Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for

Graphene Nucleation on a Surface-MoltenCopperCatalyst: Quantum Chemical Molecular Dynamics Simulations

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Contents

Movie and Figures

Movie S1. The dynamics of transformation of defect rings into hexagonal rings in trajectory 6. The total length of the movie is 2.7ps; each frame is separated by 0.1 ps. Red and yellow spheresrepresent the top terrace and low terrace copper atoms, respectively. Cyan spheres represent the carbon atoms.

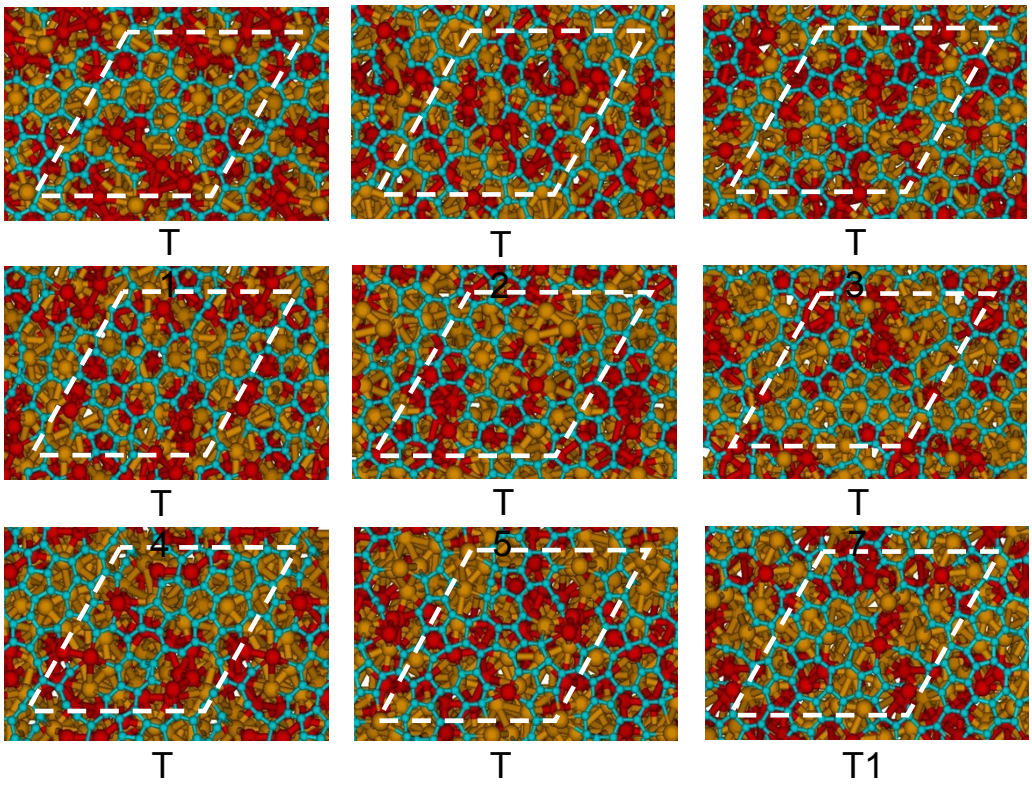


Figure S1. The snapshots (extended periodic boundary condition) of graphene flakes with metal doped point defects for the other 9 trajectories.

