Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Supplementary Information: MXenes/graphene heterostructures for Li battery applications: a first principles study

Yierpan Aierken[a], Cem Sevik[b], Oğuz Gülseren[c], François M. Peeters[a] and Deniz Çakır*[a,d]

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

Stacking of MXenes/graphene

In order to determine the ground state stacking configuration of M_2CX_2+Gr heterostructures, we calculated the binding energy of different stacking configurations by shifting the M_2CX_2 layer with respect to the unit cell of graphene on a uniform mesh. In the course of these simulations, only the interlayer distance was allowed to relax.

The binding energy per atom, E_b, was defined in Equation (1) of the main manuscript. Fig. S**??** shows the binding energy difference of each stacking type with respect to the ground state configuration of each system. In each plot, the absolute value of the ground state binding energy, $E_b(GS)$, corresponding to the configuration identified by the blue region where the strongest binding occurs are given as the text labels. The illustrated procedure for shift top layer is also depicted in Fig. S**??**(h). The calculated binding energies (i.e. E_b) are negative for all the considered heterostructures, demonstrating the stability of each system against phase separation. The $E_b(GS)$ of MXene oxides are comparable to that of bilayer graphene, whereas the hydroxides are slightly stronger bonded due to the extra hydrogen bonds. The differences of the binding energies among different MXenes that have the same functionalized group are negligible.

Peculiarly, the binding energy profiles depicted in Fig. S**??** indicate that the change in binding energy by relative motion of M_2CX_2 layer on graphene is quite small. This clearly points out the super lubricant feature of these two materials interface. The nature of the local interlayer interactions is not the same throughout the supercell. Therefore, the overall effective interaction will be small. In addition, we found that the strength of the interlayer binding and separation for a particular M_2CX_2+Gr bilayer can be tuned by changing the type of the MXene layer, suggesting that, depending on the type of the heterostructure, metal ions larger than Li (such as Na) can be accommodated between constituent the monolayers.

For the relative orientation of the two layers, we only considered the structure, in which both armchair or zigzag edges of two materials are pointing at the same direction. The symmetry of the heterostructure is the highest in this way, thus the orientation result in either the highest or lowest total energy. If one layer is arbitrarily rotated with respect to the other one, the symmetry of the system will be lowered and the total energy will be between the mentioned extremes. Therefore, in this way of the orientation of the two layers, the resulting ground state geometries always have a common reflection symmetry with respect to the [110] line as shown in Fig.1 in the main manuscript. This holds for all types of heterostructure in this study.

---

[a] Department of Physics, University of Antwerp, Groenenborgerlaan 171 , 2020 Antwerpen, Belgium; [b] Department of Mechanical Engineering, Faculty of Engineering, Anadolu University, Eskisehir, TR 26555, Turkey; [c] Department of Physics, Bilkent University, Bilkent, Ankara 06800, Turkey; [d] Department of Physics and Astrophysics, University of North Dakota, Grand Forks, North Dakota 58202, USA; Emails:yierpan.aierken@uantwerpen.be; gulseren@fen.bilkent.edu.tr; csevik@anadolu.edu.tr; francois.peeters@uantwerpen.be; deniz.cakir@und.edu (*corresponding author)

