Optimal Single-Walled Carbon Nanotube Vessels for Short-Term Reversible Storage of Carbon Dioxide at Ambient Temperatures

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Optimized light vessels composed of single-walled carbon nanotubes have high gravimetric and volumetric capacity for short-term reversible storage of CO2 at 298 K and near-ambient operating pressures. We use grand canonical Monte Carlo simulation for modeling of CO2 adsorption at 298 K and pressures up to 5.7 MPa. It is shown that both gravimetric and volumetric uptake of CO2 strongly depend on the pore size in nanotubes but not on their chiral vector. Moreover, for any operating storage pressure, a unique optimal size of carbon nanotubes is well-defined. At 1.5 MPa, the most efficient nanotubes that maximize both gravimetric and volumetric uptake of CO2 (i.e., 13.6 mmol g⁻¹ and 11.4 mol dm⁻³) have diameters of 3.8 nm. This size corresponds to the (28,28) armchair nanotubes. For a higher operating pressure of 3.5 MPa, the optimal diameter of carbon nanotubes is slightly shifted up to 4.8 nm (i.e., 25.3 mmol g⁻¹ and 16.7 mol dm⁻³). This size corresponds to the (36,36) armchair nanotubes. We demonstrate that to make an objective statement about the efficiency of CO2 storage in any nanoporous material, the complete volumetric and gravimetric adsorption data are necessary. Taking this into account, we discuss the recently reported exceptionally high capacity of metal–organic frameworks. We show that MOF-177, known as the most efficient porous material for storage of CO2 at room temperature, is characterized by very high gravimetric uptake of CO2 (i.e., 21.8 mmol g⁻¹ at 1.5 MPa and 33.5 mmol g⁻¹ at 3.5 MPa). However, the reported volumetric density of CO2 adsorbed in MOF-177 at 298 K (i.e., 8.17 mol dm⁻³ at 1.5 MPa and 12.26 mol dm⁻³ at 3.5 MPa) is lower in comparison to storage vessels composed of optimized single-walled carbon nanotubes. Our systematic study of CO2 adsorption in bundles composed of single-walled carbon nanotubes at 298 K indicates the potential of nanotubes for innovation in clean technologies.

1. Introduction

Uncontrollable release of large quantities of CO2 into the atmosphere has devastating environmental effects that include melting the polar ice caps and changing the ocean’s acidity.1–10 Thus, development of new as well as improvements of existing CO2 capture technologies (i.e., flue gas purification, CO2 geosequestration, fixation of CO2 in photosynthesis, ocean CO2 sequestration, chemical fixation of CO2, etc.)11–26 is an important and complex economic challenge. CO2 adsorption and separation using a variety of porous materials has received much attention in the last decades. The most common ordinary porous adsorbents that have been widely used in industrial separations and storage of different fluid mixtures are activated carbons and zeolites.27–34 Recently, new classes of storage vessels and membranes that can store and separate vast amounts of fluids has been discovered. Among them, crystalline metal–organic frameworks (MOFs)34,35,38–42 and ordered carbonaceous materials [such as single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), wormlike nanotubes, double-walled carbon nanotubes, single-walled carbon nanohorns, stacked-cup carbon nanofibers, doped fullerences, worm-like graphitic carbon nanofibers, bamboo-type multiwalled carbon nanotubes, activated carbon fibres, ordered porous carbons, etc.]43–56 are of great potential for reduction of CO2 emissions near ambient temperatures by capture and short-term reversible storage. However, fundamental understanding of the competition between the space available for guest molecules and the high binding energy of adsorption at the nanoscale is crucial for designing of efficient nonporous membranes as well as storage vessels. Computer simulations supplemented with fundamental theory of physical adsorption offer an alternative tool for the systematic investigation of CO2 adsorption and separation in different known and theoretical nanostructures. When the underlying physical conditions and the intermolecular potentials are known, computer simulations are convenient tools for extrapolating experimental results to conditions difficult to access experimentally (i.e., well-defined samples of nanomaterials, high purity of nanomaterials, broad spectrum of pore sizes, different operating conditions, unlimited access to different quantities characterized by the adsorption process, observation of adsorption phenomena at the molecular level, etc.).57–58