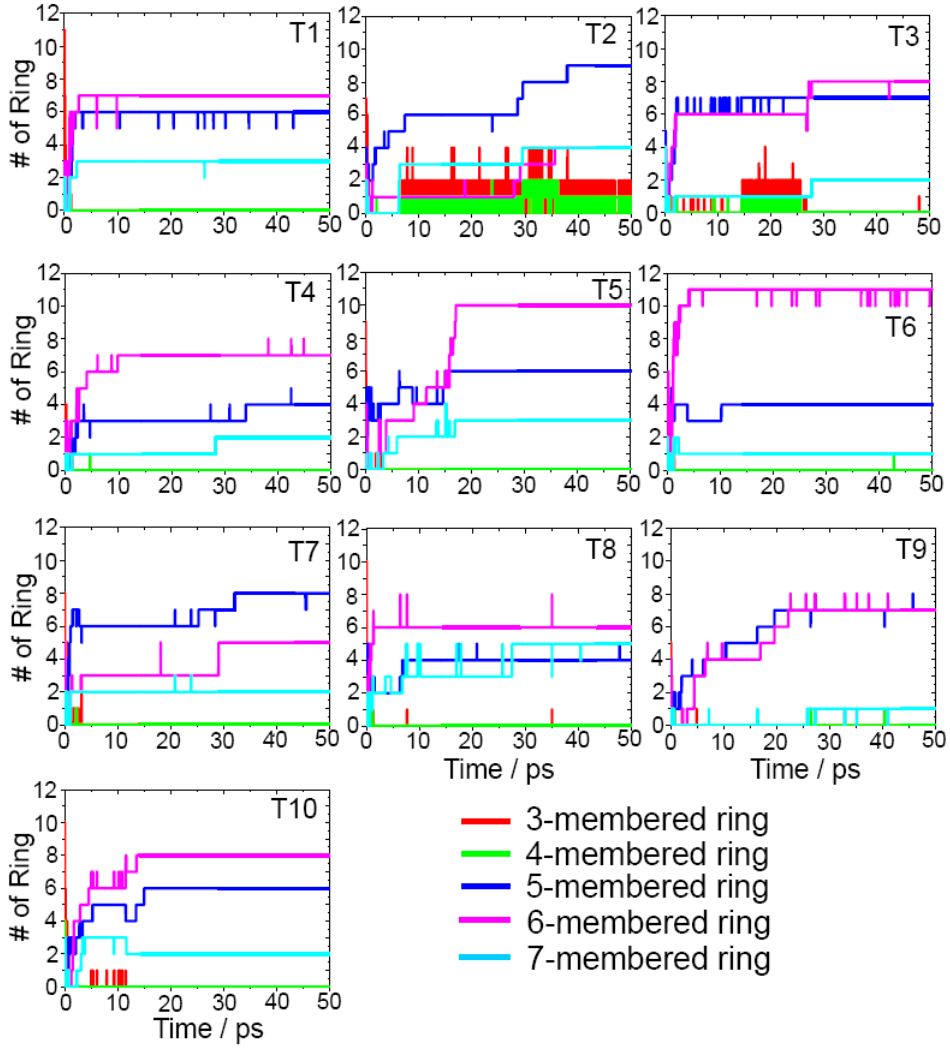


Figure S2. Polygonal carbon ring formation statistics as a function of time for each of the 10 trajectories.

1. Computational Methodology for DFTB Parameter Development

Electronic DFTB parameters for the Cu-Cu and Cu-C atom pairs are those developed by Cui *et al*.[1] However, considering the context in which these parameters were developed (*i.e.* systems of biological interest, such as Cu-containing enzymes/proteins), their benchmarking in the context of solid-state systems is warranted. To this end, we compare band structure and densities of states (DOSs) of various Cu and Cu-C systems relevant to graphene growth with plane-wave density functional theory (DFT) calculationsin included in Section 1.1. For the DFT calculations, we use the PBE exchange-correlation functional[2] with a plane-wave cutoff of 500 eV as implemented in a first principles simulation package (VASP).[3] This method was also employed for the development of a new Cu-Cu repulsive potential, described in Section 1.2 and benchmarked in Section 2.

1.1. Benchmark of the Cu-Cu/Cu-C DFTB Electronic Parameters

Benchmarks of DFTB parameters employed a four-layer Cu(111) slab with 2 x 2 atoms in one layer (a total number of copper atoms are 16) was used with each slab separated by 25 Å to avoid the interactions between neighboring slabs. A k-point sampling of 12 x 12 x 1 was chosen to ensure converged results. For all DFTB calculations, no electron smearing (via electron temperature) was employed. DFT and DFTB Band structures and DOS for this Cu(111) surface are presented in Figure S3. The slight shift observed in the Fermi level predicted using DFT and DFTB shown in Figure S3(a) is within the limits expected for the DFTB method. The DOS between -5 and -5 eV computed using DFT and DFTB is in good agreement, for both the valence and conduction bands. Band structure and DOS for the same Cu(111) surface with an adsorbed carbon atom are shown in Figure S4, and the results remain in good agreement. From both benchmarking works, we could come to the conclusion that the application of the electronic Cu-Cu/Cu-C parameters developed by Cui *et al.*[1] is reliable for our purposes.

