Supporting Information

Structure, stability and property modulations of stoichiometric graphene oxide

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In the supporting Information, we provide some additional results for better understanding our studied system, including: structural parameters of all the studied structures, and the geometric structure, stability and electronic properties of a-GMO configuration, and single layer deposition of metal atoms on z-GMO.

1. Structural parameters

We list the structural parameters in Table S1 for all the studied systems.

Table S1. Geometrical parameters of GMO and GDO (the vacuum layer is set as 15Å, the lattice parameters are given in order of a, b, c, α, β, γ).

Structure	Space group	Lattice parameters (Å)			Atom	Wyckoff positions		
z-GMO	*Pmma*(51)	2.25	2.68	15.0	C(2e)	0.7500	0.0000	0.4703
		90°	90°	90°	O(2f)	0.2500	0.5000	0.5854
a-GMO	*Pmma*(51)	5.02	2.27	15.0	C(4i)	0.4192	0.0000	0.4551
		90°	90°	90°	O(4j)	0.0100	0.5000	0.4045
ep-GMO[1,2]	*Cmmm*(65)	2.64	5.68	15.0	C(4h)	0.3259	0.0000	0.5000
		90°	90°	90°	O(4l)	0.5000	0.0000	0.5697
mix-GMO[2]	*Cm*(8)	9.42	5.27	15.0	C(4b)	0.0484	0.1415	0.4401
		90°	90°	90°	C(4b)	0.9144	0.3110	0.4319
					C(4b)	0.2856	0.6432	0.4081
					O(4b)	0.1599	0.2344	0.3906
					O(2a)	0.8976	0.5000	0.5006
					O(2a)	0.9300	0.5000	0.3644
					O(2a)	0.3230	0.5000	0.3313
					O(2a)	0.5703	0.5000	0.5203
GDO	$P\bar{4}m2$ (115)	2.34	2.34	15.0	C(1c)	0.5000	0.5000	0.5000
		90°	90°	90°	O(2g)	0.5000	0.0000	0.4587

2. The stability and properties of a-GMO configuration

As is mentioned in the main text, the total energy of the metastable a-GMO is slightly higher than z-GMO but still more energetically favorable than ep-GMO and mix-GMO. Here we present its optimized geometrical structure (Figure S1), dynamic

and thermodynamic stability (Figure S2), and electronic structure (Figure S3).

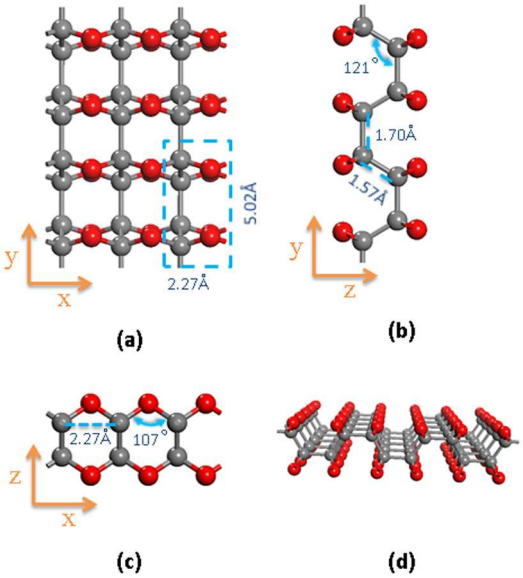

Figure S1. Different views of optimized a-GMO: (a) along z direction; (b) along x direction; (c) along y direction; (d) perspectiveview. Red and grey balls are oxygen and carbon atoms, respectively.