As was shown by Cinke et al.,59 the adsorption characteristics of raw SWNTs are strongly influenced by those of Fe2O3. The metal and metal oxide impurities drastically lower the CO2 uptake in SWNTs due to the weak CO2–Fe2O3 binding energy (i.e., type III of the CO2 adsorption isotherm on Fe2O3 according to IUPAC classification60) and high molecular weight of metal/
metal oxides in comparison to that of pure carbon. Purification of SWNTs results in almost twice larger adsorbed volumetric uptake of CO$_2$ compared to that of activated carbon (Calgon Corporation). This experimental result is particularly interesting since both studied carbonaceous materials are characterized by a similar order of apparent surface area computed from the Brunauer–Emmett–Teller method ($1617$ and $1284$ m$^2$ g$^{-1}$ for purified SWNTs and activated carbon, respectively). The enthalpy of CO$_2$ adsorption in purified SWNTs of $23.03$ kJ mol$^{-1}$ results from strong physisorption of CO$_2$ at $308$ K. High uptake of CO$_2$ of $\sim 4$ mol dm$^{-3}$ at $0.13$ MPa and $308$ K reveals the potential of purified SWNTs for greenhouse gas detection and bioremediation. Shen and Bai$^{62}$ synthesised open-ended MWNTs doped with various contents of nitrogen. These novel MWNTs possess high CO$_2$/CH$_4$ adsorption selectivity of $6\sim 13$ at zero coverage, which increases with increasing nitrogen content. Large apparent BET surface areas ($400\sim 500$ m$^2$ g$^{-1}$), uniform pore size distributions, and various contents of doped nitrogen impact the binding energy of mixture components (CO$_2$ and CH$_4$) with MWNT samples. However, one should remember that smart tuning of CO$_2$/CH$_4$ selectivity in any carbon nanotubes requires atomistic-level understanding of complex processes accompanying mixture adsorption. The experimental results of Hsu et al.$^{63}$ showed that SWNTs as well as MWNTs can be used as cost-effective sorbents for CO$_2$ capture from flue gas. As reported, adsorption capacities and physiochemical properties of studied carbon nanotubes were preserved during $20$ cycles of adsorption and regeneration. Adsorption and selective properties of these carbon nanotubes were enhanced by functionalization with amines. As pointed out by the authors, amine-modified carbon nanotubes adsorbed twice the amount compared to that of amine-doped granular activated carbon. This experimental finding seems to be very interesting because both commercialized amine-doped granular activated carbons and novel amine-doped carbon nanotubes are characterized by a similar enthalpy of CO$_2$ adsorption ($\sim 20.3$ and $14\sim 24$ kJ mol$^{-1}$ for activated carbons and amide-modified carbon nanotubes, respectively). Huang et al.$^{64}$ used grand canonical Monte Carlo (GCMC) simulations to investigate adsorption behavior of an equimolar CO$_2$/CH$_4$ mixture in carbon nanotubes. According to this study, isolated SWNTs demonstrated higher selectivity of CO$_2$ than other materials (activated carbons, zeolite 13X, and MOFs) reported in the literature. Huang et al.$^{64}$ showed that despite the change in temperature or pressure or for different carbon nanotube diameters, the selectivity is generally above $8$. At $343$ K and $1$ MPa, the selectivity reaches $11.2$ in the (6,6) carbon nanotube, which is larger than ever reported in activated carbon (selectivity of $4$) and MOFs (selectivity of $10$). This theoretical study showed the potential of SWNTs for separation of CO$_2$/CH$_4$ mixtures under assumed thermodynamic equilibrium. However, one should keep in mind that the model of the isolated carbon nanotube does not corresponds to real assembly of SWNTs. Due to action of attractive van der Waals forces between carbon atoms, individual carbon nanotubes self-assemble into a stable bundle structure.$^{65\sim 68}$ The overall selectivity of this entanglement structure depends on the selectivity of different adsorption sites, including internal and interstitial channels, grooves, and the rounded surface of the bundle. Isolation and separation of individual carbon nanotubes are difficult and expensive processes. That is why the model of the isolated carbon nanotube is a crude approximation to the real carbon nanomaterials composed of self-assembled carbon nanotubes. Chen and Johnson$^{69}$ showed that CO$_2$ adsorbed in the groove sites of SWNTs displays unique quasi-one-dimensional behavior. Interestingly, they showed that clusters containing only odd numbers of molecules are formed at finite CO$_2$ coverages and low temperatures. Following Chen and Johnson$^{69}$ this ordering is a result of a delicate balance between solid–fluid and fluid–fluid forces. Moreover, as shown by the authors, the CO$_2$ quadrupole plays a critical role in the cluster formation and orientational ordering. Concluding, previous simulations indicated that any realistic modeling of CO$_2$ adsorption and separation in carbonaceous nanomaterials composed of carbon nanotubes should employ a fully atomistic model of CO$_2$.

