Supporting Information

Adsorption and Diffusion of Sodium in Graphene with Grain Boundaries

Xiaoli Sun,[1] Zhiguo Wang,[1*] Yong Qing Fu[2*]

1 *School of Physical Electronics, Center for Public Security Information and Equipment Integration Technology, University of Electronic Science and Technology of China, Chengdu, 610054, P.R. China*

2 *Faculty of Engineering and Environment, University of Northumbria, Newcastle upon Tyne, NE1 8ST, UK*

*Corresponding author. Tel: 862883200728. E-mail: zgwang@uestc.edu.cn (Zhiguo Wang);
richard.fu@northumbria.ac.uk (Richard Yong Qing Fu)

Table S1 Adsorption energies (in eV) of Na and Li on pristine graphene calculated with cut-off energies of 180 and 250 Ry.

	Cut-off	H	B	T
Na	180 Ry	-0.67	-0.49	-0.48
	250 Ry	-0.67	-0.49	-0.48
Li	180 Ry	-1.01	-0.71	-0.67
	250 Ry	-1.02	-0.70	-0.68

Table S2 Lists of electronic configurations for pseudopotentials generation and cut-off radii (r_c in Bohrs) for orbitals (*s*, *p*, *d*, and *f*) being used; the pseudopotential generation was performed with the ATOM program within the SIESTA package.

Element	Configuration	r_c (*s*)	r_c (*p*)	r_c (*d*)	r_c (*f*)
Li	$2s^1 2p^0 3d^0 4f^0$	2.28	2.28	2.59	2.59
Na	$3s^1 3p^0 3d^0 4f^0$	2.83	2.83	3.13	3.13
C	$2s^2 2p^2 3d^0 4f^0$	1.56	1.56	1.56	1.56

The calculated lattice constants of ionic compounds of Li_2O and Na_2O are 4.58 and 5.47 Å, respectively, which are close to the experimental values of 4.619 and 5.560 Å for Li_2O and Na_2O [1], respectively, which indicates that the pseudopotential can be successfully used to describe the alkaline ionic compounds.

Table S3 Adsorption energies (in eV) of Na on pristine graphene with different supercells.

Supercells	6×6	7×7	8×8
E_{ads}	-0.67	-0.67	-0.67

Table S4 Total energies (in eV) of supercells with and without Na adsorption and adsorption energies (in eV) calculated with cut-off energies of 180 and 250 Ry and *k*-point meshes of 2×4×1 and 4×6×1.

	k-point	Cut-off		2	3	8	10	16	17
	2×4×1	180 Ry	E_{GBs+Na}	-57688.81	-57688.76	-57688.76	-57688.73	-57689.14	-57688.96
			E_{GBs}	-57680.38	-57680.38	-57680.38	-57680.38	-57680.38	-57680.38
			E_{ads}	-0.88	-0.83	-0.83	-0.80	-1.20	-1.04
	2×4×1	250 Ry	E_{GBs+Na}	-57688.76	-57688.76	-57688.79	-57688.73	-57689.13	-57688.96
GB1			E_{GBs}	-57680.38	-57680.38	-57680.38	-57680.38	-57680.38	-57680.38
			E_{ads}	-0.88	-0.83	-0.83	-0.80	-1.20	-1.04
	4×6×1	180 Ry	E_{GBs+Na}	-57688.77	-57688.77	-57688.79	-57688.75	-57689.09	-57688.93
			E_{GBs}	-57680.29	-57680.29	-57680.29	-57680.29	-57680.29	-57680.29
			E_{ads}	-0.88	-0.83	-0.83	-0.80	-1.20	-1.04
	k-point	Cut-off		5	8	13	17	27	28
	2×4×1	180 Ry	E_{GBs+Na}	-61404.62	-61404.66	-61404.66	-61404.68	-61405.06	-61404.86
			E_{GBs}	-61396.18	-61396.18	-61396.18	-61396.18	-61396.18	-61396.18
			E_{ads}	-0.89	-0.93	-0.93	-0.95	-1.32	-1.14
	2×4×1	250 Ry	E_{GBs+Na}	-61404.62	-61404.66	-61404.67	-61404.69	-61405.06	-61404.87
GB2			E_{GBs}	-61396.19	-61396.19	-61396.19	-61396.19	-61396.19	-61396.19
			E_{ads}	-0.89	-0.93	-0.93	-0.95	-1.32	-1.14
	4×6×1	180 Ry	E_{GBs+Na}	-61404.66	-61404.68	-61404.68	-61404.70	-61405.04	-61404.84
			E_{GBs}	-61396.13	-61396.13	-61396.13	-61396.13	-61396.13	-61396.13
			E_{ads}	-0.89	-0.93	-0.93	-0.95	-1.32	-1.14