1.2. Cu-Cu DFTB repulsive potential

The Cu-Cu DFTB repulsive potential was developed using the automatic parameterization scheme of Bodrog *et al.*[4] in conjunction with a model bulk fcc copper system. The supercell consisted of a single atom, 12 x 12 x 12 k-point sampling was employed to ensure adequate convergence, and the lattice parameters of the bulk Cu structure were initially optimized. In order to alleviate convergence issues, a finite electronic temperature of 40 K was employed in the DFTB calculations.

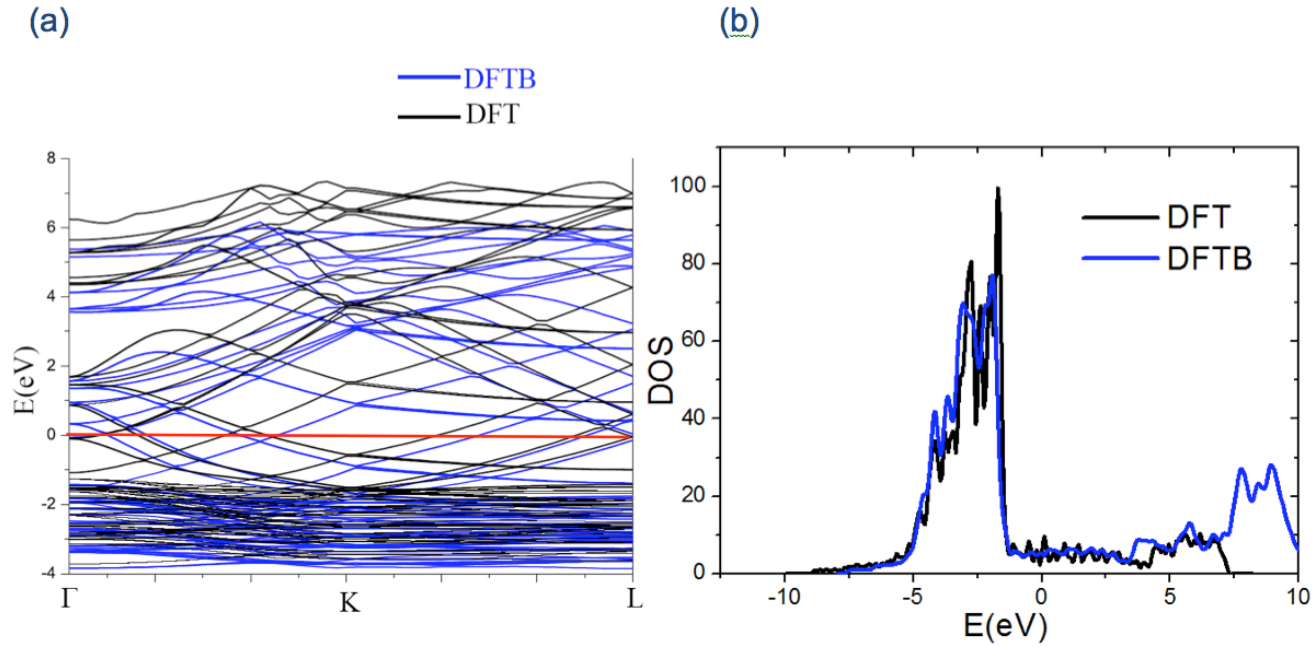


Figure S3. (a) Band structures and (b) DOS of Cu(111) surface predicted with DFT and DFTB.

