MgO-decorated carbon nanotubes for CO_2 adsorption: first principles calculations*

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The global greenhouse effect makes it urgent to deal with the increasing greenhouse gases. In this paper the performance of MgO-decorated carbon nanotubes for CO_2 adsorption is investigated through first principles calculations. The results show that the MgO-decorated carbon nanotubes can adsorb CO_2 well and are relatively insensitive to O_2 and N_2 at the same time. The binding energy arrives at 1.18 eV for the single-MgO-decorated carbon nanotube adsorbing one CO_2 molecule, while the corresponding values for O_2 and N_2 are 0.55 eV and 0.06 eV, respectively. In addition, multi-molecule adsorption is also proved to be very satisfactory. These results indicate that MgO-decorated carbon nanotubes have great potential applications in industrial and environmental processes.

Keywords: carbon nanotube, CO_2 adsorption, first principles calculations

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1. Introduction

Recently, more and more phenomena have shown a trend of global warming. Living and production processes release carbon dioxide (CO_2) into the atmosphere at all times, which is one main reason for global warming. It is increasingly recognized that there is an urgent requirement to control this CO_2 release. One effective solution is to search for materials that can capture and sequester CO_2 before it is released. Recent studies have shown that metal-organic frameworks (MOFs) are good candidates for the selective adsorption of CO_2.[1−5] Millward and Yaghi[1] assessed the viability of MOFs in CO_2 storage at room temperature through nine compounds such as MOF-505, $Cu_3(BTC)_2$ and IRMOF-11. Walton *et al.*[2] presented experimental adsorption isotherms for CO_2 in IRMOF-1 over a wide range of temperatures. In the study of Torrisi *et al.*,[3] the material $(OH)_2$-MIL-53(Al^{3+}) was investigated and shown to be an ideal candidate for improving CO_2 capture ability at low pressures. Bastin *et al.*[4] examined microporous MOF Zn(BDC) for the separation and removal of CO_2 from its binary CO_2/N_2 and CO_2/CH_4 and ternary $CO_2/CH_4/N_2$ mixtures, and their results verified that microporous MOFs are suitable for CO_2 capture. These research papers prove the validity of using MOFs as the materials for the selective adsorption of CO_2.

In the last few years, carbon nanotubes (CNTs) have demonstrated excellent versatility and wide applicability in emerging technologies. Compared with the previous MOFs, CNTs have large surface-to-volume and surface-to-weight ratios, high electrical conductivity, high thermal conductivity, chemical stability at high temperatures and other excellent features.[6,7] The tubular structure of CNTs leads to a unique surface chemistry. Varied electrical properties, depending on the tube chirality and diameter, make CNTs promising candidates for various functional materials. Until now, there has been little research on using CNTs for effective materials adsorbing CO_2. Hsu *et al.*[8] used multi-walled CNTs to study thermodynamics and regeneration of CO_2 capture from gas streams. Their results suggested that CNTs were possibly cost-effective sorbents. Huang *et al.*,[9] investigated the adsorption behaviour of an equimolar CO_2/CH_4 mixture in carbon nanotubes by grand canonical Monte Carlo simulations. Their results showed that the CNTs had a preferential adsorption of CO_2 in a binary CO_2/CH_4 mixture. Du *et al.*[10] investigated the effect of Fe doping on adsorption of CO_2/N_2 inside carbon nanotubes from first

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principles calculations, which suggested that Fe doped CNTs might be feasible for CO_2/N_2 separation.[11] However, in Ref. [10], N_2 was still shown to have a greater binding energy with CNTs than CO_2. This may be due to the fact that the doping pure metal atom is very active and its non-bonding orbital is very sensitive to the N_2 and O_2 molecules. In addition, some metal oxide compounds are sensitive to CO_2 and but show no activity in response to N_2 and O_2. CNTs decorated with such metal oxide compounds may be good candidates for the selective adsorption of CO_2.

In this paper, we investigate the performance of MgO-decorated CNTs (MCNTs) for CO_2 adsorption from first principles calculations. Results show that the MCNTs can well adsorb CO_2 and be relatively insensitive to O_2 and N_2 at the same time. The multi-molecule adsorption is also proved to be very satisfactory. These results indicate that metal-oxide-decorated CNTs are feasible materials for CO_2 capture and have great potential applications in industrial and environmental processes.

