Influence of water on the electronic structure of metal-supported graphene: Insights from van der Waals density functional theory

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Abstract: We investigate the interaction between water and metal-supported graphene through van der Waals density functional theory calculations. Our results show a systematic increase in the adsorption energy of water on graphene in the presence of underlying metal substrates. In addition, we find that the electronic nature of the graphene-metal contacts behave differently upon water adsorption: In the case of a weak, physical graphene-metal contact, the charge carrier doping level of graphene is tuned by water, resulting in a Fermi level shift on the order of ~100 meV. In the case of a strong chemical graphene-metal contact, the π and π^* bands of graphene are hardly perturbed by water adsorption. These results illustrate the correlated nature of the interactions between water, graphene, and metal substrates, and show that the electronic structure and the doping level of graphene can be tailored by water deposition.

Metal-supported graphene

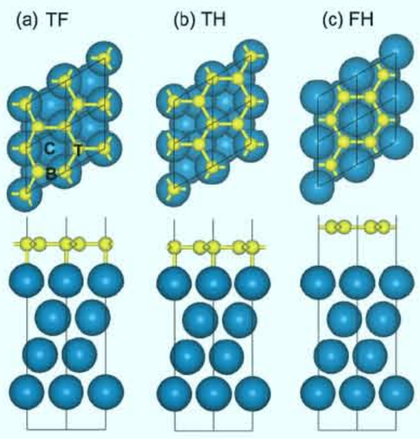

Figure 1. Three possible structures with C_{3v} symmetry for graphene on Ni(111) [or Cu(111)], shown in both top and side views. (a) top-fcc (TF), (b) top-hcp (TH), and (c) fcc-hcp (FH). Adsorbed water monomer can be placed on three different highly symmetric adsorption sites (in terms of oxygen's location) in these structures: (T) top, (B) bridge, and (C) center, with respect to graphene, which are labeled by black characters in panel (a). Yellow balls stand for C atoms, and blue for Ni (or Cu) atoms.

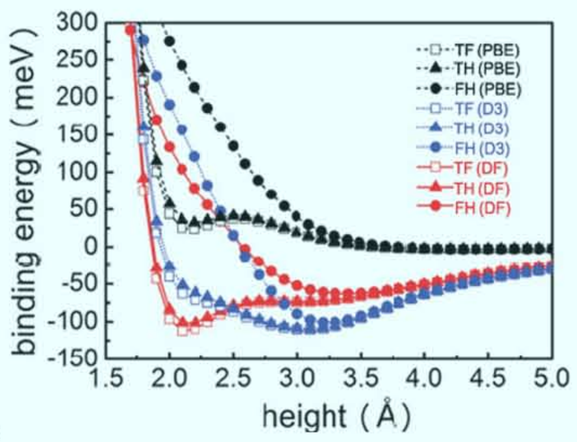

Figure 2. The binding energy versus height of the graphene sheet above Ni(111) in three adsorption structures, namely, TF, TH, and FH, using three different methods, namely, PBE, DFT-D3 (D3 for short), and optB86b-vdW (DF).

- Van der waals interactions are very important for the graphene/metal systems. OptB86b-vdW with a good vdW correction is more suitable for describing these systems than PBE and DFT-D3.
- The TF interface between graphene and Ni(111) surface with a binding distance of 2.1 Å is more stable than the other two structures [Fig. 2 and Table I].
- The interaction between graphene and Cu(111) is weaker than the graphene-Ni(111) interaction. Three structures for graphene/Cu(111) interfaces have similar binding energies and distances [Table I].

TABLE I. Binding energy ($E_{G\text{-}M}$) and the average perpendicular distances (d) between graphene and the first layer of Ni(111) [or Cu(111)] for graphene on Ni(111) [or Cu(111)] in three adsorption structures, namely, top-fcc (TF for short), top-hcp (TH), and fcc-hcp (FH). Results with three different methods, namely, PBE, DFT-D3 (D3 for short), and optB86b-vdW (DF for short) are reported. $E_{G\text{-}M}$(D3) is decomposed into two parts, E^{D3} and E^{GGA}, while $E_{G\text{-}M}$(DF) is decomposed into E^{nlc} and the remainder (E^{r} for short). A negative (positive) E means that graphene is bound (unbound) to the Ni(111) surface.