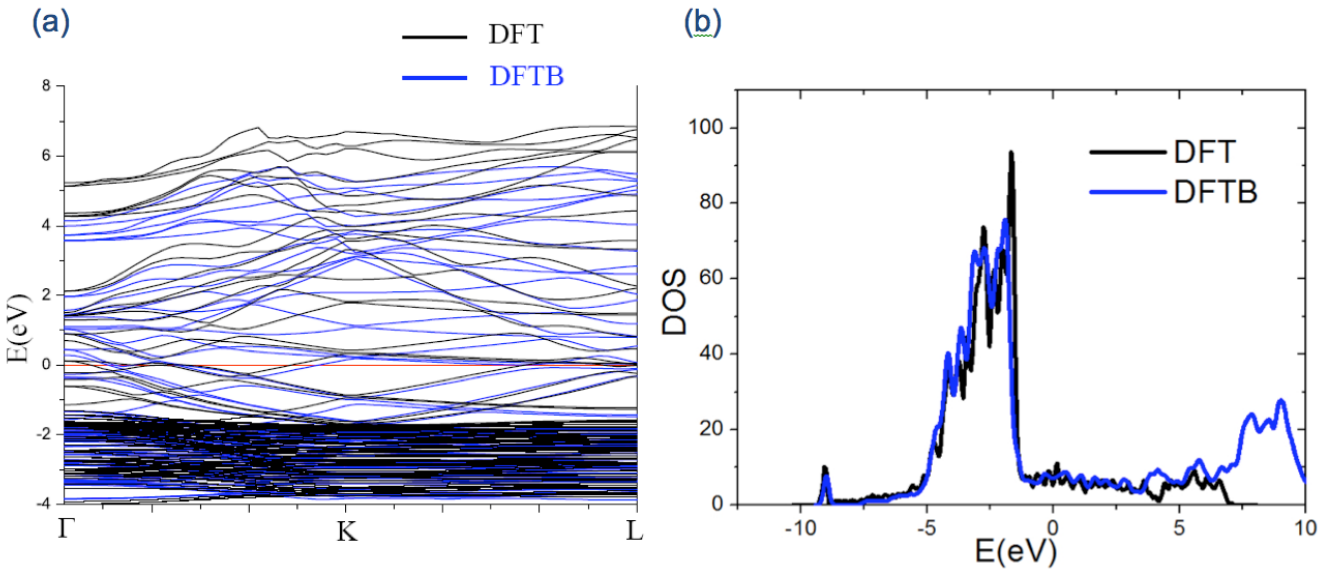


Figure S4. (a) Band structures and (b) DOS of Cu(111) surface with one adsorbed carbon atom predicted with DFT and DFTB.

2. Benchmarks of Cu-Cu parameter

2.1. Cu(111) Structural Parameters

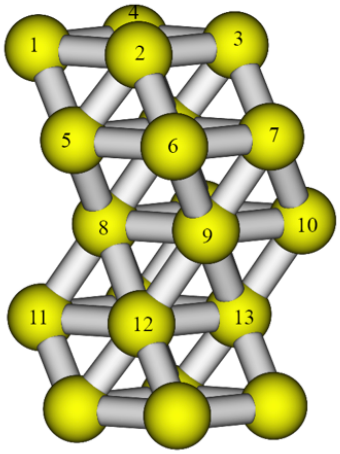
Optimized structural parameters of model 4- and 5-layer Cu(111) surfaces obtained with DFTB are compared with DFT calculations in Table S1. It is evident that Cu-Cu parameter we produced could give rise to the similar bond lengths of Cu surface compared to the DFT results.Within the “bulk” region

of the surface, the agreement is near perfect, with all bond lengths agreeing to within 0.05 Å. For the surface layer, a larger difference of 0.14 Å is observed, and is attributed to the fact that the repulsive potential was developed using bulk structural data. Nevertheless, the magnitude of this difference is sufficiently small to be disregarded.

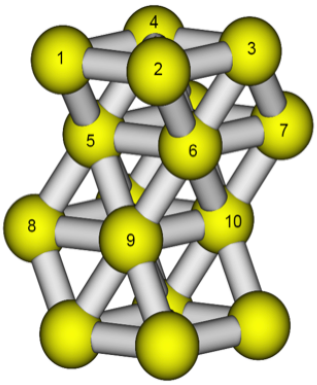
Table S1. Bond lengths of Cu(111) surfaces (four and five layers) using DFT and DFTB methods and the corresponding difference.