2. Computational details

All simulations are performed within the framework of density functional theory[11] as implemented in the plane-wave-basis-set Vienna *ab initio* simulation package (VASP).[12,13] We use the frozen-core projector augmented wave (PAW)[14] method to describe the electron–core interaction and the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE)[15] for the exchange-correlation functional. The energy cutoff for the plane-wave expansion is set to be 500 eV. A 1×1×2 supercell of (8, 0) CNT containing 64 carbon atoms is built, and an over 10 Å vacuum layer is added between the carbon atoms on adjacent nanotubes. For structural relaxation and self-consistent calculation, Brillouin-zone integrations are performed by a 1×1×11 Monkhorst–Pack k-point mesh.[16] While for the calculation of the density of states (DOS), a 1×1×21 grid is used. Moreover, the optimized structures are obtained by relaxing the atomic configurations until the calculated Hellmann–Feynman (H–F) force on each atom is smaller than 0.05 eV/Å.

3. Results and discussion

To obtain the optimized structures of the substrate MCNT, the properties of a single MgO molecule is calculated first. The bond length of a MgO molecule is found to be 1.76 Å. Then we consider the structure of the single-MgO-decorated CNT. Several initial adsorption positions of Mg are tested, *i.e.*, site above the centre of a carbon hexagon (H-site), above the midpoint of a carbon–carbon bond (B-site) and on the top of a carbon atom (T-site). The results show that the total energy of the system is lowest when the Mg atom is adsorbed on the H-site. Thus, all the following results are obtained using MCNT with Mg adsorbed on the H-site. The structure of MCNT after relaxation is shown in Fig. 1(a). From the figure, it can be found that the MgO molecule is perpendicular to the CNT. The bond length between Mg and O is 1.80 Å and increases to about 0.04 Å compared with that of isolated MgO molecule. The distances between Mg and its nearest neighbouring and second nearest neighbouring C atoms are 2.46 Å and 2.67 Å, respectively. The calculated binding energy of the decorated structure is 0.72 eV, indicating stable chemical adsorption.

Next we consider the gas molecules adsorbed on the MCNTs. Optimized structures of CO_2, O_2 and N_2 adsorption are presented in Figs. 1(b), 1(c) and 1(d), respectively. For CO_2 adsorption, compared with the case of non-adsorption configuration, the Mg atom moves slightly toward the CNT and the distance between Mg and its nearest neighbouring C atoms decreases to 2.33 Å. As seen from Fig. 1(b), the geometry of CO_2 molecule changes significantly. C atom and the other two O atoms are no longer on a line. The C1–O1 and C1–O2 bond lengths are 1.35 and 1.26 Å, respectively. For O_2 adsorption, the MgO molecule is no longer perpendicular to the CNT. The Mg–O bond length of the molecule becomes 1.84 Å and the Mg atom moves away from the CNT. The distance between Mg1 and O1 is 1.97 Å. For N_2 adsorption, it can be found that the N_2 molecule is far from the substrate and the geometries of both the MCNT and the N_2 molecule almost have no change. The N_2 molecule is about 3.1 Å away from O1 (see Fig. 1(d)).

The binding energies for CO_2, O_2 and N_2 are 1.18, 0.55 and 0.06 eV, respectively. The relatively high binding energy for CO_2 suggests that CO_2 can be well adsorbed on the MCNT. The binding energy of O_2 is less than half that of CO_2, so CO_2 is much easier to adsorb than O_2. The small binding energy for N_2 demonstrates that the adsorption of N_2 is very weak. In conclusion, the MCNT is sensitive to CO_2 but insensitive to N_2/O_2. The selective adsorption behaviour suggests that the MCNT is a good candidate for CO_2 capture.

