First-principles study of CO_2 and NH_3 adsorption on armchair graphene nanoribbon

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Graphene is a most attractive candidate for high sensitivity gas sensor because graphene has highest surface-to-volume ratio. In this research, First-principle calculations are performed to study the adsorption of CO_2 and NH_3 gas molecules on armchair graphene nanoribbons (AGNR). The electronic and transmission properties are calculated based on Density functional Theory (DFT) and Non equilibrium green function formalization based on DFT implemented in the OpenMX package [1]. A system consisting of a central region connected to the left and right leads of infinite size, as shown in Fig. 1, is considered in this work. The structure given in Fig. 2 was used for initial configuration of the CO_2 adsorbed on AGNR.

To find the optimum distance between the molecule and the AGNR channel, adsorption energy calculations were performed. The adsorption energy is defined as $E_{Ads}=E_{AGNR-Gas}-(E_{AGNR} + E_{Gas})$, where $E_{AGNR-Gas}$ is the total energy of the AGNR with the gas molecule adsorption. E_{AGNR}, E_{Gas} are the energies of the isolated AGNR and the isolated corresponding gas molecule, respectively. The calculated adsorption energies of the CO_2 and NH_3 molecules are -0.1861 eV and -0.1528 eV, respectively. These results indicate that both CO_2 and NH_3 gas molecules are physisorptions nature on AGNR with the low adsorption energies.

In order to understand the charge transfer mechanism between the molecules and AGNR, the Mulliken population analyses were performed. The Table given in Fig. 3 shows the Mulliken population of each atom of the CO_2 and NH_3 molecules. It gives the values of the atomic charge transfer of each atom and the net charge transfer between the molecule and AGNR. For the CO_2 adsorption, we can see that there is small amount of 0.008679 e charge transfer from the AGNRs to the CO_2 molecule. This indicates that CO_2 adsorption acts as acceptor. In contrast, there is 0.088381e charge transfer from the NH_3 molecule to the AGNR, which indicates that NH_3 act as donor.

Fig. 4 and Fig 5 show the density of states (DOS) and the transmission spectra of the pristine AGNR, AGNR with CO_2 adsorption and AGNR with NH_3 adsorption. In the case of the CO_2 adsorbed on AGNR, the DOS is modified weakly because the interaction between CO_2 molecule and ANGR is weak as indicated by the mulliken population analysis. The corresponding transmission spectrum shows the reduction of the transmission. However, the DOS and the transport spectrum are changed considerable in the case of NH_3 adsorption. The emergence of the mid-gap state and the reduction in the transmission can be noticed for the NH_3 adsorption, which is consistent with the strong interaction between the NH_3 molecule and the AGNR indicated by the mulliken population analysis. Fig. 6 shows the IV characteristics of the AGNR device with a CO_2 and NH_3 molecules. Even though a small charge transfer occurs in the CO_2 adsorption the reduction in the current is remarkable, which is attributed to the remote Coulomb scattering [2].

The analysis of the charge transfers demonstrate that NH_3 and CO_2 absorbed on AGNR exhibit n-type and p-type doping, respectively. The remarkable reduction of the current with the CO_2 adsorption indicates the dominant nature of the remote Coulomb scattering.

REFERENCES

[1] http://www.openmx-square.org/
[2] Y Sato, K Takai, T Enoki Nano letters, 11, 3468–3475, 2011

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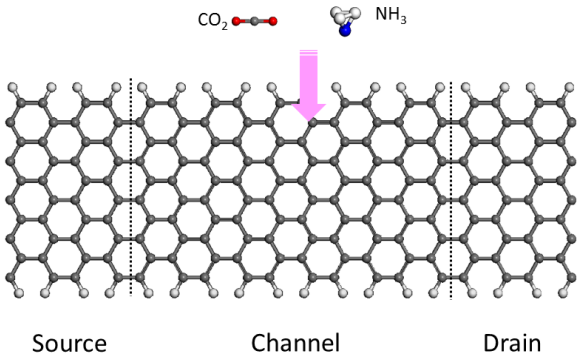

Fig. 1. The Configuration of the AGNR device treated by the transport calculation.

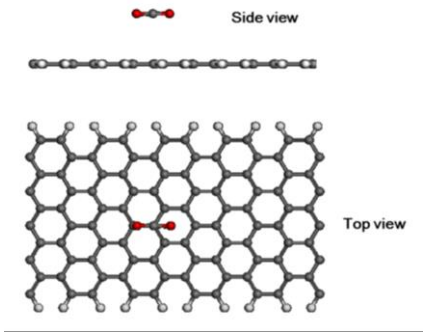

Fig. 2. Side view, and top view of the initial configuration of CO_2 molecule on the AGNR channel.

	CO_2			NH_3			
	C	O(1)	O(2)	N	H(1)	H(2)	H(3)
Mulliken population (e)	3.999	6.004	6.003	5.879	0.676	0.676	0.6766
Total charge transfer (e)	-0.008848 -> Acceptor-like			0.1346 -> Donor-like			

Fig. 3. Mulliken population analysis result of the CO_2 and NH_3 molecules on the AGNR channel.

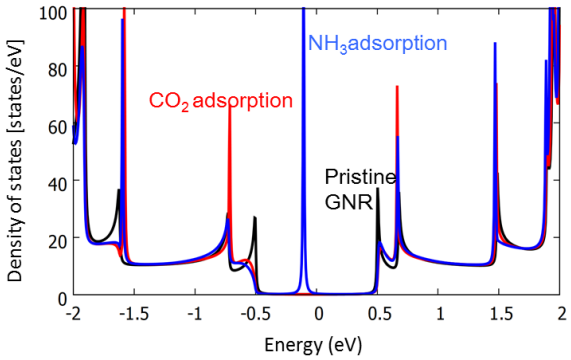

Fig. 4. Density of states of the Pristine AGNR, the AGNR with a single CO_2 molecule adsorption, and the AGNR with a single NH_3 molecule adsorption.

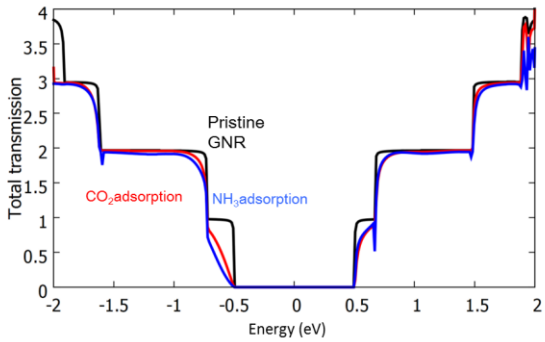

Fig. 5 The transmission spectrum of the Pristine AGNR, the AGNR with a single CO_2 molecule adsorption, and the AGNR with a single NH_3 molecule adsorption.

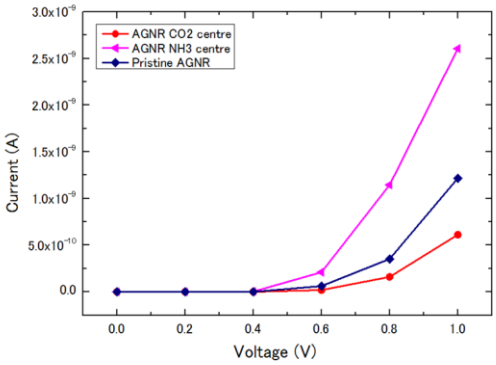

Fig. 6 I-V characteristics of a single molecule of CO_2, NH_3 adsorbed on AGNR and the pristine GNR.