4–3 potential. The GCMC simulations are carried out using established procedures;

It should be pointed out that in our calculations endohedral adsorption is expressed as the amount adsorbed per unit weight (or volume) of bundle, whereas exohedral adsorption is calculated as the amount adsorbed per unit external surface area of the bundle; if the latter value is multiplied by the specific external surface area of the bundle, \( S_{p} \), the adsorption isotherm for the external surface becomes expressed per unit weight. Thus, the calculation of the total adsorptive contribution from the external surface of the bundle requires the estimation of \( S_{p} \). In our previous work, a method for estimating \( S_{p} \) was developed. Briefly, plotting the experimental adsorption isotherm versus the simulated exohedral adsorption isotherm yields a curve, whose slope of the linear asymptote at high loading is the value of \( S_{p} \).

Third, once the endohedral and exohedral isotherms for each homogeneous bundle have been calculated, they are weight-averaged according to the tube-diameter distribution obtained from the relative peak intensity at each RBM frequency. This provides theoretical isotherms, \( q_{i}^{\text{sim}} \) and \( q_{s}^{\text{sim}} \), incorporated with sample-specific heterogeneity:

\[
\{q_{i}^{\text{sim}}, q_{s}^{\text{sim}}\} = \frac{1}{n_{k}} \sum_{D} \sum_{D} w_{L,D}(q_{i}^{\text{sim},D}, q_{s}^{\text{sim},D}),
\]

where

\[
\sum_{D} w_{L,D} = 1
\]

Here, \( q_{i}^{\text{sim}}(P/P_{0}) \) and \( q_{s}^{\text{sim}}(P/P_{0}) \) are the adsorption isotherms for the external surface (\( s \)) and internal volume (\( i \)) of an homogeneous bundle of tube diameter \( D \), expressed as a function of relative pressure \( P/P_{0} \); \( \Sigma_{D} \) denotes summation over the \( n_{k} \) excitation energies probed in the Raman-scattering experiments; \( w_{L,D} \) is the tube-diameter distribution obtained at a particular
excitation energy $\lambda$, which can be estimated from the relative ratio of peak heights at the corresponding $\omega_{\text{RBM}}$ in the Raman spectrum.

The total adsorption isotherm for the sample, $q_{\text{sim}}(P/P_0)$, is then expressed as

$$q_{\text{sim}}(P/P_0) = (1-\eta)q_{\text{sim}}^1(P/P_0) + S_q q_{\text{sim}}^2(P/P_0) + \frac{S_q q_{\text{sim}}^3(P/P_0)}{(\text{endohedral})} + \frac{S_q q_{\text{sim}}^3(P/P_0)}{(\text{exohedral})} + \frac{\eta q_{\text{sim}}^4(P/P_0)}{(\text{impurities})} \tag{2}$$

where $\eta$ is the weight fraction of impurities in the sample, $S_q$ is the external surface area of SWNTs in the sample (m$^2$/g); $S_e$ is the surface area of impurities (m$^2$/g), and $q_{\text{sim}}^1(P/P_0)$ is the adsorption isotherm on nonporous carbon, which is assumed to be representative of the adsorptive contribution from carbon-coated impurities. In a related work, it has been shown that most impurities present in SWNT samples can be modeled as the planar surface of a nonporous carbon and $S_e$ can be calculated by a least-square fitting of eq 2 to the experimental adsorption isotherm. Note that the first term on the rhs of eq 2 is the total endohedral adsorption in the nanotube bundles; the other two terms account for adsorption outside of the internal accessible porous volume of the nanotubes, that is, adsorption on the external surface and adsorption on impurities.

ii. Sample Information. The integrated experimental-simulation strategy procedure was applied to several commercially available SWNT samples; Table 1 lists their suppliers. Samples identified as EA95 and CVD80 were purchased from MER Corporation in 2001 and Carbon Nanotechnologies Inc. in 2002, respectively. Our previous work focused on these two samples only. The nomenclature for these samples has not been changed to maintain consistency. All other samples were purchased in 2006. Whenever possible, multiple samples were purchased from the same supplier in order to reveal the effects, if any, of samples extracted from the same as-produced soot generated during the nanotube synthesis process. Here, each new sample is identified using an alphanumeric nomenclature consisting of letters and numerals. The letters are the initials of the supplier, and the numerals denote the sample purity. For example, CS40, CS70, and CS80 denote three samples with, respectively, 40%, 70%, and 80% purity, purchased from Carbon Solutions (CS) Inc.