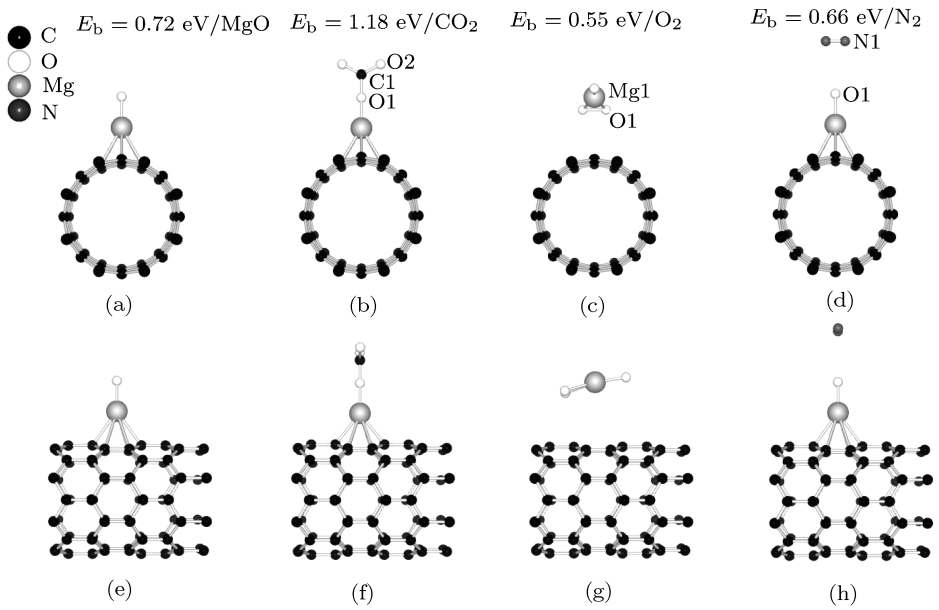


Fig. 1. Optimized structures of MCNTs and their gas adsorption. E_b is the corresponding binding energy. (a)–(d) cross-sectional view of MCNTs, (e)–(h) the corresponding side view of (a)–(d). (a), (e) Without gas adsorption; (b), (f) with CO_2 adsorbed; (c), (g) with O_2 adsorbed; (d), (h) with N_2 adsorbed.

To show the reason for the selective adsorption behaviour, partial desities of states (PDOSs) of different structures are calculated. It is found that the interactions between MgO and gas molecules play a key rule in the adsorption properties of different gases. The PDOSs of atoms labeled in Fig. 1 for different adsorbed MCNTs are given in Fig. 2. For CO_2 adsorption, a strong hybridization between O1 and the C atom of CO_2 can be observed and indicated by the sharp peaks of PDOSs for both atoms at −21.6, −18.6, −8.3 and −5.2 eV. The strong hybridization stabilizes the CO_2 molecule on the MCNT. For O_2 adsorption, hybridization between MgO and the gas molecule also exists, since the PDOSs of Mg1 and O1 have some common peaks. But the overlap is very small, as can be seen in Fig. 2(b). Hence, the small binding energy of O_2 results from the weak hybridization. For N_2 adsorption, the PDOSs of O1 and N1 have no common peaks, so there is no hybridization between O1 and the N_2 molecule. This leads to the insensitivity of the MCNT to N_2.

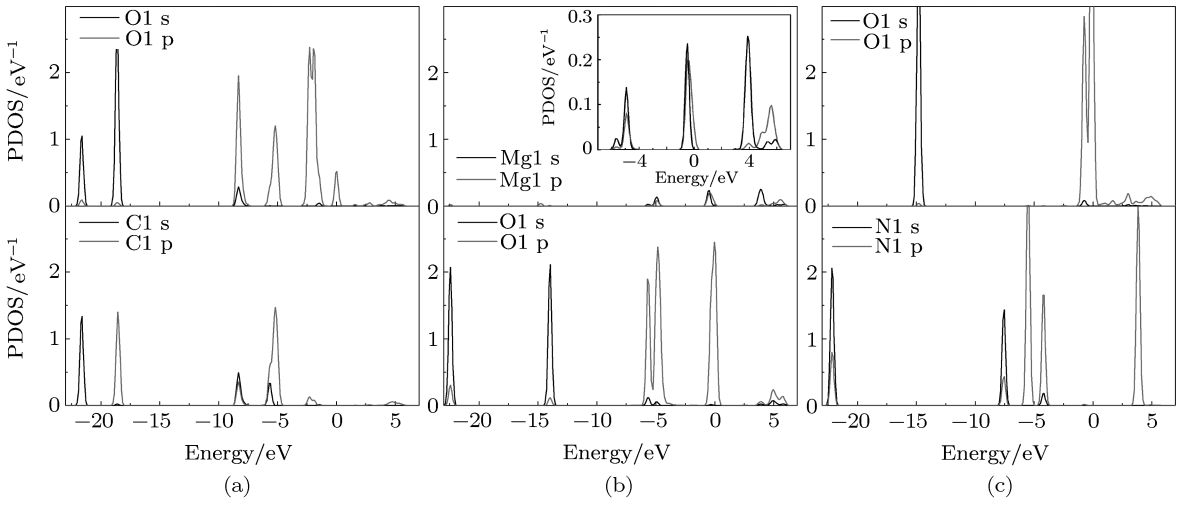


Fig. 2. PDOSs of atoms labeled in Fig. 1: (a) O1 and C1 for CO_2 adsorbed on MCNT, (b) Mg1 and O1 for O_2 adsorbed on MCNT (insert is the zoom for Mg1), (c) O1 and N1 for N_2 adsorbed on MCNT.