The above-quoted experimental and theoretical results indicate that various pure and modified carbon nanotubes are promising for innovations in CO$_2$ short-term reversible storage, separation, and sensing technologies. The transportation of CO$_2$ from the power plant to the place of its geosequestration exceeds $90\%$ of the overall cost. Thus, reversible short-term storage of CO$_2$ in nanoporous materials is an interesting alternative for high-energy consumption processes accompanying CO$_2$ transportation, such as compression or liquefaction. Experimental results clearly show that various pure and modified carbon nanotubes adsorbed more CO$_2$ in comparison to commercial granular activated carbons, regardless of similar apparent surface area or enthalpy of adsorption. Nevertheless, no general conclusions or clear future directions connected with the optimal size of carbon nanotubes for short-term reversible storage of CO$_2$ near ambient conditions have been presented. That is why the atomistic-level understanding of the CO$_2$ adsorption mechanism in realistic SWNTs bundles seems to be very important for optimization of potential CO$_2$ storage vessels, molecular sieves, and sensors. In the current work, we want to find answers to the following questions: (1) What is the optimal size of carbon nanotubes for short-term reversible storage of pure CO$_2$ at $298$ K? (2) Does an optimal size of carbon nanotubes for adsorption of pure CO$_2$ depend on the operating storage pressure? (3) What is the magnitude of volumetric and gravimetric uptake of CO$_2$ in optimized SWNT bundles? (4) What is the potential of carbon nanotubes for CO$_2$ capture in comparison to selected MOFs, zeolites, and activated carbons? To answer these questions, we performed extensive computer simulations of CO$_2$ adsorption at $298$ K and pressures up to $5.7$ MPa in realistic bundles composed of different SWNTs. In the section 2, we briefly present simulation details including intermolecular potentials, simulation details, and macroscopic quantities characterized by the adsorption process. Next, we present our theoretical results in close relation to known experimental data. Here, we compare and discuss the CO$_2$ adsorption properties of studied SWNT bundles and other novel and ordinary porous materials. Finally, we present conclusions. Our simulation results can be interesting for postcombustion CO$_2$ capture and short-term reversible storage.

2. Simulation Methodology

2.1. Interaction Potentials. Carbon dioxide was modeled by a three-center rigid model (with a fixed C–O bond length of $0.1162$ nm).$^{13,70}$ Each center was the (12,6) Lennard-Jones one (LJ) as well as the point charge ($Q$). The total energy of interactions between a pair of CO$_2$ molecules A and B can be written as$^{13,70}$