Table 1: SWNT Samples Analyzed in the Present Work

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Sample Identifier</th>
<th>Sample Description</th>
<th>$\lambda = 532$ nm</th>
<th>$\lambda = 633$ nm</th>
<th>$\lambda = 785$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MER Corp.</td>
<td>EA95$^a$</td>
<td>Electric arc produced, 0% metal</td>
<td>1.37, 1.54</td>
<td>1.25, 1.30</td>
<td>1.15, 1.40, 1.52</td>
</tr>
<tr>
<td>Carbon Nanotechnologies Inc.</td>
<td>CVD80$^a$</td>
<td>Carbon monoxide catalytic cracking</td>
<td>0.92, 1.56</td>
<td>0.8, 0.84</td>
<td>0.92, 1.02, 1.07</td>
</tr>
<tr>
<td></td>
<td>CN95</td>
<td>Same process, &lt; 5% Fe</td>
<td>0.9, 1.11, 1.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Solutions Inc.</td>
<td>CS40$^a$</td>
<td>Electric arc, as-produced sample</td>
<td>1.46, 1.60</td>
<td>1.25, 1.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS70</td>
<td>Electric arc, 70–90% SWNT, 7–10% Ni/Y</td>
<td>1.46, 1.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CS80</td>
<td>Electric arc, 80–90% SWNT, 5–10% Ni/Y, 4–6 atomic % carboxylic acid</td>
<td>1.25, 1.35, 1.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbolex Inc.</td>
<td>CL60$^a$</td>
<td>Electric arc, as-produced sample</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BU80$^d$</td>
<td>Chemical vapor deposition</td>
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<td>BuckyUSA Inc.</td>
<td>BU90</td>
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$^a$ The diameter distribution was obtained by Raman scattering ($\lambda = 785, 633, and 532$ nm). $^b$ Numerals denote the wt% of SWNTs in the sample, as provided by the manufacturer. $^c$ These samples were purchased in 2001 and 2002; their characterization details are presented elsewhere. Previous GCMC modeling of these samples was based on a narrower diameter distribution obtained from Raman scattering at $\lambda = 785$ nm. $^d$ As-produced samples.

Purity. The value of sample purity enters the GCMC calculations via parameter $\eta$ in eq 2. Our characterization method requires a reasonably good estimate of sample purity. In the present work, $\eta$ was calculated from the purity value provided by the manufacturer. However, we specifically tested the purity of samples EA95 (MER Corp.) and CN95 (Carbon Nanotechnologies Inc.) by thermogravimetry because of the exceptionally high levels of purity reported (Figure 2).

iii. Sample Analyses. Samples were analyzed for purity by thermogravimetry, diameter distribution by Raman spectroscopy, and experimental N$_2$ adsorption isotherms by standard volumetric adsorption at 77 K.

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The area under the curve corresponded to 95–98% of sample mass. Furthermore, the peak appears at approximately 550 °C, which denotes the characteristic onset temperature for nanotubes. Thus, it can be reasonably concluded that the two samples consisted of almost pure SWNTs with compositions similar to those reported by the manufacturer.

**Diameter Distribution.** All samples were analyzed for tube-diameter distribution by Raman scattering at multiple excitation energies (Table 1). The modeling study reported in our previous work was based on a narrower tube-diameter distribution obtained by Raman characterization at λ = 785 nm only. Those experiments were performed on a liquid suspension of individually dispersed SWNTs in a 10 wt % surfactant solution in pure water. The diameter, \( D \), was calculated from \( \omega_{\text{RBM}} = 12.5 + 223.5/D \) (nm). However, it is known that Raman scattering by single excitation energy may be insufficient to explore all nanotube diameters. In the present work, additional Raman-scattering experiments were performed on all samples listed in Table 1 at \( \lambda = 532 \text{ nm and } \lambda = 633 \text{ nm (T6400 Raman research system by JY Horiba, and Renishaw 100 MicroRaman System, respectively). These experiments were performed on solid samples, and } D \text{ was calculated by the relation } \omega_{\text{RBM}} = 10.0 + 234.0/D \) (nm), which accounts for the slight shift in RBM frequencies due to nanotubes present in bundles as opposed to individually dispersed.