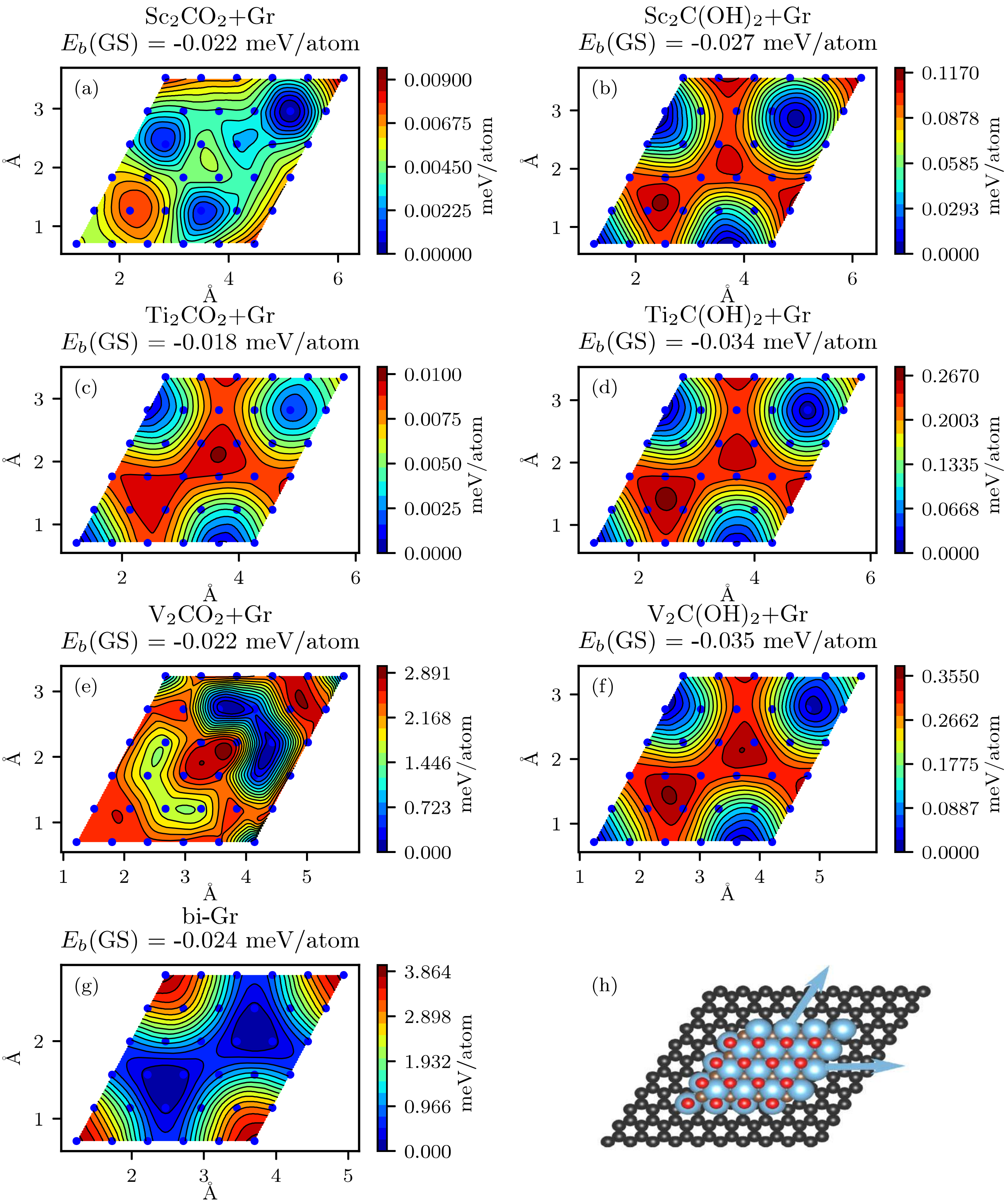

Fig. 1 (Color online) The binding energy difference of different stackings with respect to the ground state stacking binding energy, E_b(GS), in M$_2$CX$_2$+Gr heterostructure and bilayer graphene. Dots are the original data, contour maps are the interpolated results. (h) The directions toward which top layer is shifted stepwise.

Table 1 Single Li binding energy E_b^{Li} (eV/Li atom) at different inequivalent positions between heterostructures given as the difference from the strongest binding energy marked in red. Numbers are arranged in accordance with Li atom position in the structures shown in the Fig. S??. Note: Sc_2CO_2+Gr+Li is not stable since it involves strong structure distortion.

Heterostructure	Oxides (X=O)					Hydroxides (X=OH)				
			15.614					0.084		
Sc_2CX_2+Gr+Li		0.033	0.013				0.059	0.046		
	0.014	0.000	14.859			0.000	0.014	0.064		
				0.005					0.159	
			0.004	0.010				0.123	0.105	
Ti_2CX_2+Gr+Li		0.008	0.002	0.020			0.095	0.135	0.029	
	0.028	0.025	0.001	0.000		0.000	0.027	0.115	0.032	
					0.623					0.131
				0.361	0.198				0.148	0.181
V_2CX_2+Gr+Li			0.327	0.358	0.331			0.181	0.135	0.082
		0.350	0.334	0.351	0.331		0.049	0.142	0.062	0.042
	0.370	0.352	0.000	0.192	0.365	0.000	0.010	0.089	0.137	0.055

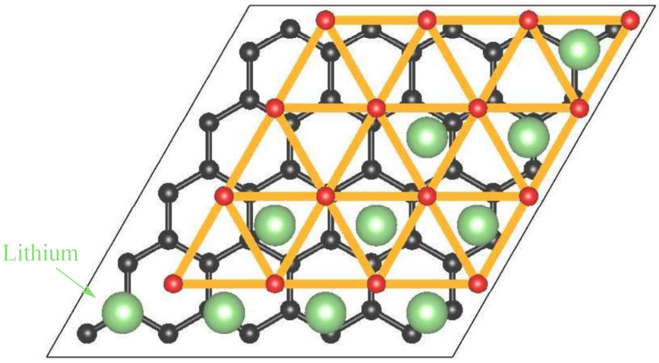

Fig. 2 (Color online) Lithium intercalation between 4×5 Ti_2CO_2+Gr heterostructure.

Single Li intercalation and its binding energy

In order to make sure that the reported Li binding energy in the main manuscript is the largest one (i.e. the ground state adsorption site), here we calculated all the possible adsorption sites between the two layers, as shown in Fig. S??. The calculated binding energy differences with respect to the ground state binding energy are listed in Table S??. This information is also important to show how the underlying graphene pattern influences the binding of Li atoms, since if it were for pure M_2CX_2 without graphene, the difference in the binding energy among the different sites should be zero, because they are equivalent sites. However, we not only can see the obverse difference in binding energies, but also see the average difference of the binding energy in each system increases when going from Sc to Ti to V, indicating that the influence of graphene become more important following the same order. As for the strongest adsorption position, $M_2C(OH)_2$+Gr+Li prefers Li on top of a C atom from graphene despite the large distance between these two atoms. This is independent of the type of M. However, this position is not preferred for the M_2CO_2+Gr+Li systems, and they shows different favorable sites depends on the type of M.