$$U_{j(A,B)}^{\text{FF}} = \sum_{i=1}^{3} \sum_{j=1}^{3} [U_{1j}^{\text{LJ}}(r_{ij}) + U_{Q}^{\text{A,B}}(r_{ij})]$$  (1)
where $U_{ij}^{(B)}(r_{ij})$ is the energy of dispersion interactions between center $i$ on molecule $A$ and center $j$ on molecule $B$. The dispersion interactions were computed from the truncated $(12,6)$ LJ potential\(^1\)

$$U_{ij}^{(B)}(r_{ij}) = \begin{cases} \frac{4\epsilon_{ij}}{\sigma_{ij}} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} & \text{if } r_{ij} < r_{\text{cut,LJ}} \\ \frac{4\epsilon_{ij}}{\sigma_{ij}} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 & \text{if } r_{ij} \geq r_{\text{cut,LJ}} \end{cases}$$

(2)

where $\sigma_{ij}$ and $\epsilon_{ij}$ are the collision diameter and depth of the potential well (see Table 1), and $r_{\text{cut,LJ}}$ denotes the cutoff distance for dispersion interactions.

The second term in eq 1 is the energy of electrostatic interactions between point charge $i$ on molecule $A$ and point charge $j$ on molecule $B$. We calculated electrostatic interactions from Coulomb’s law\(^1\)

$$U_{ij}^{(A,B)}(q_i,q_j) = \begin{cases} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} & \text{if } r_{ij} < r_{\text{cut,Q}} \\ 0 & \text{if } r_{ij} \geq r_{\text{cut,Q}} \end{cases}$$

(3)

where $r_{\text{cut,Q}}$ is the distance between the centers of mass of the molecules $A$ and $B$, $q_i$ and $q_j$ denote the values of the point charges, and $\varepsilon_0$ ($8.8543 \times 10^{-12}$ C$^2$ J$^{-1}$ m$^{-1}$) is the permittivity of the free space. We use the cutoffs for electrostatic interactions, but for all molecules, if the centers of the mass of two molecules are located at a distance smaller than the cutoff for electrostatic interactions ($r_{\text{cut,Q}}$ assumed to be equal to 1.5 nm), the sum of the energy of interactions between all pairs of charges occurring in the molecules is calculated; otherwise, the electrostatic interactions are neglected\(^1\). At this cutoff distance, the energy of interactions of a pair of molecules is negligibly small because the energy of electrostatic interactions for CO$_2$ molecules (having quadrupole moments) decreases proportionally to the fifth power of the distance.\(^7\)

Total solid–fluid interactions between CO$_2$ molecule $A$ and carbon nanomaterial include only dispersion interactions\(^1\)

$$U_{\text{SF}}^{(A)} = \sum_{i=1}^{N_C} \sum_{j=1}^{3} U_{ij}^{(A)}(r_{ij})$$

(4)

where $N_C$ denotes the number of carbon atoms in the simulation box. For all $(12,6)$ LJ interactions, the cutoffs were placed at $r_{\text{cut,LJ}} = 5\sigma_{ij}$\(^1\). All parameters used in computer simulations are displayed in Table 1. As previously, we used Lorentz–Berthelot mixing rules for all cross-term interactions.\(^7\)

Althought application of the Lorentz–Berthelot mixing rule for calculation of cross-term interactions is justified for mixtures of nobles gases, our previous simulation results indicate that this mixing rule correctly reproduces the fundamental adsorption properties of fluids in various nanoporous materials. To justify used solid–fluid LJ parameters, we compared CO$_2$ adsorption properties computed for selected values of the LJ well depth. Increasing of the solid–fluid LJ well depth predicted from the Lorentz–Berthelot mixing rule by 5% has negligible impact on the computed absolute value and en-thalphy of CO$_2$ adsorption in optimized carbon nanomaterials (see Figure 1S and 2S in the Supporting Information).