Figure 3 depicts the RBM region of the Raman spectra for samples EA95 and CN95, showing that the latter sample is clearly more heterogeneous and has a higher concentration of smaller nanotubes. Each spectrum shows the presence of multiple diameters specific to the laser energy used in the Raman-scattering experiments. Similar spectra were obtained for all samples. The discrete values of \( D \) calculated for all samples are listed in Table 1.

**3. Results and Discussion**

i. **Effect of Diameter Distribution.** The theoretical \( N_2 \) isotherms at 77 K for endohedral adsorption (including interstitial channels) and adsorption on the external surface of the bundles (including external groove sites), \( q_{\text{end}}(P/P_o) \) and \( q_{\text{ext}}(P/P_o) \), were determined using the Glissone and Harkins-Dekker-Hale (GHD) equations. The experimental \( N_2 \) adsorption isotherms for all samples (Table 1) were obtained by standard \( N_2 \) adsorption at 77 K using an Autosorb-1-C Chemi-Physisorption Surface Area Analyzer (Quantachrome Instruments). The instrument is fitted with a special 1 Torr transducer that allows accurate adsorption measurements at as low as \( 10^{-6} P/P_o \), where \( P_o \) is the saturation pressure of \( N_2 \) at 77 K. Experimental measurements at such low pressures are essential for probing pores smaller than 2 nm. For each run, 25–30 mg of sample was outgassed at 140 °C under a vacuum of 1 mTorr for a continuous 24 h period. The sample was cooled to 77 K using liquid \( N_2 \). Isotherms were obtained over a relative pressure range of \( 10^{-6} < P/P_o < 0.99 \) by controlled dosing of ultrahigh-purity \( N_2 \) and volumetrically measuring adsorption capacity from the loss in cell pressure at each equilibrium point. The resulting isotherms, \( q_{\text{exp}}(P/P_o) \), are presented later in the manuscript. The surface area and pore volumes are listed in Table 2.
**TABLE 2: Surface Area and Pore Volume of All Samples, as Determined from Simulations and N₂ Adsorption Experiments**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>% α</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA95</td>
<td>1117</td>
<td>0.62</td>
<td>50</td>
</tr>
<tr>
<td>CVD80</td>
<td>876</td>
<td>0.86</td>
<td>53</td>
</tr>
<tr>
<td>CN95</td>
<td>950</td>
<td>0.65</td>
<td>28</td>
</tr>
<tr>
<td>CS40</td>
<td>677</td>
<td>0.47</td>
<td>6</td>
</tr>
<tr>
<td>CS70</td>
<td>1241</td>
<td>0.86</td>
<td>55</td>
</tr>
<tr>
<td>CS80</td>
<td>771</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>CL60</td>
<td>745</td>
<td>0.44</td>
<td>10</td>
</tr>
<tr>
<td>BU80</td>
<td>973</td>
<td>0.59</td>
<td>0</td>
</tr>
<tr>
<td>BU90</td>
<td>828</td>
<td>0.66</td>
<td>2</td>
</tr>
</tbody>
</table>

*Notes:*
- Total (T) and external (Ex) surface areas are expressed in m²/g; total pore (TP) and micropore (MP) volumes are expressed in cm³/g.
- All nanotubes are assumed to be open-ended.
- α is the estimated vol % of open-ended nanotubes in the samples.
- S is the area of external surface of the bundles.
- R is the estimated vol % of open-ended nanotubes in the samples.
- S is the surface area of impurities.
- As-produced samples.
- Calculated at 0.77 P/P₀ (cm³/g).
- Calculated at 0.99 P/P₀ (cm³/g).
- The experimental micropore volumes presented here were determined by the standard t-plot technique incorporated in the Quantachrome software.

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**Figure 4.** (a) Endohedral and (b) exohedral isotherms calculated for homogeneous bundles with tube-diameter sizes typically found in the experimental samples. Similar isotherms were obtained for all values of D listed in Table 1. The figures on the right are snapshots taken from the simulation box for nitrogen adsorption at 77 K (D = 10.0 Å, P/P₀ = 10⁻⁶).

