Self-assembled metallic nanoparticle superlattices on large-area graphene thin films: growth and evanescent waveguiding properties

Electronic Supplementary Information

Tianhao Ouyang [1], Arash Akbari-Sharbaf [1], Jaewoo Park [1], Reg Bauld [1], Michael G. Cottam[1,2], and Giovanni Fanchini[1,2,3]

[1] *Department of Physics and Astronomy, University of Western Ontario, 1151 Richmond St, London, ON N6A 3K7, Canada*

[2] *Centre for Advanced Materials and Biomaterials Research (CAMBR), University of Western Ontario, 1151 Richmond St, London, ON N6A 5B7, Canada*

[3] *Department of Chemistry, University of Western Ontario, 1151 Richmond St, London, ON N6A 5B7, Canada*

S1 Variable periodicity along the y-axis

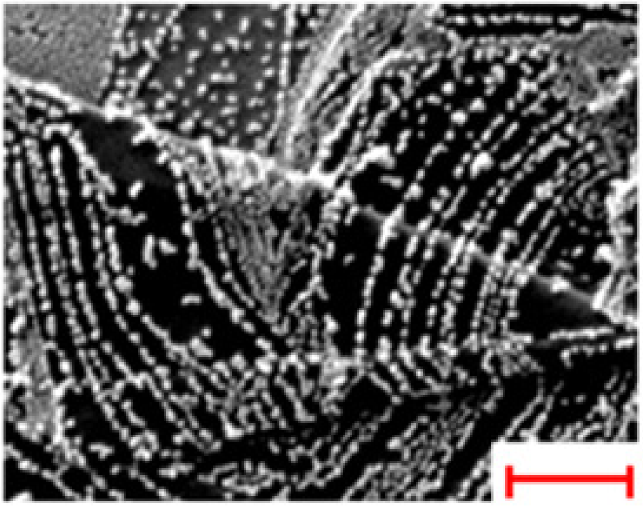

Figure S1: SEM micrograph of curved lines of Cu-np's formed at the inter- section of an armchair and zigzag edge (30^0 angle, clearly visible on the right end of the image) on a sample annealed at 360˚C for 5 hrs (scale bar = 200 nm).

Different arrangements along the y-axis are obtained on graphene-based thin films in specific locations. These arrangements are mostly associated with a combination of annealing conditions and the underlying graphene structures. As discussed in detail in the paper, lines of Cu-np's typically align along armchair edges and crystallographic directions of a graphene flake, which are normally more naturally abundant than their zigzag counterparts. A remarkable exception occurs in the proximity of the intersection of an armchair and zigzag edge, which is normally indicated by angles of 30^0 or 90^0 between two boundaries, as opposed to angles of 60^0, 120^0 and 180^0, which are typical of intersections between two armchair directions**. Figure S1** shows curved lines of Cu-np's at relatively constant interline spacing, which are typical of this situation.

S2 Superlattices obtained at higher temperatures and shorter times

Figure S2: Partially ordered Cu-np lines (500˚C annealing for 3 hrs). Fluctuations of the interline spacing, Δy, are larger than at the most optimal superlattice formation conditions (500˚C, 8 hrs) (scale bar = 500 nm)

Superlattices also form under other conditions, different from 360^{o}C and 8 hrs annealing, such as higher temperatures at short times and lower temperatures and long times, with variations in particle diameters, Δx and Δy. However superlattices in these cases, if formable, appear to have smaller Δx and Δy at short annealing times, especially at the areas near the armchair edges. A superlattice obtained in an annealing attempt at 500 ^{o}C and 3 hrs, shown in the **Figure S2**, displays a supportive Δy (11±2 nm) and a less distinguishable Δx.

S3 Distribution along armchair direction

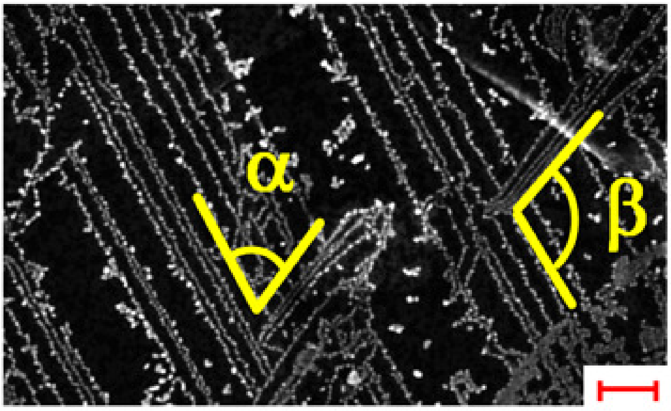

Figure S3: SEM images taken from sample obtained at 335˚C and 8 hrs. When lines intersected with each other, under most circumstances observed, they formed an angle of approximately α = 60±3˚ or β=120±4˚, indicating a strong distributing dependence along armchair directions of the underlying graphene flake (scale bar = 200 nm).

