

DFT investigation of electron-induced cross-linking of aromatic SAM on Au(111): formation of graphene nanoribbons

Pepa Cabrera-Sanfelix,¹ Andrés Arnau^{2,3} and Daniel Sánchez-Portal²

¹ Donostia International Physics Center (DIPC)-UPV/EHU, Paseo Manuel de Lardizabal 4, San Sebastian 20018, Spain

² Unidad de Física de Materiales, Centro Mixto CSIC-UPV, Apdo. 1072, San Sebastián 20080, Spain

³ Departamento de Física de Materiales UPV/EHU, Facultad de Química, Apdo. 1072, San Sebastián 20080, Spain

We have performed a density functional theory study of the possible layered geometries occurring after dehydrogenation of a self-assembled monolayer (SAM) of biphenyl-thiol molecules (BPTs) adsorbed on a Au(111), as it has been experimentally observed for low energy electron irradiated SAMs of 4'-nitro-1,1'-biphenyl-thiol adsorbed on a Au(111) surface.¹ Cross-link formation between the BPT molecules has been analyzed using different models with different degrees of complexity. We start by analyzing the bonding between biphenyl (BP) molecules in a lineal dimer and their characteristic vibrational frequencies. Next, we consider the most stable cross-linked structures formed in an extended free-standing monolayer of fully dehydrogenated BP molecules. Finally, we analyze a more realistic model where the role of the Au(111) substrate and sulphur head groups is explicitly taken into account. In this more complex model, the dehydrogenated BPT molecules are found to interact covalently to spontaneously form “graphene-like” nanoflakes. We propose that these nanographenes provide plausible building-blocks for the structure of the carbon layers formed by electron irradiation of BPT-SAMs.² In particular, in our calculations we observe the formation of ultrathin graphene nanoribbons as a result of the coalescence of such graphene nanoflakes. Therefore, we focus on the electronic and magnetic properties of perfectly ultrathin zigzag terminated nanoribbons, depending on their head and tail groups, and the presence or absence of the substrate.³

¹ W. Eck, V. Stadler, W. Geyer, et al., *Advanced Materials* **12**, 805 (2000).

² P. Cabrera-Sanfelix, A. Arnau, and D. Sanchez-Portal, *Physical Chemistry Chemical Physics* **12**, 1578 (2010).

³ P. Cabrera-Sanfelix, A. Arnau, and D. Sanchez-Portal, (In preparation).