$q_{\text{sim}}^{\text{int},D}(P/P_0)\text{ and } q_{\text{sim}}^{\text{ext},D}(P/P_0)$, respectively, were determined by GCMC simulation for all values of D listed in Table 1. For each isotherm, adsorption capacities were calculated at 20 intermediate values of $P/P_0$ in the pressure range of $10^{-6} < P/P_0 < 0.9$. This is the typical range commonly scanned in standard N₂ adsorption experiments (Figure 4). Endohedral adsorption in arrays of smaller tube diameter ($D < 9.0$ Å) saturates at much-lower values of $P/P_0$. As D increases, both the saturation capacity, $q_{\text{sim}}^{\text{int},D}(P/P_0 = 1)$, and the minimum value of $P/P_0$ at which complete pore filling occurs, also increase (Figure 4a). Exohedral adsorption starts in the external grooves located on the periphery of the bundles. Adsorption on the external surface is observed only after complete filling of the grooves (Figure 4b).

Individual isotherms for the discrete values of D relevant to a given sample were averaged according to eq 1. As a typical example of this procedure, Figure 5 shows the total internal adsorption, $q_{\text{sim}}^{\text{int}}(P/P_0)$, as well as adsorption on the bundle surface, $q_{\text{sim}}^{\text{ext}}(P/P_0)$, for samples EA95 and CN95. Also plotted in Figure 5 are the average isotherms estimated using the tube-diameter distribution explored only by single excitation, $\lambda = 785$ nm. Numerous observations can be made here. First, at any given vapor pressure, adsorption in sample EA95 is much-
higher than that in sample CN95. This is irrespective of whether the isotherms are calculated for a tube-diameter distribution estimated by using single or multiple excitation energies. This is because sample EA95 has larger nanotubes than sample CN95, which is evident from the calculated diameters (Table 1) and also from Figure 3 where the majority of the RBM peaks for EA95 are observed at a lower Raman shift. This essentially means that samples containing large-diameter nanotubes exhibit higher endohedral adsorption at gas pressures that give rise to near pore filling and thus are more suitable for potential applications such as gas-storage media.

Second, for both samples, $q_{i}^{\text{sim}}(P/P_o)$ based on a tube-diameter distribution obtained from multiple excitation energies ($\lambda = 532, 633, \text{and } 785 \text{ nm}$) is not drastically different from that calculated from a single excitation energy ($\lambda = 785 \text{ nm}$). Although a diameter distribution explored by multiple excitation energies provides a more-accurate method of calculating adsorption, because it gives a better representation of sample heterogeneity, it is needless to say that Raman-scattering experiments at a single excitation energy are less-complicated and more-common than those using multiple excitation energies. Therefore, for all practical purposes, integration of sample morphology into our GCMC modeling approach can be simplified greatly when sample morphology is obtained from Raman analysis using single excitation energy. In the present work, however, the theoretical adsorption isotherms were calculated using the tube-diameter distribution obtained by multiple excitation energies as listed in Table 1.

Third, it is noticed that for both samples $q_{i}^{\text{sim}}$ increases by approximately 10,000 times, whereas $q_{i}^{\text{exp}}$ increases by only 2–5 times over the same pressure range. Therefore, at high relative pressures ($P/P_o > 10^{-3}$) adsorption on the external surface of the bundles could become extremely sensitive to pressure changes and could contribute significantly to total adsorption. It should also be pointed out that although at any given relative pressure $q_{i}^{\text{sim}}$ is much less than $q_{i}^{\text{exp}}$, a true comparison between external adsorption and adsorption inside the nanotubes can only be drawn when $q_{i}^{\text{sim}}$ (cm$^3$ [STP]/m$^2$) is multiplied by the total external surface area, $S_i$ (m$^2$/g), of the bundles. For example, the value of $S_i$ for sample EA95 was found to be 186 m$^2$/g (Table 2); therefore, at $P/P_o = 0.1$ adsorption on the external surface of the bundles for this sample is 48.4 cm$^3$ [STP]/g ($= S_i q_{i}^{\text{sim}}$), whereas that inside the SWNTs is 202 cm$^3$ [STP]/g ($= q_{i}^{\text{sim}}$). Thus, as much as 20% of the observed adsorption capacity at $P/P_o = 0.1$ is attributed to adsorption on the outer surface of the bundles. This fraction of total adsorption increases with increasing $P/P_o$ and will be more-apparent for samples with larger external surface areas.

