Supporting Information

Formation of CO_2 Hydrates within Single-Walled Carbon Nanotubes at Ambient Pressure: CO_2 Capture and Selective Separation of CO_2/H_2 Mixture in Water

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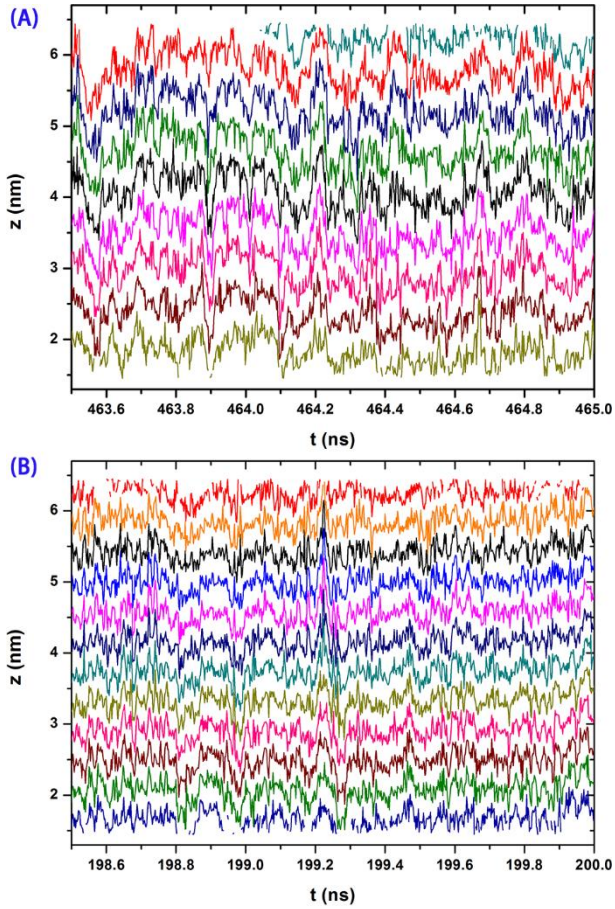

Figure S1. Motions z(t) of individual CO_2 molecules along the nanotube axis shown as colored lines, inside the nanochannel of Q1D (A) octagonal and (B) nonagonal CO_2 hydrates.

1. Computational Details

The zigzag SW-CNTs with two open ends are immersed into the dilute CO_2 (or CO_2/H_2) aqueous solution. All zigzag SW-CNTs have the length of 5.112 nm and their length is fixed during the simulations. And the lengths of (10, 10) and (12, 9) SWCNTs are 4.919 and 5.183 nm, respectively. Water molecules are described by the TIP3P model.[S1] Carbon atoms of SW-CNTs are modeled as uncharged Lennard-Jones (LJ) particles with graphite parameters of ε_C = 0.3598 kJ/mol and σ_C = 0.34 nm.[S2] H_2

molecules are described by a rigid two-center LJ model with a bond length of 0.074 nm and with the LJ parameters of ε_H = 0.1039 kJ/mol and σ_H = 0.259 nm.[S3] The aqueous solution includes 4858 water molecules and 15 CO_2 molecules (and additional 15 H_2 molecules for the dilute CO_2/H_2 aqueous solution). We also study the effect of the gas concentration difference. The results also show the high selectivity of CO_2 over H_2. Indeed, the 1D gas hydrates in SW-CNTs are the ice nanotubes with gas molecules occupying the nanochannels. And the reason for the high selectivity of CO_2 over H_2 in the mixture solution is due to the much lower free-energy barrier of CO_2 to enter the SW-CNTs. Therefore, the formation of 1D gas hydrates within SW-CNTs and high selectivity of CO over H_2 are less affected by the ratio of number of water and guest molecules in the solution.

2. Calculation of CO2 weight storage efficiency

The CO_2 weight storage efficiency for Q1D hydrate within SW-CNT is defined as:

$$\text{wt\%} = \frac{m_{CO2}}{m_{CO2}+m_{water}+m_{CNT}} \times 100\% \quad (1)$$

Here m_{CO2} and m_{water} are the masses of CO_2 and water within SW-CNTs, and m_{CNT} is the mass of SW-CNT.

3. Potential of Mean Force (PMF) Calculation

The free-energy profile along the tube axis for the gas molecules is calculated by using the umbrella-sampling algorithm.[S4,S5] The force constant adopted for the harmonic biasing potential is 200 kJ $mol^{-1}nm^2$ due to the weak interactions between gas molecule and water, particular between H_2 and water. The target positions vary from 0.4 nm to 3.6 nm at increments of 0.1 nm (the coordinate of the SW-CNT end is z ~ 1.5 nm). A total of 32 simulations yield overlapping windows of density

probability. Each window is sampled for 4 ns and the last 2 ns of data are analyzed using the weighted histogram analysis method (WHAM).[S4] Note that all the umbrella-sampling simulations are carried out for the system being at a low temperature (200 K) with a stable polygonal ice nanotube when pulling the gas molecule.

Supporting References

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