To achieve a high efficiency of CO_2 capture, configurations with two and four MgO molecules in a CNT supercell are constructed to explore their stabilities and capacities of CO_2 collection. The fully relaxed structures are shown in Fig. 3. The calculated binding energies are 0.64 eV for a MgO molecule and 0.54 eV/MgO for two MgO and four MgO-decorated CNTs, respectively. This is adequate to stabilize MgO molecules on CNTs, though the binding energy decreases compared with that of single-MgO-decorated CNTs. Therefore, CNTs with high MgO coverage are able to be synthesized. The binding energies are 1.06 eV for CO_2 and 0.98 eV/CO_2 for CNTs with two and four MgO molecules decoration respectively, which is rather large and satisfactory for CO_2 capturing. According to these results, a high efficiency of CO_2 capturing can be expected for MCNTs.

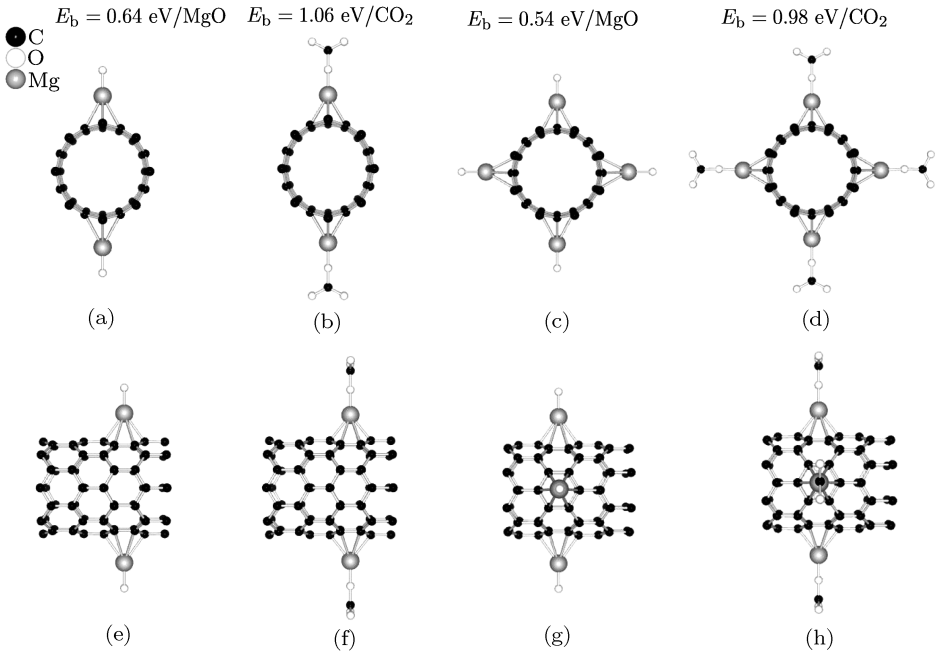


Fig. 3. Optimized structures of CNTs with two and four MgO molecules decoration and their corresponding structures of CO_2 adsorption: (a) the cross-sectional view of the CNT with two MgO molecule decoration, (b) the structure of two MgO-decorated CNT with the adsorbed CO_2, (c) and (d) the four MgO molecule decoration, (e)–(h) the corresponding side views of (a)–(d). E_b is the corresponding binding energy.

4. Conclusion

The performance of MCNTs for CO_2 adsorption is studied from first principles calculations. The results show that MCNTs exhibit a selective adsorption behaviour. CO_2 can be well adsorbed on MCNTs due to the large binding energy, while the binding energy is relatively small for O_2 and nearly zero for N_2. The strong hybridization between MgO and CO_2 molecules leads to the stable chemical adsorption of CO_2 on MCNT. Multi-MgO-decorated CNTs also exhibit good capacities of CO_2 collection, promising high efficient device for CO_2 capture based on MCNTs.

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