**ii. Simulation vs Experimental Isotherms.** Total adsorption for a sample was estimated by eq 2. Figure 6 shows the total isotherm, $q_{\text{sim}}(P/P_o)$, calculated for samples EA95, CN95, CS70, and CS80. Similar isotherms were obtained for the other samples listed in Table 1. We are able to generate the characteristic type-II adsorption isotherm for all samples. This isotherm shape is common for SWNT samples. It denotes the presence of mesoporosity (2 nm < pore size < 50 nm) in addition to microporosity (pore size < 2 nm). The typical diameter of an individual SWNT ranges between 0.7 to 2.0 nm. This is well within the microporous range; thus, the presence of any mesoporous characteristic would be counterintuitive. The source for mesoporosity in SWNTs is the wide interbundle space between adjacent bundles (Figure 7); therefore, by calculating the external contribution, $q_{\text{exp}}(P/P_o)$, we are essentially modeling the adsorption in the void space between bundles. It is worth pointing out, however, that this mesoporous space has some microporosity attached to it, which is due to the external grooves. Once these sites get completely filled with adsorbate molecules, which happens at very-low pressure, their influence is suppressed. The surface area and pore volume information for all samples were extracted from the calculated total isotherm and are listed in Table 2 along with the experimental values for comparison.

A striking feature is observed when the total adsorption isotherm determined by simulation, $q_{\text{sim}}(P/P_o)$, is compared with the experimental one, $q_{\text{exp}}(P/P_o)$. For all samples, the two isotherms are identical in shape, which corroborates our strategy of modeling heterogeneous bundles as smaller fractions of several homogeneous bundles. The simulated isotherms appear to be parallel to the corresponding experimental isotherms. However, the isotherms were found shifted vertically toward larger loading values, exhibiting more adsorption than experimentally measured at each $P/P_o$. The explanation for this shift is as follows. Our calculations were carried out with the implicit assumption that all SWNTs are open or unblocked to allow unrestricted access for N$_2$ molecules. This assumption is not unrealistic given the fact that sonication and oxidation are routine practices in purification of as-produced nanotubes; these techniques are believed to cut the nanotubes to shorter lengths and oxidize their ends to allow easier access to their endohedral volume. Therefore, the simulated isotherm (left panel, Figure 6) and the corresponding surface area and pore volumes (Table 2) of any given sample represent its maximum achievable adsorption capacities and related physical properties.

**Volume Fraction of Open-Ended SWNTs.** Assuming that not all SWNTs are open-ended or accessible for adsorption implies that the endohedral adsorption must be scaled down. Other
Figure 6. Simulated and experimental N\textsubscript{2} adsorption isotherms (77 K) for samples (a) EA95, (b) CN95, (c) CS70, and (d) CS80, as predicted by GCMC modeling of heterogeneous bundles and their comparison with experimental isotherms. The left panel shows the isotherms for samples calculated with the implicit assumption that all nanotubes are open ($\alpha = 1$). The right panel shows the same isotherms after adjusting the endohedral adsorption by the scaling parameter $\alpha < 1.0$, which represents the fraction of open-ended nanotubes. $\alpha$ reduces the total adsorptive contribution from the internal pore volume of the bundles while maintaining all other contributions unchanged. Perfect overlap with experimental values is achieved.
adsorptive contributions remain unchanged because adsorption on the external surface the bundles and on the impurities is unaffected by whether the nanotubes are open or closed. A scaling parameter, \( \alpha \), is introduced into our calculations, such that eq 2 is now modified as follows

\[
q_{\text{sim}}(P/P_o) = \alpha(1 - \eta) q_{\text{sim}}^i(P/P_o) + S_p q_{\text{sim}}^e(P/P_o) + \frac{S_c \eta}{(\text{impurities})} q_{\text{sim}}^c(P/P_o)
\]

where the new parameter \( 0 \leq \alpha \leq 1 \) is a structural property of the sample. It should be independent of \( D \) and \( P/P_o \) for most generality. It is particular only to a sample. This parameter can be estimated by trial and error to yield an isotherm, \( q_{\text{sim}}(P/P_o) \), that overlaps the experimental isotherm or it can be determined by least-square fitting of eq 3, or it can be taken as the ratio of the experimental micropore volume of the sample and the micropore volume calculated from simulations. The three methods result in comparable values. Here, we define \( \alpha \) as the volume fraction of open-ended nanotubes:

\[
\alpha = \frac{q_{\text{exp}}^i(P/P_o \rightarrow 1)}{(1 - \eta) q_{\text{sim}}^i(P/P_o \rightarrow 1)}
\]