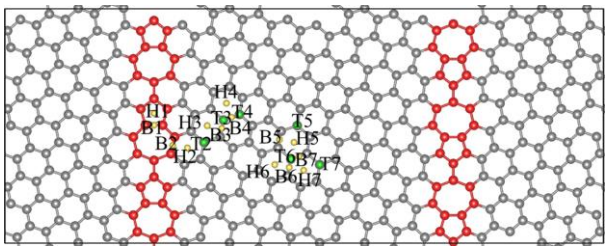

Fig. S1 Adsorption sites of Na on graphene with zig-zag oriented GB.

Table S5 Adsorption energies (in eV) of Na on graphene with zig-zag oriented GB as shown in Fig. S1.

	1	2	3	4	5	6	7
H	-1.04	-0.98	-0.90	-0.86	-0.80	-0.80	-0.79
B	-0.95	-0.87	-0.69	-0.67	-0.62	-0.62	-0.61
T		-0.73	-0.67	-0.64	-0.60	-0.60	-0.61

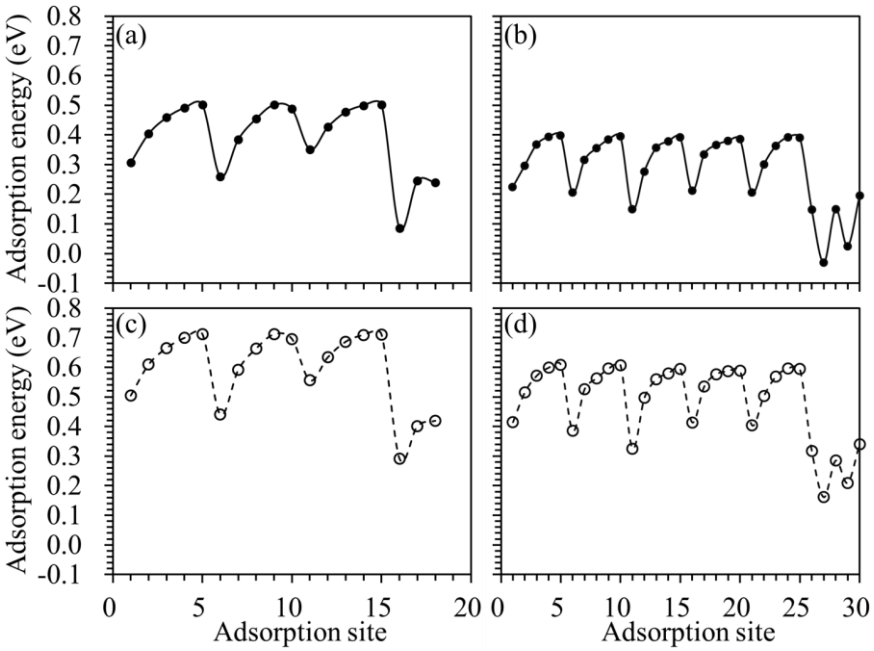

Fig. S2 Adsorption energies of sodium/lithium on graphene with (a)/(c) zigzag- and (b)/(d) armchair-oriented GBs using the reference to bulk metal as the reference state.