2.2. Simulation Details. We simulated CO$_2$ adsorption isotherms by the GCMC method\(^1\). We adopted our previous setup for GCMC simulation of adsorption in bundles composed of SWNTs, that is, a cubic simulation box of size $L_x \times L_y \times L_z$ ($L_x = 4.23$ nm for $(n,0)$ nanotubes, and $L_x = 4.3959$ nm for $(n,n)$ nanotubes) with periodic boundary conditions and minimum image convention for computing molecular interactions in $x$, $y$, and $z$ directions, as presented in Figure 1.\(^7\) We kept atomistic carbon nanotubes rigid in our computer experiments. Overall, we computed 28 CO$_2$ adsorption isotherms at 298 K and pressures from $1 \times 10^{-6}$ to 5.7 MPa. More precisely, we studied CO$_2$ adsorption in nine bundles of SWNTs composed of the following armchair nanotubes: (8,8), (10,10), (12,12), (16,16), (20,20), (24,24), (28,28), (32,32), and (36,36). For comparison, we investigated CO$_2$ adsorption at 298 K in 19 SWNTs built up from the following chiral nanotubes: (12,0), (18,0), (24,0), (30,0), (36,0), (42,0), (48,0), (54,0), (60,0), (72,0), (84,0), (96,0), (108,0), (120,0), (132,0), (144,0), (156,0), (168,0), and (180,0). All simulated adsorption isotherms of CO$_2$ consisted of 94 points and covered the range of nanotube pore diameters, $D_{\text{Cyl}} \in [0.93,14]$ nm.

As previously, the diameter of carbon nanotubes forming the bundle assembly was selected based on the assumed carbon–carbon bond length of $d_{cc} = 0.141$ nm, and given by the equation\(^6\)

$$D_{\text{Cyl}} = \frac{d_{cc}\sqrt{3(n^2 + n \cdot m + m^2)}}{\pi}$$

(5)

where $(n,m)$ denotes the chiral vector of carbon nanotubes forming a bundle assembly. All studied bundles of SWNTs were constructed by using Nanotube Modeler software.\(^7\) The grand canonical ensemble simulations utilized $5 \times 10^7$ configurations; the first $2.5 \times 10^7$ configurations were discarded to guarantee equilibration.

2.3. Gravimetric and Volumetric Storage of Carbon Dioxide. Packing of linear CO$_2$ molecules into studied carbon nanomaterials is essential for microscopic understanding of storage efficiency. The optimal porous materials for storage should maximize both gravimetric and volumetric uptake of CO$_2$ at given operating conditions. Thus, any objective statement about the storage efficiency of nanoporous material taken only from volumetric or gravimetric experimental measurements or computational experiments is incomplete. Some nanoporous materials can enhance the gravimetric density of adsorbed fluid significantly. However, at the same time, the pore density of trapped fluid can be quite low (for details, see Kowalczyk et al.\(^6\)).

To determine the volumetric uptake of adsorbed CO$_2$ in studied carbon nanomaterials, we computed the absolute value of adsorption from the following formula\(^6,7\)

$$\rho_{abs} = \frac{\langle N \rangle}{V \cdot N_A}$$

(6)
where \( \langle N \rangle \) is the ensemble average of the number of CO2 in the simulation box of volume \( V = L_xL_yL_z \) and \( N_{AV} \) denotes Avogadro’s number.

The gravimetric uptake of CO2 adsorbed in studied carbon nanomaterials is simply given by\(^{76,77}\)

\[
\Gamma = \frac{\langle N \rangle}{N_C \cdot M_C}
\]  

where \( N_C \) denotes number of carbon atoms in the simulation box and \( M_C \) is the molecular mass carbon. The enthalpy of CO2 adsorption was calculated from the theory of fluctuations.\(^{76,77}\)

