Supporting Information

Ordered Three-fold Symmetric Graphene Oxide/Buckled Graphene/Graphene Heterostructures on MgO (111) by Carbon Molecular Beam Epitaxy

Chad Ladewig[1,‡], Tao Cheng[2,‡], Michael D Randle[3], Jonathan Bird[3], Opeyemi Olanipekun[1], Peter A. Dowben[4], Jeffry Kelber[1,], and William A. Goddard III[2,]**

1Deptartment of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, TX USA

2Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA

3Department of Electrical Engineering, University at Buffalo, the State University of New York, Buffalo, NY 14260-1900, USA

4Department of Physics and Astronomy, Nebraska Center for Nanostructures and Materials, University of Nebraska-Lincoln, Lincoln, NE 68588-0299, USA

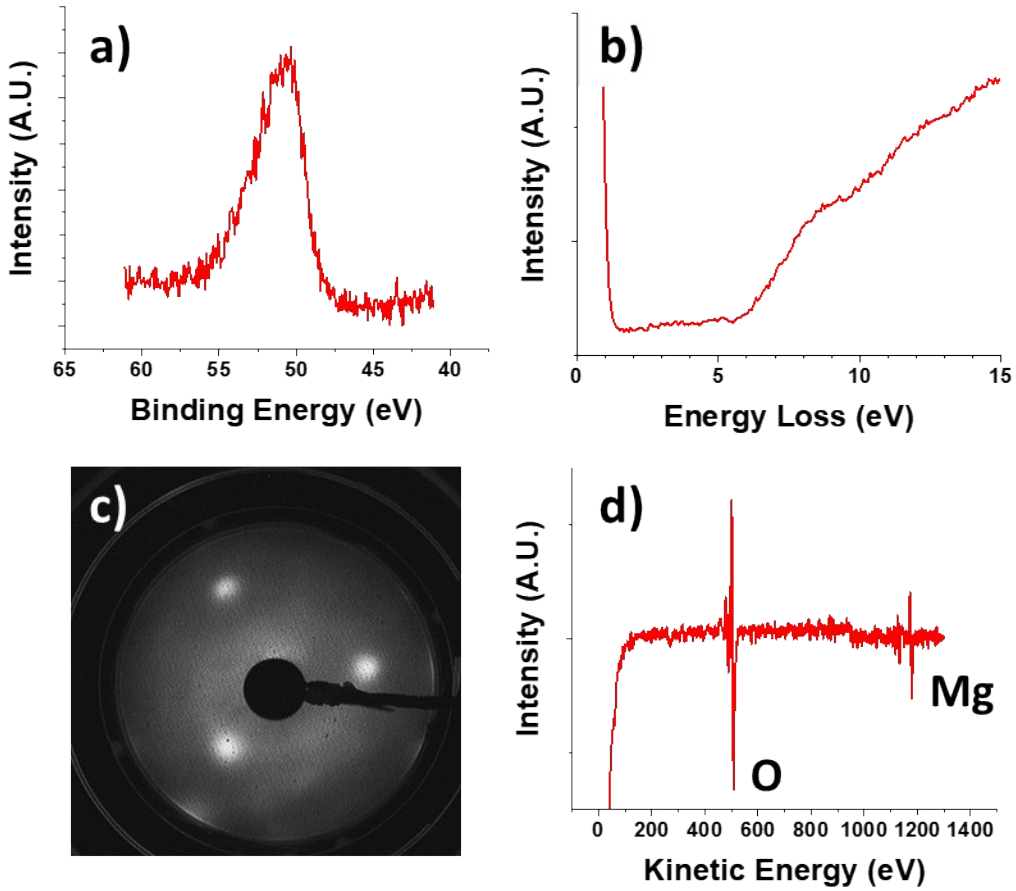

Fig. S1: (a) O 1s and (b) Mg 2p XPS spectra, (c) EELS spectrum and (d) LEED pattern for a clean hydroxylated MgO (111) single crystal. (e) AES of DC sputter deposited MgO film on Ru (0001). EELS and LEED were acquired at a beam energy of 100 eV.