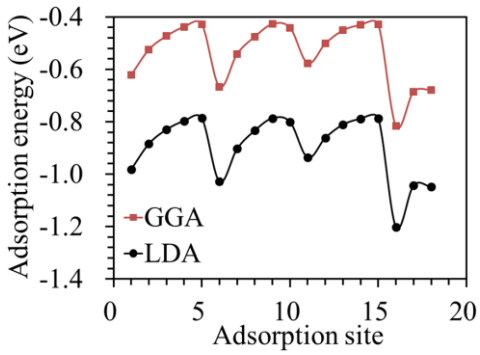

Fig. S3 Adsorption energies of sodium on graphene with zig-zag oriented GB calculated with the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional. Sodium atom shows the same adsorption behavior with those from LDA and GGA calculations expect for the absolute values. We can conclude that the calculations using LDA do not affect the conclusion of this work.

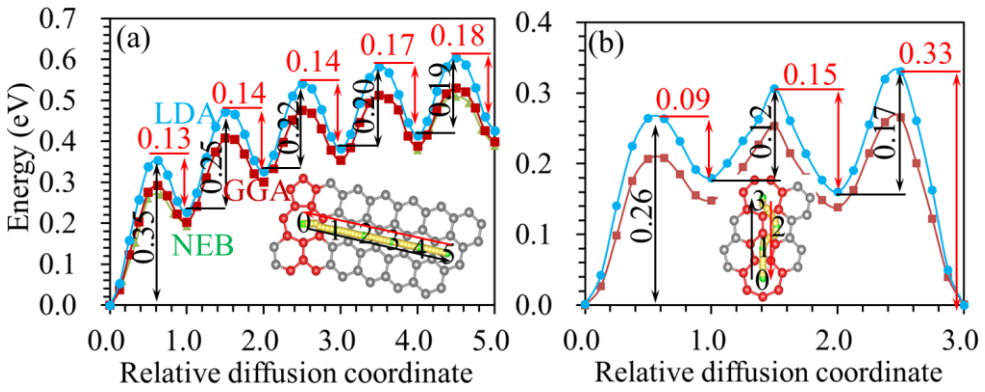

Fig. S4 Energy curves for sodium diffusion on graphene with zig-zag oriented GB calculated with tGGA functional. Sodium atom shows the same diffusion behavior with those from LDA and GGA calculations expect for the absolute values. The energy curves for sodium atoms diffusing from site 0 to site 1 and from site 4 to site 5 calculated using climbing image nudged elastic band (CI-NEB) theory also shown.

Adsorption of Na clusters on graphene with GBs. We have further investigated more sodium atoms adsorbed on graphene with GBs. We have only studied the adsorption behavior of planar structure of Na cluster, so Na_n (n=1-5) were investigated. The cluster structures of ground state geometries of free Na clusters were considered. For Na_3, Na_4, and Na_5 the corresponding isomers are an isosceles triangle, a rhombus, and planar C_{2v} isomer. The clusters are placed on graphene assumed that the hollow site is energetically favorable for each Na atoms, i.e. all the Na atoms are in contact with the graphene surface. After optimization, structural changes can be clearly observed (typical optimized atomistic configurations are shown in Fig. S5). Na dimer can keep its two Na atoms which are in contact with the graphene surface except the change of dimer bond length either the Na dimer absorbed at the GBs or far away from the GBs. Na_3 can keep its triangular shape, but the two Na

atoms are in contact with the graphene surface after relaxation. The adsorption of Na_4 and Na_5 cluster leads to a significant distortion from planarity. A pyramid structure is finally formed. The adsorption energies for Na clusters are listed in Table S6. The Na dimer has larger adsorption energy at GBs than those at the sites far away from GBs. For example, the adsorption energies are -1.01 and -0.75 eV for the dimers adsorbed at 28-29 and 19-25 (see Fig. 1), respectively, which indicates that the adsorption of Na dimers can also be enhanced by GBs. Na_3, Na_4, and Na_5 also have larger adsorption energies at GBs than those at sites far away from GBs. The graphene can keep its honeycomb structures with more sodium atoms adsorbed at GBs although the curvature is increased as shown in Figs. 3b and 3c. The results indicate that graphene with GBs can store more sodium atoms with a larger Na/C ratio, which agrees well with the recent report that the curvature can enhance the adsorption of lithium atoms on graphene [2].