	$E_{G\text{-}M}$(PBE) (meV)	d(PBE) (Å)	$E_{G\text{-}M}$(D3) (meV)	E^{D3} (meV)	E^{GGA} (meV)	d(D3) (Å)	$E_{G\text{-}M}$(DF) (meV)	E^{nlc} (meV)	E^{r} (meV)	d(DF) (Å)
Ni-TF	~–3[a]	~4.36	–107	–147	40	3.25	–112	–277	165	2.12
Ni-TH	~–3	~4.40	–106	–143	37	3.28	–103	–272	169	2.14
Ni-FH	~–3	~4.46	–97	–134	37	3.40	–63	–109	46	3.41
Cu-TF	~–2	~4.39	–113	–151	38	3.33	–67	–125	58	3.24
Cu-TH	~–2	~4.44	–113	–152	39	3.32	–66	–130	64	3.19
Cu-FH	~–2	~4.52	–106	–139	33	3.34	–61	–116	55	3.30

[a]"~" is placed before all the PBE numbers, because PBE gives essentially no binding and only very shallow minima within the limits of the numerical accuracy of our simulations.

Adsorption of water overlayers

- The adsorption energy differences between H-up and H-down ice bilayers on each surface are all very small. Adsorption energies of the H-up bilayers are all slightly more stable than for H-down bilayers.
- Electric field induced by the ice bilayer shifts the Dirac point of graphene relative to the Fermi level, thus altering the electron doping level of the graphene/metal interface [Fig. 5].
- The three components of the water-graphene-metal composite are correlated in their mutual interactions: both water and the metal substrates play a role in modifying the electronic structure of graphene, and they themselves are mutually influenced via graphene as a bridge.

Water monomer adsorption

- Water adsorption at the center of a carbon hexagon [Fig. 3] is the most stable for four surfaces, where the water molecule stands vertically with two O-H bonds pointing toward two neighboring carbon atoms.
- The adsorption energy of water monomer increases by 11%–31% when graphene is supported on the metal substrates, compared to the single graphene. The increase for G/Ni-TF is larger than G/Ni-FH and G/Cu-TF.
- Metal substrates provide a nearly-free electron gas in the vicinity of graphene, which enhances the induced electron density of graphene in response to the dipole of adsorbed water [Fig. 3 and Fig. 4].

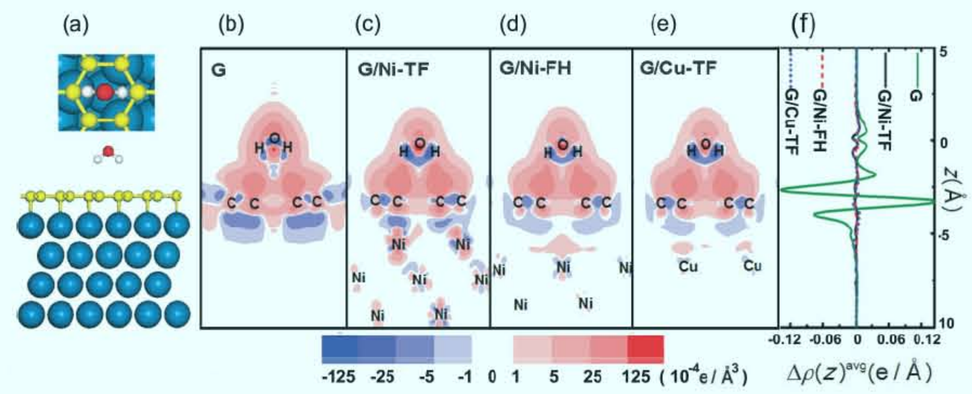

Figure 3. (a) The most stable adsorption structure of a water monomer on graphene/Ni-TF. In this structure the water is in a vertical orientation at the center of a C hexagon with the O-H bonds directed to two neighboring carbon atoms. Similar structures are seen for water on graphene, graphene/Ni-FH, and graphene/Cu-TF. Red balls represent the O atoms, white the H atoms, yellow the C atoms, and blue the Ni atoms. 2D slice of the charge density difference (obtained with the optB86b-vdW functional) for water monomer on (b) graphene, (c) graphene/Ni-TF, (d) graphene/Ni-FH, and (e) graphene/Cu-TF, through the plane of the adsorbed water molecule. (f) Plane-averaged electron density differences, $\Delta\rho^{avg}(z)$, of the four systems. The vertical position z is given relative to the O atom of water monomer (zero point). A (5×5) supercell of graphene was used, but only a portion of it is shown in panels (b)–(e).

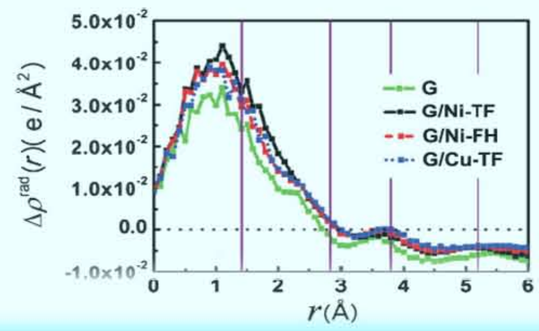

Figure 4. The lateral radial electron density differences in the proximity of graphene for four systems. The green solid line represents free graphene, the black solid line graphene/Ni-TF, the red dashed line graphene/Ni-FH, and the blue dotted line graphene/Cu-TF. r is the lateral radial distance from the origin of the x-y plane, which is set to the location of O in water molecule. The purple bold lines indicate the positions of C atoms in the graphene in the model system.