If the endohedral isotherm, \( q_{\text{sim}}^i \), is scaled by \( 0 \leq \alpha < 1 \), then it results in a near-perfect fit between the total simulated isotherm and the experimentally measured one, for all samples (right panel, Figure 6). The surface area and pore volumes have been recalculated from the adjusted simulated isotherm and are listed in Table 2. The recalculated values are now comparable to the corresponding experimental values, which corroborates an accurate estimation of the volume fraction of open-ended nanotubes and the applicability of this concept to a variety of SWNT samples.

The volume fraction of open-ended nanotubes in the test samples ranges between 0 and 55%. Among the most open samples are EA95, CVD80, and CS70 from MER Corp., Carbon Nanotechnologies Inc., and Carbon Solutions Inc., respectively. The BET surface area of these samples is relatively high, 507, 609, and 970 m\(^2\)/g, with only 50–55% open nanotubes in each of these samples. This means that in spite of a high adsorption capacity nearly half of the microporous volume (pores < 2 nm) remains inaccessible. The BET surface area for these samples could reach up to 1100–1200 m\(^2\)/g if every nanotube was open-ended and unblocked.

Among the least-open samples are CS40, CL60, and BU80, which have 6%, 10%, and 0% open-ended nanotubes, respectively (Table 2). These samples were procured from Carbon Solutions Inc., Carbolex Inc., and BuckyUSA. According to the manufacturers, these samples consisted of as-produced nanotubes. It is known that as-produced SWNTs are mostly closed-ended, which would explain the extremely low volume fractions of open nanotubes found in these samples. However, it was noticed that sample CS80 also had 0% open nanotubes. According to Carbon Solutions Inc., this is a purified and highly oxidized SWNT sample. Purification opens some nanotubes; consequently, \( \alpha \) should be greater than zero for this sample. Therefore, \( \alpha = 0 \) can only mean that excessive functional groups were blocking the probe molecules and preventing them from penetrating into the internal pore volume of the bundles. Adsorption observed for this sample is, therefore, taking place on the external surface of the bundles, and not inside the nanotubes. This is also apparent from the fact that the experimental isotherm for this sample overlaps the simulated external adsorption isotherm almost perfectly (left panel, Figure 6d). Therefore, based on the above observations, it can be said that our method of estimating the fraction of open-ended nanotubes includes every possible scenario of gas molecules not being able to utilize the adsorption capacity of SWNTs, even the extreme possibility of complete blockage of the internal pore volume.

4. Conclusions

We have developed an integrated experimental-simulation characterization technique for practical modeling of heterogeneous SWNT bundles for adsorption applications. Our approach results in a perfect reproduction of experimental \( N_2 \) adsorption isotherms at 77 K for several commercially available SWNT samples. Typical experimental isotherms only provide total adsorption capacities without differentiating between adsorption on the various structural components of a sample. With our technique, we are able to deconvolute the experimentally observed adsorption capacities into several components and accurately quantify adsorption inside the nanotubes, adsorption on the external surface of the bundles, and adsorption on impurities. We are also able to estimate the volume fraction of open-ended nanotubes in several samples. The fraction of open-ended nanotubes is a structural property that is specific to a sample. It cannot be estimated by typical analytical techniques used in the characterization of carbon nanotubes. Therefore, adsorption is perhaps the most-appropriate method to quantify this structural property, much like the widespread use of adsorption for estimating the surface area of a material. This new information should convey that many advances are still needed in the synthesis and processing of carbon nanotubes. It is also essential for a fair assessment of adsorption capabilities and limitations of carbon nanotubes for any practical use in adsorption and gas-storage applications.

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References and Notes