Parameters	DFT	DFTB	ΔR	%ΔR
$R_{1\text{-}5}$	2.55 (2.56)	2.42 (2.42)	-0.13 (-0.14)	-5.28% (-5.44%)
$R_{5\text{-}8}$	2.56 (2.56)	2.57 (2.59)	0.01 (0.03)	0.46% (1.20%)
$R_{8\text{-}11}$	2.56	2.57	0.01	0.48%

* The data in the parenthesis is the parameters of Cu(111) with four layers;
* ΔR is the data of $R_{(DFTB)}-R_{(DFT)}$;
* %ΔR is the data of $[R_{(DFTB)}-R_{(DFT)}]/R_{(DFT)}$ * 100%;
* The symbols of bond length are shown in the below schemes of Cu(111) with five and four layers respectively.



five layer



four-layer

2.2. Cu Energetic Parameters

In order to verify that the Cu-Cu parameters provide reasonable energetic results, we have calculated the cleavage energy of copper atoms in Cu(111), Cu(110), and Cu(100) surfaces. This energy is defined as the difference of surface copper (E_{slab}) and bulk copper (E_{bulk}). The formula is:

$$E_{cleavage}(eV)=\frac{1}{2}[E_{slab}-n*E_{bulk}]$$

where n is the number of the copper atoms in the slab, E_{bulk} is the energy we got above with one copper atom model. Cleavage energies of these three copper facets are given in Figure S5. Both DFT and DFTB predict that the Cu(111) surface has the lowest cleavage energy, while the Cu(110) has the largest cleavage energy. Thus, while DFTB underestimates the DFT cleavage energy, trends predicted using DFT and DFTB are nevertheless in qualitative agreement. This is generally the case for other transition metals as well, as illustrated by the comparison of Ni(110), Ni(100) and Ni(111) cleavage energies computed using DFT and DFTB, shown in Figure S5b.

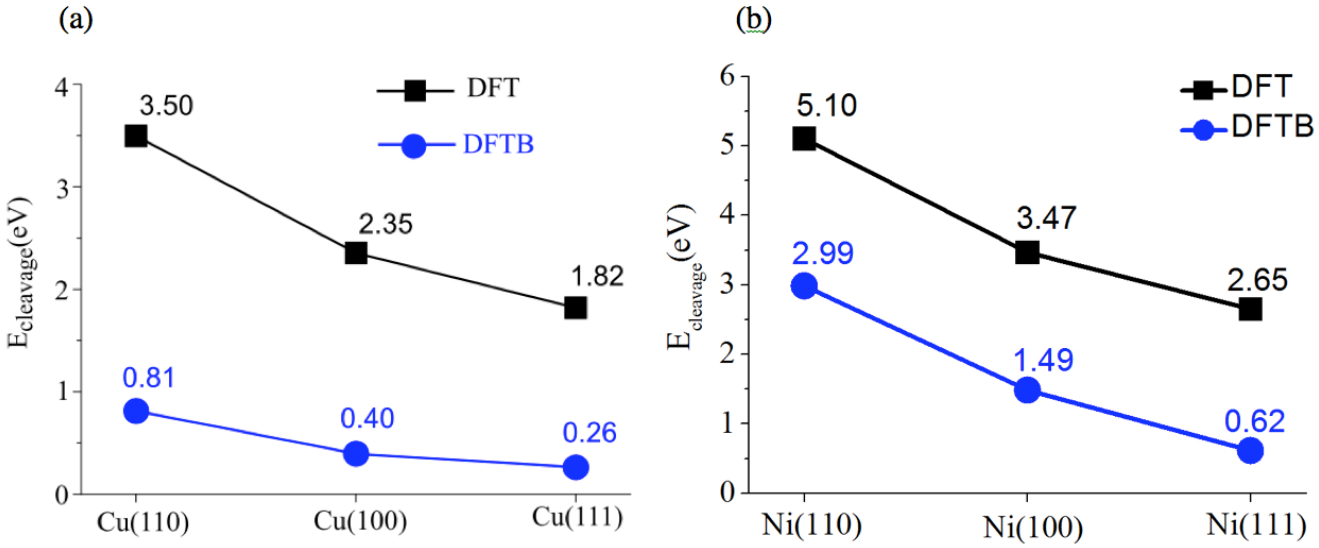


Figure S5. The cleavage energy of (111), (110), and (100) (a) Cuand (b) Ni surfaces, computed using DFT and DFTB, respectively. The Ni DFTB calculations use the existing trans3d-0-1 parameter set.[2]