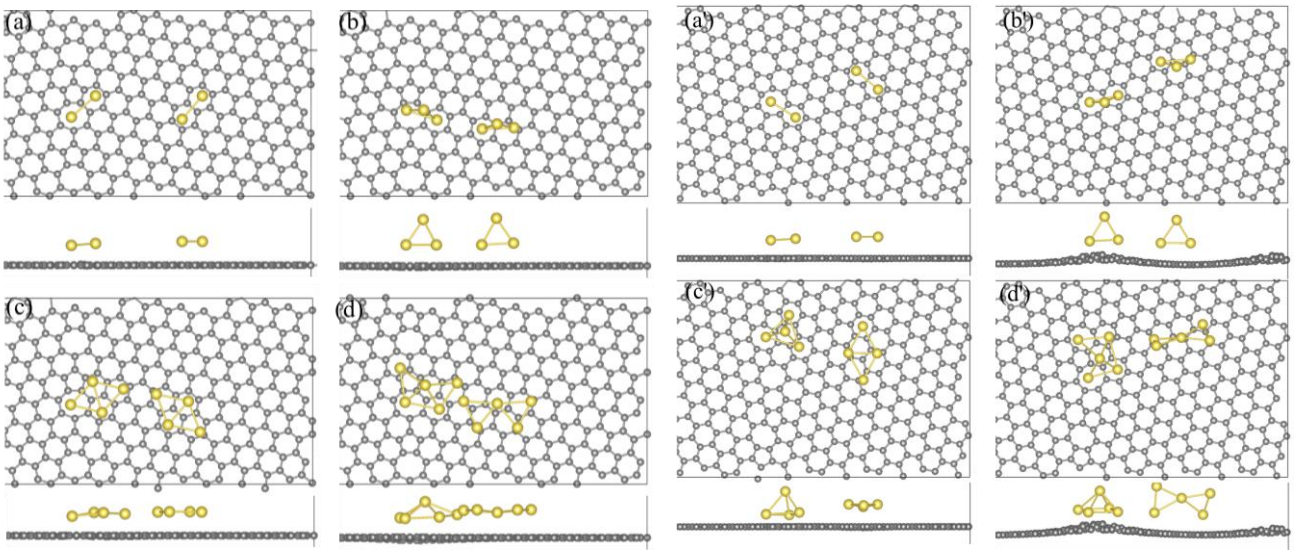

Figure S5 Optimized (a)/(a') Na_2, (b)/(b') Na_3 ,(c)/(c') Na_4 and (d)/(d') Na_5 clusters on graphene with zigzag/archair-oriented GBs shown from two perspectives.

Table S6 Adsorption energies of Na clusters adsorbed on graphene with GBs

Na_2	GB1	Configuration	16-17	16-6	16-1	17-6	17-18	6-1	6-18	15-10
		E_{ads} (eV)	-0.86	-0.87	-0.84	-0.81	-0.83	-0.79	-0.83	-0.70
	GB2	Configuration	27-11	27-16	27-21	27-28	28-11	28-29	29-11	19-25
		E_{ads} (eV)	-0.97	-0.91	-0.96	-0.99	-0.85	-1.01	-0.99	-0.75
Na_3	GB1	Configuration	6-11-17		16-6-1		6-17-18		3-4-9	
		E_{ads} (eV)	-1.14		-1.12		-1.07		-1.05	
	GB2	Configuration	6-28-29		16-21-27		27-28-29		14-15-19	
		E_{ads} (eV)	-1.27		-1.28		-1.32		-1.19	
Na_4	GB1	Configuration	1-6-7-16		6-7-11-18		4-5-9-10			
		E_{ads} (eV)	-1.04		-1.00		-0.87			
	GB2	Configuration	11-16-27-29		1-6-12-29		1-6-11-29		15-18-20-24	
		E_{ads} (eV)	-1.34		-1.33		-1.30		-0.92	
Na_5	GB1	Configuration	1-6-7-16-17		6-11-16-17-18		6-7-11-17-18		3-4-8-9-10	
		E_{ads} (eV)	-1.03		-1.00		-0.99		-0.94	
	GB2	Configuration	6-11-16-27-29		16-26-27-28-29		1-6-28-29-30		14-15-18-20-20	
		E_{ads} (eV)	-1.23		-1.21		-1.15		-1.09	