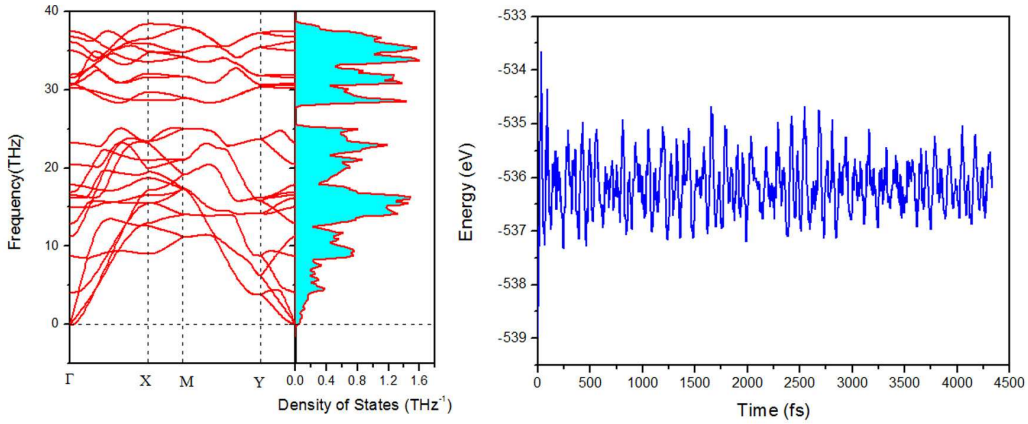

Figure S2. (a) Phonon dispersion band structures and the corresponding phonon density of states of a-GMO. The high symmetric Brillouin zone points are Γ (0, 0, 0), X (1/2, 0, 0), M (1/2, 1/2, 0), and Y (0, 1/2, 0). (b) Total energy fluctuation with respect to time during molecular dynamics simulations within a (3×3) supercell at the constant temperature of 300K.

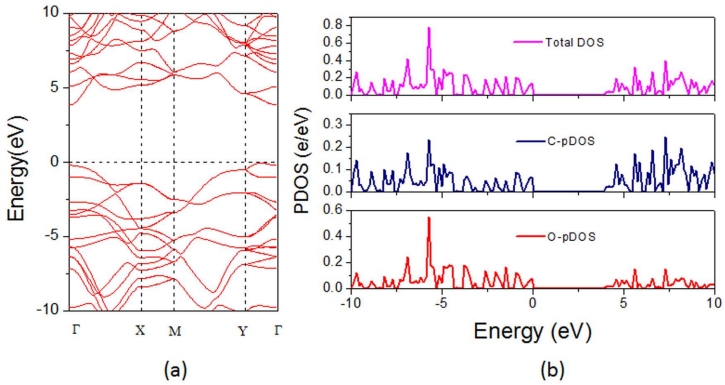

Figure S3. (a) Electronic band structure and (b) PDOS of a-GMO. The high symmetric Brillouin zone points in (a) are Γ (0, 0, 0), X (1/2, 0, 0), M (1/2, 1/2, 0) and Y (0, 1/2, 0).

The a-GMO structure (consisting of armchair carbon chains linked by O atoms) is a metastable state. It is interesting to note that the armchair carbon nanotubes are more metallic-like than the zigzag one, but a-GMO shows much larger energy band gap (3.90 eV) as compared with z-GMO (0.90 eV). Moreover, we found a-GMO dispalys larger anisotropy in its in-plane elastic modulus (See Table 1 in the main text). Since a-GMO can be stable up to 2000 K as the z-GMO does, and energy difference is quite small, a-GMO is also expected to be observed in experiment. The big differences between z-GMO and a-GMO in energy band gap and in-plane elastic modulus clearly indicate that the properties of graphene oxide are very sensitive to the structural details and synthesis details even in stoichiometric condition.

3. Deposition of metal atoms on z-GMO

Due to the special configuration of oxygen in z-GMO, the following question would be asked: is it possible to use z-GMO as a substrate for the single layer deposition of metal atoms? To explore this, we extensively studied the stability of

metal atoms on z-GMO including Li, Be, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni Cu and Zn. We found that only Li can be stably absorbed on the z-GMO forming a single layer without clustering (Figure S4 in SI), where (1×2) reconstruction occurs resulting in slight bucklings. This is because the Li-O ionic bond (341 kJ/mol bond dissociation energy) is much more stable than Li-Li metal bond (106 kJ/mol bond dissociation energy). The stability of Li-z-GMO is verified through *ab initio* molecular dynamics simulations under 300 K for 5 ps.

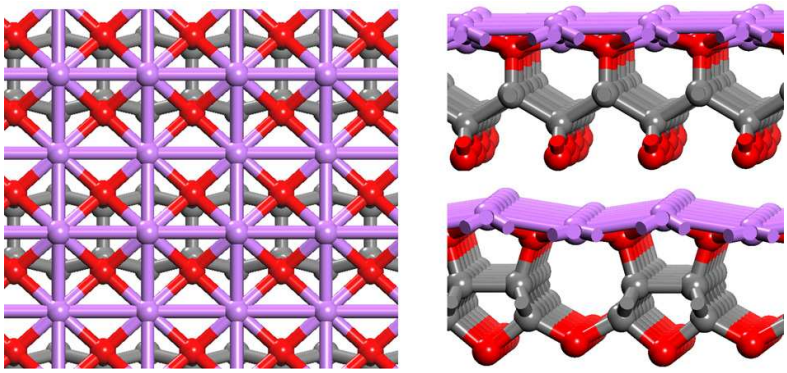

Figure S4. Different views of optimized geometry for Li-z-GMO.

REFERENCES

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