2.3. Carbon adsorption on copper surfaces

For carbon adsorption on Cu(111), DFTB predicts that the bridge-site is the most favourable, with Cu-C bond length of 1.96 Å. Based on this optimized structure from DFTB calculation, we re-optimized it using DFT method, we found the bond length is shortened by 0.11 Å, as show in Figure S6. Similar agreement is obtained for the Cu(100) and Cu(110) facets (data not shown). These results are in exact agreement with previous results regarding the relative stability of C-adsorption sites on Cu(111).[5]

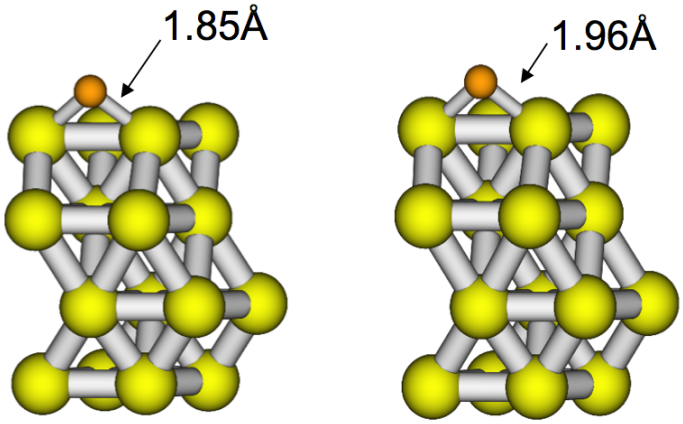


Figure S6. Carbon atom adsorption on Cu(111) surface predicted using PBE (left) and SCC-DFTB (right).

The potential energy surface for this adsorption (as a function of Cu-C bond length) is depicted in Figure S7. This figure shows that over a wide range of Cu-C bond distances, DFTB remains consistent with DFT.

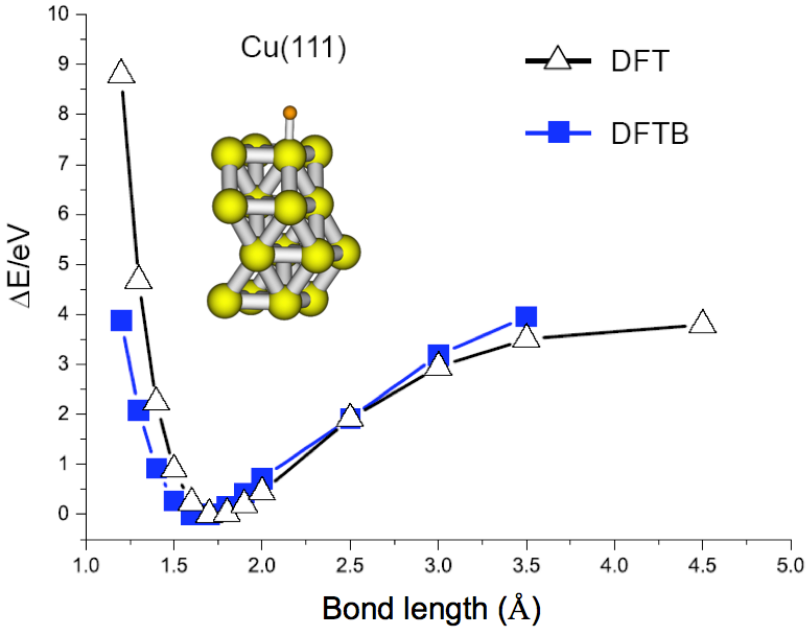


Figure S7. The potential energy surface for C-atom - Cu(111) interaction.

3. References

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