3. Results and Discussion

The accuracy of computer simulations strongly depends on the applied force field. In the current paper, we study the thermodynamic properties of CO2 adsorbed in various nanoporous, microporous, and mesoporous carbon nanomaterials at 298 K. Note that this temperature is very close to 304 K (i.e., CO2 critical temperature). Thus, the validation of the applied force field against known experimental data near the CO2 bulk critical temperature is necessary. As one can see from Figure 2, the force field proposed by Nguyen\(^{78}\) reproduces experimental data reasonably well.\(^{79}\) The experimental CO2 equation of state is quantitatively reproduced at 298, 320, and 340 K. Next, as shown in Figure 2, almost quantitative prediction of isothermal expansivity is achieved for CO2, either in the vapor, liquid, or near-critical phase. Below the saturation pressure at 298 K, CO2 is in the vapor state, and its thermal expansivity increases with increasing pressure. For very low pressures, the isothermal expansion would be expected to be \( 1/T = 1/(298 \text{ K}) = 0.00336 \text{ K}^{-1} \) due to the perfect gas law, which is correct at low pressures.\(^{76,77}\) Our simulation results predicted the isothermal expansion of CO2 of 0.00334 K\(^{-1}\) at 0.1 MPa and 298 K, in agreement with the ideal gas law. Above the saturation pressure, isothermal expansivity is reduced since CO2 is in a liquid state, and the density slowly increases with the increasing pressure, as displayed in Figure 2. Above the critical temperature of the CO2 simulation, results clearly indicate that the isothermal expansivity is reduced (i.e., the single peak broadens and moves...
to the higher values of pressures, in good agreement with the experimental data. Concluding, we are confident that the applied force field correctly reproduces thermodynamic properties of CO$_2$ near its critical temperature.

Selected CO$_2$ adsorption isotherms at 298 K on studied carbon nanomaterials composed of armchair SWNTs are displayed in Figure 3. First, we find that both volumetric and gravimetric uptake of CO$_2$ at 298 K strongly depend on the size of the nanotubes but not on their chiral vectors (i.e., detailed arrangement of carbon atoms on the nanotube surface). At the high temperature studied, adsorbed CO$_2$ molecules do not see details of the carbon surface because of their high kinetic energy. As expected, for all studied sizes of carbon nanotubes, the simulated adsorption isotherms exhibit type I behavior according to IUPAC classification. However, widening of carbon nanotubes results in gradual CO$_2$ adsorption uptake, suggesting the presence of wider microporosity and small mesoporosity. This transformation of adsorption isotherms stems from a “cooperative pore filling” mechanism of CO$_2$ adsorption in wider carbon nanotubes and interstitial channels. More precisely, for carbon nanomaterials built up from small nanotubes, the adsorption is governed by the “micropore filling” mechanism. Gaseous CO$_2$ fills the internal and interstitial channels at low pressures because the strong solid–fluid potential alters vapor–liquid transformation of the adsorbed fluid. Interestingly, CO$_2$ molecules adsorbed in interstitial channels between carbon nanotubes form quasi-one-dimensional dense structures stabilized by the strong solid–fluid potential (see Figure 4 and the movie in the Supporting Information). At higher pressures, adsorbed CO$_2$ molecules are only slightly compressed due to geometric restrictions and the contribution of repulsive forces. In contrast, in carbon nanomaterials composed of wider nanotubes, the adsorption mechanism corresponds to the filling process by the CO$_2$ molecules in the mono- and multilayer-coated micropore walls (see Figure 5 and the movie in the Supporting Information). Similarly, in wider interstitial channels, the formation of discrete CO$_2$ layers occurs at low pressures. As the external pressure increases, the interstitial channels are filled by CO$_2$ molecules.

The highest enthalpy of CO$_2$ adsorption at 298 K and zero coverage of ∼31 kJ mol$^{-1}$ corresponds to bundles composed of (12,12) and (16,16) carbon nanotubes (equivalent pore diameters of 1.62 and 2.16 nm, respectively). As expected,
widening of carbon nanotubes reduces the enthalpy of CO₂ adsorption at zero coverage because of the rapid decrease in the solid–fluid interaction potential, as shown in Figure 6.