S4 Theoretical model

Decorating the surface of graphene with metal atoms can serve as a method for doping graphene without dramatically altering its bond and geometrical structure. On the one hand, metal atoms decorated on the surface of graphene act as electron donors. On the other hand metallic contacts absorbed on graphene can act as acceptors or donors depending on the metal. Additionally, absorption of some metal contact (such as Co, Ni and Pd) on graphene significantly alter the bond and electronic structure of graphene by forming chemical bonds, while for other metals (e.g. Al, Cu, Ag, Au, and Pt) only weak van der Waals type forces between graphene and the metal contact take place, preserving the bond structure of graphene.[1]

The preservation of bond structure when decorating the surface of graphene with metal atoms allows us to implement a simple tight-bind model to describe the electronic properties of the system. The tight-binding Hamiltonian in second-quantization notation is given by

$$H = \sum_{i} \varepsilon_i c_i^{+} c_i + \sum_{i,j} t_{i,j} c_i^{+} c_j \qquad \text{(S-1)}$$

where c^{+} (c) indicate the creation (annihilation) operators, ε_i is the ionization energy of the π-electron at lattice site i, and $t_{i,j}$ is the hopping integral between sites i and j taken to be nonzero between nearest neighbour sites. The presence of a metal atom on a graphene surface is expected to alter the hybridization of π-electrons in the immediate vicinity of the metal atom. This leads to a modified ionization energy and hopping integral for the affected sites. **Figure S4** depicts a metal atom located at the centre of a hexagon on the graphene lattice. Due to the short-range nature of the electronic wave functions, the π-electron bonds most affected by the presence of the metal atom are modelled as shown in **Figure S4**. The C=C bonds in which both C atoms interact with a Cu atom (red) and to a lesser extent the C=C bonds in which only one C atom interacts with a Cu atom (blue) may also be affected in terms of hopping parameters, as suggested in Ref [S2]. Specifically, for our job we utilize $t_0 = 2.90$ eV (as customary for unperturbed C=C bonds [S2-S3]) and $t_1 = t_0$ and $t_2 = 1.5t_1$ as recently proposed to successfully reproduce Kelvin-probe force measurements in graphene materials decorated by Cu nanoparticles [S3].

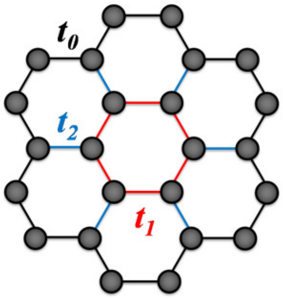

Figure S4: Hopping parameters in the presence of metal atoms on graphene, under the assumption that the six C atoms forming the central hexagon on the graphene lattice directly interact with the metal. Hopping parameters can be modified to take into account such interaction, with modified values for t_1 (C=C bonds in which both atoms interact with metal atoms) and t_2 (C=C bonds in which only one C atom interacts with metal atoms) [S2].

We qualitatively inferred the modifications of the electronic properties of graphene associated with overlapping Cu atoms on top of them by noticing that, since metal atoms act as electron donors, an increase in the both the ionization energy and hopping integral is expected [S3]. We thus simulated the density of states and formation energy for various distributions of metal atoms on the surface of graphene.

