Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

DFT calculations of the synergistic effect of λ-MnO_2/Graphene composites for electrochemical adsorption of lithium ions

Huixin Zhang,[a] Xiao Du,[a] Shengqi Ding,[a] Qiang Wang,[a] Lutong Chang,[a] Xuli Ma,[a] Xiaogang Hao**[a] and Changjun Peng[b]*

[a]Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China.

[b]State Key Laboratory of Chemical Engineering and Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, P. R. China

*Corresponding author: duxiao@tyut.edu.cn (*Xiao Du*)
**Corresponding author: xghao@tyut.edu.cn (*Xiaogang Hao*)

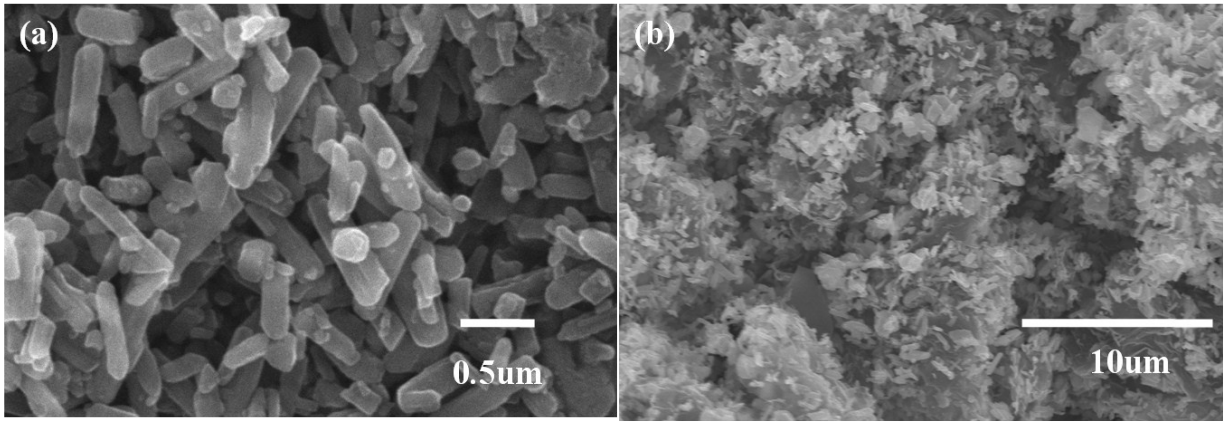

Fig. S1 SEM images of (a) λ-MnO_2 and (b) λ-MnO_2/Graphene.

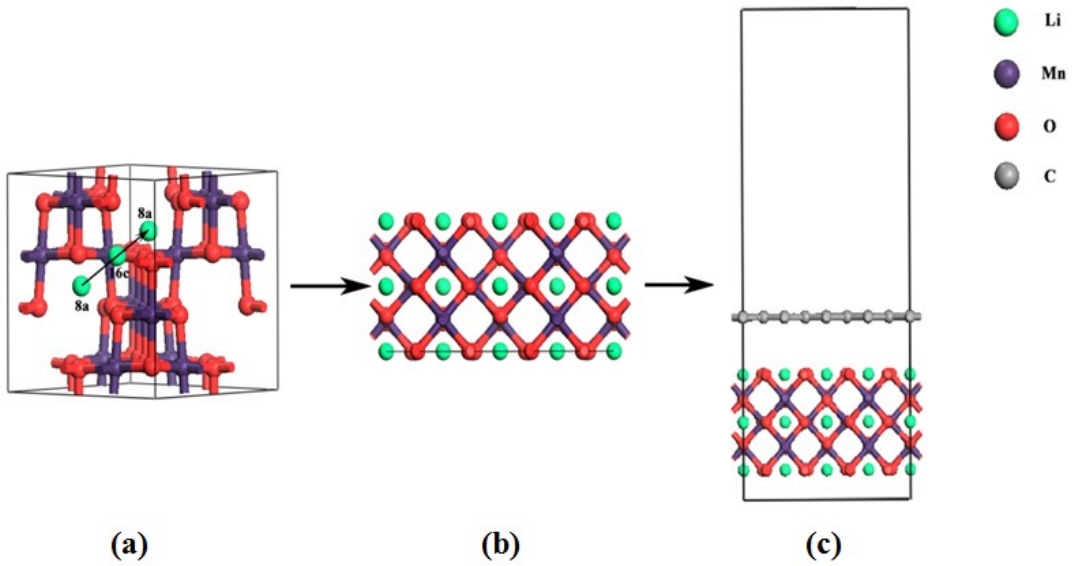

Fig. S2 The building process of λ-MnO_2/Graphene with Li model: (a) the diffusion path of Li in λ-MnO_2; (b) the (1 0 1) crystal plane of $LiMn_2O_4$; (c) the building model of λ-MnO_2/Graphene with Li.