Reduction in nanotube sizes decreases the enthalpy of CO₂ adsorption at 298 K and zero converge as well. This is caused by the imperfect packing of adsorbed rod-shaped CO₂ molecules in restricted geometries as well as the contribution of repulsion forces in very small nanospaces. We want to point out that the enthalpy of CO₂ adsorption at 298 K and zero converge corresponding to bundle composed of (10,10) SWNTs of 23 kJ mol⁻¹ coincides with experimentally reported values of 22.5–23 kJ mol⁻¹. This is because the bundles of (10,10) and similar nanotubes are the most abundant ones.

Detailed inspection results of CO₂ local densities in selected carbon nanomaterials and operating conditions are displayed in Figures 7 and 8. We find that near ambient operating pressures, the adsorbed and compressed CO₂ form two and three dense concentric solid-like layers in carbon nanotubes of pore diameter ≈ 2 nm. As we showed above, this size of carbon nanotubes corresponds to the highest enthalpy of CO₂ adsorption at 298 K and zero coverage. That is why the carbon nanomaterials composed of nanotubes with the quoted pore diameter maximized volumetric storage of CO₂ at 298 K, as shown in Figure 9. One can conclude that these carbon nanomaterials are optimal for short-term reversible storage of CO₂ near ambient operating conditions. However, this is not the case because the maximum of volumetric CO₂ uptake does not correspond to maximum CO₂ uptake per mass of carbon nanomaterial. We studied this important issue in detail.
Both gravimetric and volumetric storage of CO$_2$ at studied operating conditions strongly depend on the size of the carbon nanotubes (see Figure 9). The highest average density of adsorbed and compressed CO$_2$ exceeds 17.6 mol dm$^{-3}$ (i.e., density of liquid CO$_2$ at 298 K). Further, both volumetric and gravimetric CO$_2$ uptake slightly depend on the selected operating pressure. More precisely, the highest volumetric storage of CO$_2$ at 1.5 MPa ($\sim$19–20 mol dm$^{-3}$) corresponds to nanotube diameters of $\sim$1.4–2.3 nm. For a higher operating pressure of 3.5 MPa, these densities of adsorbed CO$_2$ can be achieved in a wider range of nanotube sizes (i.e., nanotube diameter $\approx$1.4–3.7 nm). In contrast, the gravimetric storage of CO$_2$ is continuously increasing with the mass of carbon (i.e., the size of carbon nanotubes composing the bundle structure), as displayed in Figure 9. In carbon nanomaterials composed of wider nanotubes, CO$_2$ is only adsorbed in the interstitial channels between carbon nanotubes and slightly in the internal cylindrical pores (see the discrete concentric layers of adsorbed CO$_2$ shown in Figures 7 and 8). Almost all internal cylindrical carbon pores are filled by gaseous CO$_2$. Taking both volumetric and gravimetric CO$_2$ uptake, we concluded that the optimal size of carbon nanotubes for assumed operating pressures can be uniquely defined. At

Figure 9. Gravimetric and volumetric CO$_2$ uptake at 298 K in studied carbon nanomaterials composed of armchair nanotubes (black circles) and chiral nanotubes (open squares and circles). The external pressures are 1.5 (left panel) and 3.5 MPa (right panel). Note that the density of liquid CO$_2$ at 298 K is 17.6 mol dm$^{-3}$.

Figure 10. Comparison of gravimetric and volumetric CO$_2$ uptake at 298 K in studied carbon nanomaterials (black circles: armchair nanotubes; open squares and circles: chiral nanotubes) and selected ordinary and novel nanoporous materials. Note that the experimental density of CO$_2$ in MOF-177 at 1.5 and 3.5 MPa indicates that the adsorbed CO$_2$ is in a compressed gas state at 298 K.
1.5 MPa and 298 K, the most efficient nanotubes that maximize both gravimetric and volumetric uptake of CO₂ (13.6 mmol g⁻¹ and 11.4 mol dm⁻³) have diameters of 3.8 nm, as presented in Figure 9. This size corresponds to the (28,28) armchair nanotubes. For a higher operating pressure of 3.5 MPa, the optimal diameter of carbon nanotubes is slightly shifted up to 4.8 nm (25.3 mmol g⁻¹ and 16.7 mol dm⁻³). This size corresponds to the (36,36) armchair nanotubes. Concluding, the optimal carbon nanomaterials for short-term reversible storage of CO₂ at 298 K and near ambient operating pressures are composed of wider nanotubes. Further, the enthalpy of CO₂ adsorption cannot be used as a unique measure of storage efficiency because of the subtle balance between the binding energy and excluded volumes.