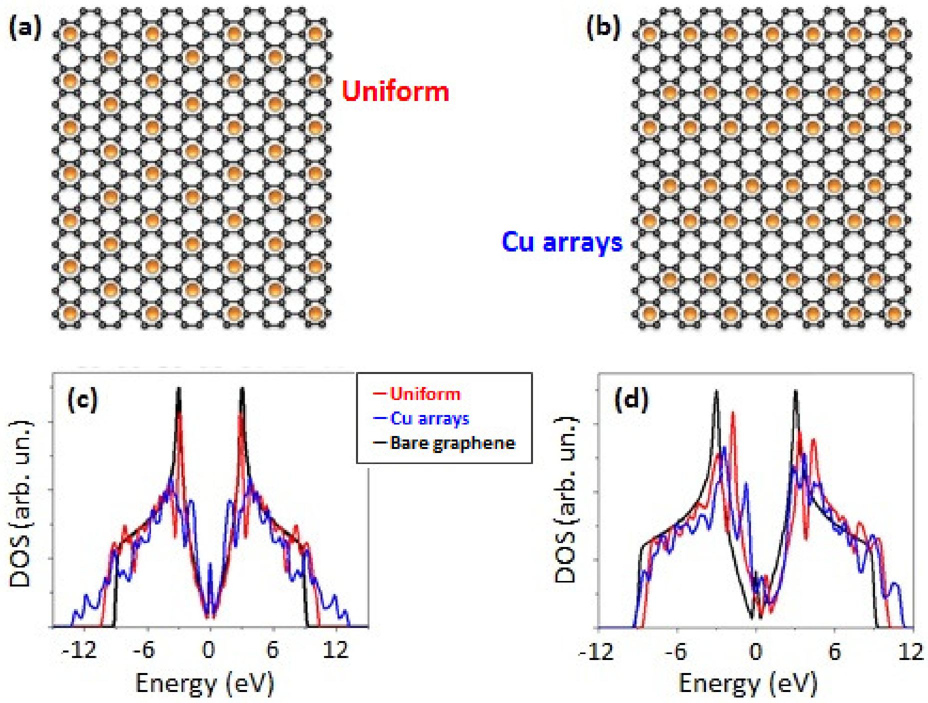

Figure S5: Comparison of the density-of-states (DOS) for two different sets of distributions of Cu atoms on single-layer graphene: **(a)** uniform (red) vs. **(b)** arrays of Cu atoms along an armchair direction (blue). The DOS of bare graphene (black) is also reported on each panel as a reference. **(c)** In this panel, the DOS is calculated by using, in eq. (S-1), the same ionization energy (ε_i = 0) for all C atoms irrespectively of their contact or non-contact with Cu atoms. Hopping parameters t_0 = t_1 = 2.90 eV and t_2 = 4.35 eV were used. **(d)** In this panel, the DOS is calculated by using different ionization energy (ε_i = 0) for C atoms in contact with Cu ($\varepsilon_{i,Cu}$ = +0.5 eV). t_0 = t_1 = 2.90 eV and t_2 = 4.35 eV.

The self-assembly of copper nanoparticles (Cu-np's) is governed by the energy landscape of the graphene surface. We can qualitatively deduce most of the features observed in our superlattices using the modified tight-binding Hamiltonian described by eq. (S-1). To illustrate the influence of Cu distribution on the formation of specific arrangements of Cu atoms that may form superlattices upon thermally-induced nucleation, we considered the formation energy of a uniform distribution of Cu atoms on graphene (**Figure S5a**) and we compared it to a distribution of Cu atoms consisting of a series of arrays along the armchair direction, as shown in **Figure S5(b)**. In both configurations, the C:Cu atomic ratio was set equal to 8:1.

The density of π-electron bonds interacting with Cu atoms is equal in both configurations when we set $\varepsilon_i = 0$ as in **Figure S5(c)**. This allows us to perform a comparison between the two structures while ensuring that the total number of bonds influenced by the metal atoms is equivalent. More accurate calculations, using both ionization energies ($\varepsilon i = +0.5$ eV) and hopping integrals ($t_2 = 4.35$ eV) that are specific for C atoms in contact with Cu [S3] indicate (**Figure S5d**) that the DOS for graphene with Cu atoms arranged in arrays is different from the DOS of graphene with uniform distribution of Cu atoms. The broadening of the DOS features of graphene with Cu lines reduces the formation energy of the system making this structure more energetically favorable. Our findings are consistent with DFT (density functional theory) calculations for the arrangement of other metals on graphene [S2].

Experimental observations for our samples suggest chains of Cu-np's form preferentially along the armchair direction of graphene. To validate these observations we consider a single line of Cu atoms arranged along the armchair and zigzag directions of graphene, as shown in **Figure S6**. Using the same tight-binding parameters ($\varepsilon_{i,Cu}$ = +0.5 eV, $t_0 = t_1$ = 2.90 eV and t_2 = 4.35 eV) we deduce that the formation energy of a single array of Cu atoms oriented along the armchair direction is lower than along the zigzag direction, which explains the preferential orientation of our Cu-np superlattices.

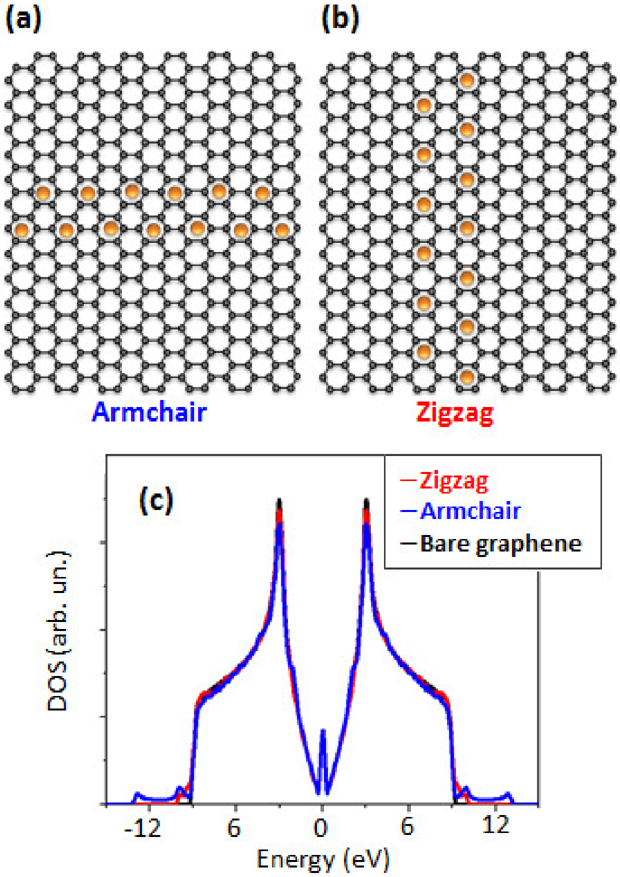

Figure S6: Comparison of two different sets of arrays of Cu atoms: **(a)** along armchair vs. **(b)** along zigzag crystallographic directions of a graphene flake. **(c)** DOS of the two configurations, which was used to determine and compare the formation energies of arrays of Cu atoms on graphene.

References

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