Comparison of binding energies of Na cluster with adsorption energies. The binding energies for small Na_n clusters (n=2, 3, 4, 5, 6 and 7) [3] are shown in Fig. S6a, and atomistic configurations of Na_n clusters are shown as the inset in Fig. S6a. Clearly the binding energies increase with cluster sizes. The binding energy is -0.95 eV/Na for a Na_7 cluster, which is smaller than the values of adsorption energies of Na on the sites far away from GBs (-0.79 eV for Na adsorbed at sites of 5, 9 and 15 on graphene with zigzag-oriented GB, and -0.90 eV or Na adsorbed at sites of 5, 10, 15, 20 and 25 on graphene with armchair-oriented GB). The result indicates that Na clusters may form on pristine graphene. Whereas the binding energies of Na_n clusters are smaller than the adsorption energy of the sodium atoms at GBs as shown in Fig. 3a, such as -1.20 and -1.32 eV for sodium atoms adsorbed at site 16 on graphene with zigzag-oriented GBs and site 27 on graphene with armchair-oriented GBs. Therefore, the existence of GBs could prevent formation of Na clusters on graphene.

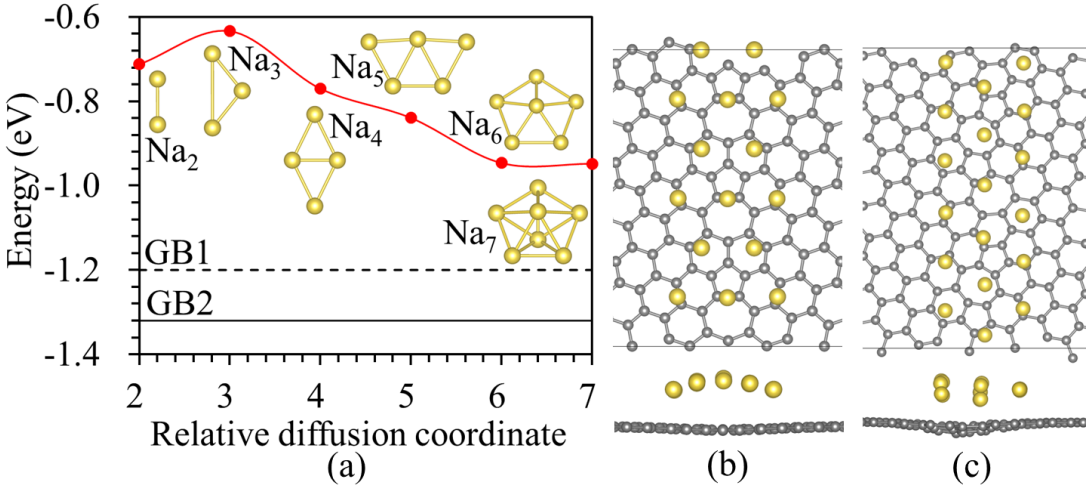

Figure S6 (a) Binding energies for small Na_n clusters (*n*=2, 3, 4, 5, 6 and 7). Atomistic configurations for more sodium atoms adsorbed at (b) zig-zag and (c) armchair-GBs.

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[3] P. Calaminici, K. Jug, A.M. Köster, Static polarizabilities of Na_n($n\leqslant 9$) clusters: An all-electron density functional study, J. Chem. Phys. 111 (1999) 4613-4620.