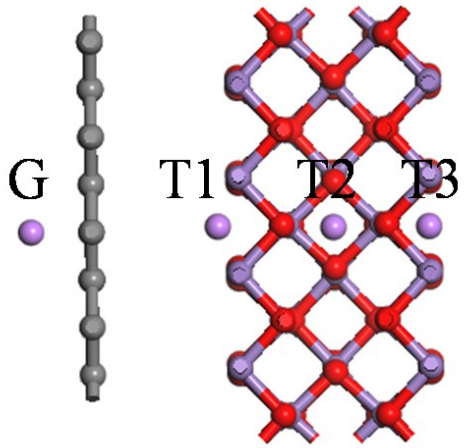

Fig. S3 The adsorption sites of the Li atoms in λ-MnO_2/Graphene.

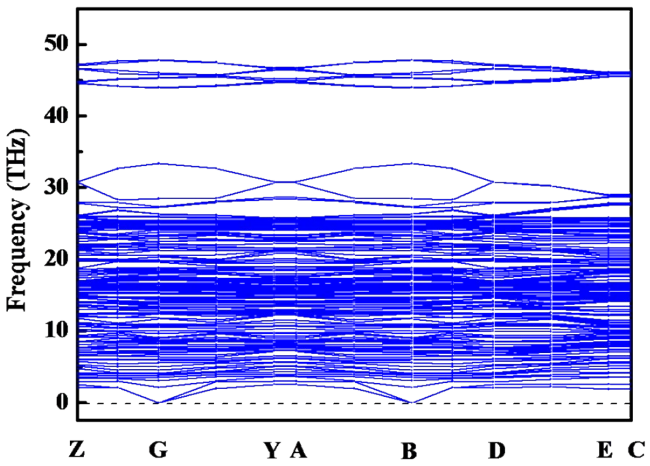

Fig. S4 Calculated phonon dispersion curves of λ-MnO_2/Graphene.

Table S1 Distance and energy before and after optimized λ-MnO_2/Graphene

Distance of λ-MnO_2/Graphene (Å)	Optimized distance of λ-MnO_2/Graphene (Å)	Energy of λ-MnO_2/Graphene (eV)
5	4.845	-35396.419
4.5	4.306	-35396.435
4	3.895	-35396.677
3.5	3.406	-35396.948
3	3.008	-35396.627
2.5	2.609	-35395.077
2	2.558	-35392.794

Table S2 The binding energies of Li at different positions of λ-MnO_2/Graphene

Position of Li	Bonding energy (eV)
G	-2.0234728
T1	-5.6050328
T2	-4.9601237
T3	-5.0477628
T1	-5.6017268 (With dipole correction)

Table S3 The values of L_{Mn-O} and d_{Li-O} in $LiMn_2O_4$ bulk and $LiMn_2O_4$/Graphene interface

	L_{Mn-O} (Å)	d_{Li-O} (Å)
Inside of $LiMn_2O_4$	1.967	1.911
Interface of $LiMn_2O_4$/Graphene	1.943	1.934

Table S4 Mulliken charges population and bond population for MMn_2O_4 (M = Li, Na, Mg)

M		Mulliken population analysis
Li	Li (e)	1.06
	Li-O	0
Na	Na (e)	0.84
	Na-O	0.13
Mg	Mg (e)	1.79
	Mg-O	-1.38

Table S5 The electrode values of graphene, λ-MnO_2 and λ-MnO_2/Graphene in EIS

Electrode	Graphene	λ-MnO_2	λ-MnO_2/Graphene
R_e (Ω)	35.42	29.96	27.88
C_L (F)	$2.999*10^{-5}$	$8.046*10^{-5}$	$2.119*10^{-5}$
R_{ct} (Ω)	43.12	21.03	16.25
Z_w (Ω)	$2.164*10^{-3}$	$7.624*10^{-3}$	$5.255*10^{-2}$
C_{dl} (F)	$1.878*10^{-3}$	$2.477*10^{-2}$	$1.810*10^{-1}$