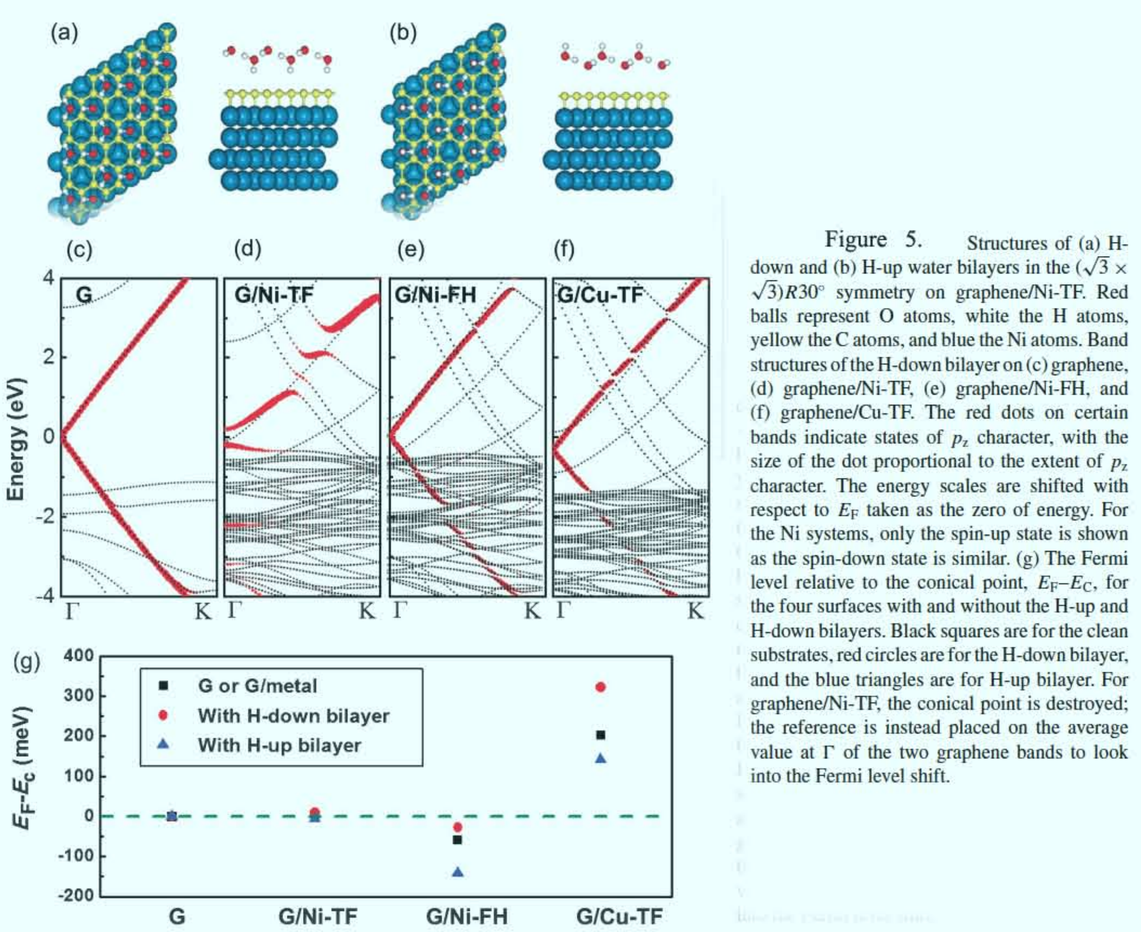

Figure 5. Structures of (a) H-down and (b) H-up water bilayers in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ symmetry on graphene/Ni-TF. Red balls represent O atoms, white the H atoms, yellow the C atoms, and blue the Ni atoms. Band structures of the H-down bilayer on (c) graphene, (d) graphene/Ni-TF, (e) graphene/Ni-FH, and (f) graphene/Cu-TF. The red dots on certain bands indicate states of p_z character, with the size of the dot proportional to the extent of p_z character. The energy scales are shifted with respect to E_F taken as the zero of energy. For the Ni systems, only the spin-up state is shown as the spin-down state is similar. (g) The Fermi level relative to the conical point, E_F–E_C, for the four surfaces with and without the H-up and H-down bilayers. Black squares are for the clean substrates, red circles are for the H-down bilayer, and the blue triangles are for H-up bilayer. For graphene/Ni-TF, the conical point is destroyed; the reference is instead placed on the average value at Γ of the two graphene bands to look into the Fermi level shift.