A Theoretical Study of Gas Adsorption on Silicene Nanoribbons and Its Application as a Highly Sensitive Molecule Sensor

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Electronic Supplementary Information

Computational Methods Details

All the calculations are carried out based on first-principles DFT combined with nonequilibrium Green's function (NEGF) implemented in Atomistix ToolKit (ATK) package.[70-72] The Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) with a double-ζ polarized basis set is adopted to solve Kohn-Sham equations and to expand electronic density. The density mesh cut off is set to be 150 Rydberg. The Grimme vdW correction (DFT-D2)[73] is also employed to describe long-range vdW interactions.[74] In order to take into account the vdW interactions, an additional term (E_{vdW}) is added to the DFT total energy (E_{DFT}):

$$E_{DFT-D2} = E_{DFT} + E_{vdW}$$

The E_{vdW} is calculated using an attractive semi-empirical pair potential (V^{PP}):

$$E_{vdW} = 0.75 \sum_{\mu p \mu'} V^{PP}(Z_\mu, Z_{\mu'}, r_{\mu,\mu'})$$

The V^{PP} between two atoms, for example atoms 1 and 2, which are located at a distance r apart can be defined as:

$$V^{PP}(Z_1, Z_2, r_{12}) = \frac{\sqrt{C_6(Z_1)C_6(Z_2)}}{r_{12}^6} f(\frac{r_{12}}{R_0(Z_1) + R_0(Z_2)})$$

here C_6 and R_0 are the element-specific parameters and $f(x)$ is a cut-off function which is defined as:

$$f(x) = \frac{1}{1 + e^{-dx}}$$

Typically, d (damping parameter) is set to be 20. Besides vdW interactions, since our systems have two subsystems: the SiNR (A) and the gas molecule (B), so-called basis set superposition errors (BSSE) are expected due to the incompleteness of the Linear Combination of Atomic Orbitals (LCAO) basis set. In an isolated A system, only the basis orbitals in the A system are responsible to describe it. While, A and B are coupled, the basis orbitals in the system B will also be used to describe system A, resulting in a larger available basis set for system A. Consequently, there will be an artificial interaction which decreases the total energy. To eradicate BSSE, a counterpoise (cp) correction is added to the total energy:[75]

$$E_{BSSE} = E_{DFT} + E^{cp}$$

here E_{DFT} is the total energy of the system AB and E^{cp} is the counterpoise corrected energy which is:

$$E^{cp} = (E_A - E_{AB'}) + (E_B - E_{A'B})$$

where $E_{AB'}$ ($E_{A'B}$) is the energy of system A (B) using the AB basis orbitals, which is obtained by considering so-called ghost orbitals at the atomic positions in the system B (A). Ghost atoms have no charge and no mass; however, they have basis orbitals. E_A (E_B) is the total energy of an isolated system A (B) using the A (B) basis orbitals. Finally, the total energy of the system considering the long-range vdW interactions and artificial attractions between two subsystems is:

$$E_{Total} = E_{DFT} + E_{vdW} + E^{cp}$$

To avoid the mirroring interactions, a vacuum space of 25 Å is considered in *x* and *y* directions in which the structures are not periodic. The electronic temperature is kept constant at 300 °K. All the structures are completely relaxed, prior to the calculations, up until the force and stress are less than 0.01 eV/Å and 0.005 eV/ Å³, respectively. 1×1×21 *k*-points in the Brillouin zone are sampled for geometry optimization and 1×1×121 *k*-points for total energy, band structure, charge transfer, and electron transport calculations.

To investigate the charge transfer and transport properties, the gas sensing system is divided onto three regions: two electrode regions (left and right) and a scattering region (the central region), as illustrated in Fig. 1. To match the effective potential of central region with bulk electrodes, the perturbation of the scattering region should be screened out. To this end, a sufficient fraction of the electrode regions should be repeated in the scattering region. To calculate the non-equilibrium electron distribution in the central region, the NEGF method is employed. The charge density of the system based on the occupied eigenstates can be defined as

$$n(r) = \sum_{\alpha} |\psi_{\alpha}(r)|^2 f(\frac{\varepsilon_{\alpha} - \varepsilon_f}{kT})$$

here $f(x)=1/(1+e^x)$ is the Fermi function, ψ is the wave function, ε_f is the Fermi energy, *T* is the electron temperature, and *k* is the Boltzmann constant. Conveniently, *n(r)* can be presented in term of density matrix (D_{ij})

$$n(r) = \sum_{\alpha} D_{ij}\phi_i(r)\phi_j(r)$$

where D_{ij} is defined by basis set expansion coefficients

$$D_{ij} = \sum_{\alpha} c_{\alpha i}^* c_{\alpha j} f(\frac{\varepsilon_{\alpha} - \varepsilon_f}{kT})$$

The density matrix is divided into left and right contributions

$$D = D^L + D^R$$

where $D^{L(R)}$ is calculated using NEGF theory by

$$D^{L(R)} = \int \rho^{L(R)}(\varepsilon) f(\frac{\varepsilon_{\alpha} - \mu_{L(R)}}{k_B T_{L(R)}}) d\varepsilon$$

Where $\rho^{L(R)}(\varepsilon)$,the spectral density matrix, is

$$\rho^{L(R)}(\varepsilon) \equiv \frac{1}{2\pi} G(\varepsilon)\Gamma^{L(R)}(\varepsilon)G^{\dagger}(\varepsilon)$$

Here $\Gamma^{L(R)}$ is the broadening function of the left (right) electrode which defined as

$$\Gamma^{L(R)} = \frac{1}{i}(\sum{}^{L(R)} - (\sum{}^{L(R)})^{\dagger})$$

where $\Sigma^{L(R}$,the left (right) electrode self-energy, is

$$\sum{}^{L(R)} = V_{S/L(R)} g_{L(R)} V_{L(R)/S}$$

where $g_{L(R)}$ is the surface Green's function for the semi-infinite electrodes and $V_{L(R)/S} = V^\dagger_{S/(L/R)}$ are the coupling matrix elements between electrodes and the scattering region. Furthermore, the key quantity to calculate is *G*, the retarded Green's function matrix,

$$G(\varepsilon) = \frac{1}{(\varepsilon + i\delta_+)S - H}$$

where δ_+ is an infinitesimal positive number. S and H are the overlap and Hamiltonian matrices of the entire system, respectively. The Green's function is only required for the central region and can be calculated from the Hamiltonian of the central region by adding the electrode self-energies

$$G(\varepsilon) = [(\varepsilon + i\delta_+)S - H - \sum{}^L(\varepsilon) - \sum{}^R(\varepsilon)]^{-1}$$

The transmission amplitude t_k, defines the fraction of a scattering state k propagating through a device. The transmission coefficient at energy ε is obtained by summing up the transmission from all the states at this energy,

$$T(\varepsilon) = \sum_k t_k^\dagger t_k \delta(\varepsilon - \varepsilon_k)$$

The transmission coefficient may also be obtained from the retarded Green's function using

$$T(\varepsilon) = G(\varepsilon)\Gamma^L(\varepsilon)G^\dagger(\varepsilon)\Gamma^R(\varepsilon)$$

At $T_R = T_L = 0$ (electron temperature) the conductance is determined by the transmission coefficient at the Fermi Level,

$$C(\varepsilon) = G_0 T(\varepsilon)$$

where $G_0 = 2e^2/h$ is the quantum conductance, in which e is the electron charge and h is Planck's constant.