Finally, we compare our simulation results with experimental CO₂ data reported in the literature. Unfortunately, in almost all experimental reports, the adsorption data are incomplete. The experimentalists usually report gravimetric uptake of CO₂ without any additional information about the average density of adsorbed fluid. As one can see from Figure 9, very high gravimetric uptake of CO₂ can be easily achieved in carbon nanomaterials composed of large-diameter carbon nanotubes. At the same time, the volumetric CO₂ is drastically reduced due to a rapid decrease of the solid-fluid dispersion energy. To critically discuss the applicability of different materials for short-term reversible storage of CO₂, the complete volumetric and gravimetric adsorption data are necessary. Taking into account both gravimetric and volumetric CO₂ uptake, we find that carbon nanomaterials composed of optimized SWNTs are superior storage vessels in comparison to ordinary porous materials, such as Norit RB2 and zeolite 13X (see Figures 9 and 10). The gravimetric uptake of activated carbons is superior storage vessels in comparison to that of the studied carbon nanomaterials composed of the optimized single-wall carbon nanotubes. Further, the enthalpy of CO₂ adsorption cannot be used as a unique measure of storage efficiency because of the subtle balance between the binding energy and excluded volumes.

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4. Conclusions
Light nanomaterials composed of optimized SWNTs have high gravimetric and volumetric capacity for storage of CO₂ at 298 K and near ambient operating pressures. Both gravimetric and volumetric storage of CO₂ strongly depend on the pore size in nanotubes. We show that for any operating storage pressure, a unique optimal size of carbon nanotubes is well-defined. Therefore, at 1.5 MPa, the most efficient nanotubes that maximize both gravimetric and volumetric uptake of CO₂ (13.6 mmol g⁻¹ and 11.4 mol dm⁻³) have diameters of 3.8 nm. This size corresponds to the (28,28) armchair nanotubes. At 3.5 MPa, the optimal diameter of carbon nanotubes is slightly shifted up to 4.8 nm (25.3 mmol g⁻¹ and 16.7 mol dm⁻³). This size corresponds to the (36,36) armchair nanotubes. We clearly demonstrate that to make an objective statement about the efficiency of CO₂ storage in any nanoporous material, the complete volumetric and gravimetric adsorption data are necessary. We show that very high gravimetric CO₂ uptake can be achieved in carbon nanomaterials composed of large-diameter nanotubes. However, for the same operating conditions, the density of adsorbed CO₂ is very low in comparison to its liquid one. Taking this insight into account, we critically discuss the exceptionally high capacity of MOFs reported recently. We show that MOF-177, known as the most efficient porous material for storage of CO₂ at room temperature, is characterized by very high gravimetric uptake of CO₂ (i.e., 21.8 mmol g⁻¹ at 1.5 MPa and 33.5 mmol g⁻¹ at 3.5 MPa). However, the volumetric density of CO₂ in MOF-177 at 298 K (i.e., 8.17 mol dm⁻³ at 1.5 MPa and 12.26 mol dm⁻³ at 3.5 MPa) is lower in comparison to that of the studied carbon nanomaterials composed of optimized nanotubes. CO₂ molecules adsorbed in MOF-177 are not in the liquid but compressed gas state.

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Supporting Information Available: Snapshots of CO₂ adsorbed in selected carbon nanomaterials composed of SWNTs. Additional simulation results for selected values of the solid-fluid LJ well depth (Figure 1S and 2S). It should be noted that some figures (showing the snapshots of the animations, i.e. Figure 1, 4, and 5) and all movies in the Supporting Information were created using the VMD program. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