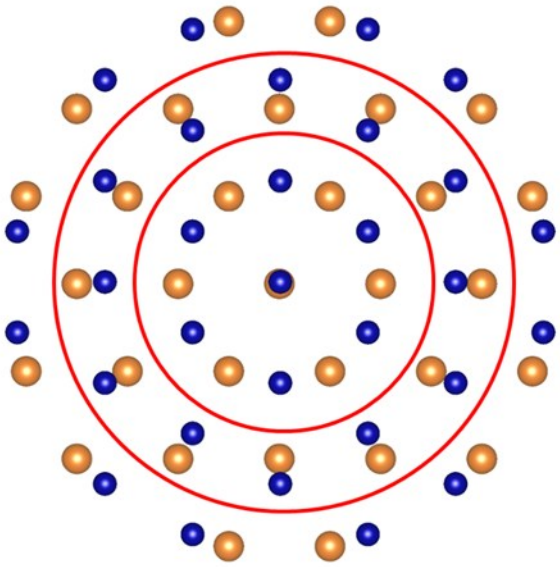

Fig. S2: Simple representation of two stacked lattices rotated 30^{O} from one another. Image shows ring composed of twinned atoms similar to that observed for the LEED image of the DC sputtered MgO(111) film. (Fig. 5d.) Red lines are guides to the eye.

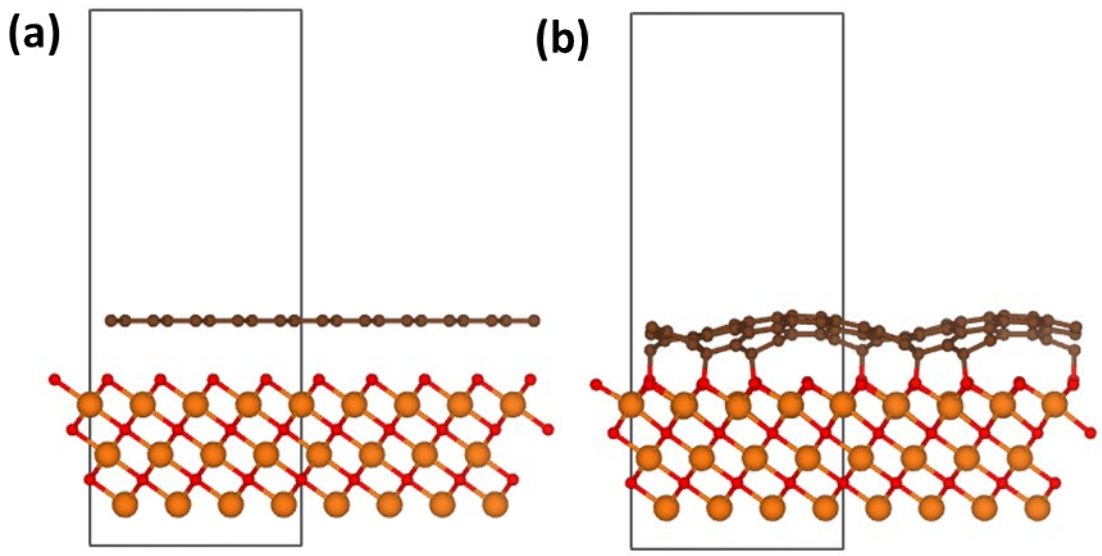

Fig. S3: The first layer of graphene on MgO (111) surface (a) flat graphene (before optimization) and (b)buckled graphene (after optimization)

We started the simulation from a flat graphene (5×5) on Mg (111) surface (4×4) as shown in Fig. S2(a). After optimization, the graphene automatically buckled with three carbon atoms forming valence interaction with surface oxygen. Considering that 5×5 graphene is 3.07% larger than 4×4 MgO (111), we suspected that the curved graphene layer may attribute to the surface mismatch. Thus, we removed one of the bonded carbon atoms to reduce the surface mismatch by 2%, leading to a defected first layer graphene. The optimized structure is as shown in Fig. 1, which is also buckled. Accordingly, we confirm that the curved surface comes from the valence interaction between first layer graphene, instead of surface mismatch.

The formation energy of curved graphene is -0.21 eV/C atom according to equation 1. Instead, the formation energy of defected graphene is -0.28 eV/C atom. Thus, the defected graphene is energetically more favorable, which also processed C3V symmetry.

We estimated the vacancy formation energy (E_v) as follows:

$$E_1 = \sum_i^N E_i = N \cdot E_{coh}^1 \tag{S1}$$

$$E_2 = \sum_i^{N-1} E_i = (N-1) \cdot E_{coh}^2 \tag{s2}$$

$$E_v = (N-1) \cdot (E_{coh}^1 - E_{coh}^2) = E_2 - \frac{N-1}{N} \cdot E_1 \tag{s3}$$

Here, E_1 is $E_{full} - E_{MgO(111)}$ and E_2 is $E_{defect} - E_{MgO(111)}$. The formation energy of the vacancy is thus -4.03 eV.