

## On the formation of early graphene nuclei on Cu(111) during CVD of graphene using benzene and toluene as C-precursors

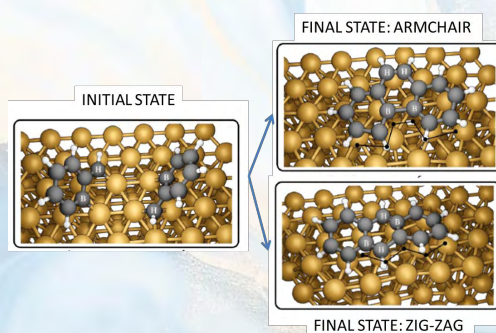
Onofrio Tau<sup>1</sup>, Paola Prete<sup>1</sup>, Nico Lovergine<sup>\*1</sup>

<sup>1</sup>Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Lecce (Italy)

\*email: [nicola.lovergine@unisalento.it](mailto:nicola.lovergine@unisalento.it)

The CVD growth of graphene from methane requires temperatures in the range 800-1000°C. The use of liquid aromatic hydrocarbons precursors (e.g. benzene and toluene) may allow reduced temperatures, while preserving high-quality graphene [1,2]; however, the effectiveness of such precursors in the synthesis of graphene is still debated [3]. Here we investigate through density functional theory (DFT-D3) calculations the molecular-level formation of early graphene nuclei on Cu(111). We estimate the stability of adsorbed benzene and toluene and identify most-likely reaction pathways through the climbing-image nudged-elastic band (CI-NEB) method, leading to the formation of anthracene and biphenyl by recombination reactions of intermediate active species.

Benzene and toluene adsorb preferentially on hcp surface sites of Cu(111) with binding energies of 0.88 eV and 0.97 eV respectively, much higher than that found for CH<sub>4</sub> (0.20 eV) [4]. Early decomposition reactions of benzene and toluene may lead to the formation of active intermediate species by consecutive dehydrogenation steps. C-H bond dissociation within the methyl group constitutes the preferred low-temperature decomposition pathway of toluene since its activation energy is 1.20 eV, leading to the abundant formation of benzyl (C<sub>7</sub>H<sub>7</sub>) radicals adsorbed onto Cu surface as primary active carbon species. The as-formed benzyl radical can undergo further dehydrogenation steps producing active species like C<sub>7</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>5</sub> and C<sub>7</sub>H<sub>4</sub>, whose energy barriers do not exceed ~1.6 eV [5]; given the relatively low energy cost, these processes could occur during low-temperature CVD of graphene. The formation of such intermediates can trigger the nucleation of anthracene (C<sub>14</sub>H<sub>10</sub>). The ideal case is the condensation of two C<sub>7</sub>H<sub>5</sub> radicals, in which two C=C double bonds forms. Two stereoisomers can be produced, namely, the (i) 'zig-zag' or (ii) 'armchair' anthracene shown in Figure 1. Despite the first C=C double bond is almost inexpensive for both structures, the zig-zag configuration is favored over the armchair one since the energy cost for the formation of the second C=C double bond is much higher for the latter due to steric hindrance.



**Figure 1.** Condensation reactions of two C<sub>7</sub>H<sub>5</sub> radicals forming the zig-zag and armchair anthracene on Cu(111). The atomic geometries of the initial and final states are shown only.

### References:

- [1] Jang J., Son M., Chung S., Kim K., Cho C., Lee B. H., Ham M. H., *Sci. Rep.*, 5 (2015) 17955.
- [2] Zhang B., Lee W. H., Piner R., Kholmanov I., Wu Y., Li H., Ruoff R. S., *ACS Nano*, 6 (2012) 2471.
- [3] Khan M. H., Moradi M., Dakhchoune M., Rezaei M., Huang S., Agrawal K. V., *Carbon*, 153 (2019) 458.
- [4] Tau O., Lovergine N., Prete P., *Carbon*, 206 (2023) 142
- [5] Tau O., Lovergine N., Prete P., *Procs. of SPIE* 13114 (2024) 1311409.