

From Self-assembled Brominated Diphenylacetylene Molecules to On-surface Organic Nanowires

M. M. S. Fakhrabadi*, F. Sedona**, and M. Sambini***

* Dipartimento di Scienze Chimiche, Università Degli Studi di Padova, Padova, Italy,
mirmasoud.seyyedfakhrabadi@unipd.it

** Dipartimento di Scienze Chimiche, Università Degli Studi di Padova, Padova, Italy,
francesco.sedona@unipd.it

*** Dipartimento di Scienze Chimiche, Università Degli Studi di Padova, Padova, Italy,
mauro.sambi@unipd.it

ABSTRACT

The paper reports on the on-surface synthesis of a novel organic nanowire starting from the deposition of 1,2-bis(4-bromophenyl) ethyne on the Ag (110) surface in ultra-high vacuum conditions. The molecular precursors self-assemble on the surface after evaporation and form organo-metallic nanowires, wherein the silver atoms replace the bromine atoms at the two ends of the self-assembled molecules. The intermediate organometallic species eventually evolve to form all-organic ordered polymers by annealing the substrate at a higher temperature, which causes the release of silver adatoms and the formation of direct C-C bonds between adjacent molecular units.

Keywords: on-surface synthesis, scanning tunneling microscopy, nanowires, brominated diphenylacetylene

1 INTRODUCTION

Nanotechnology can best be defined as a pool of deliberate activities at atomic or molecular levels including fabrication, manipulation and characterization with nanometric resolution. All of the mentioned research areas have their own specialized instruments adapted for specific purposes with certain limitations and challenges. Although during the recent years scientists have made attempts to untangle the problems one by one, there are still many open issues to deal with. For example, the fabrication of nanomaterials and nanosystems is one of the pivotal challenges that researchers face up with. With the current trend of device miniaturization, this problem has been emphasized very perceptibly in the last years due to the inherent and practical limitations of top-down techniques frequently applied to fabricate nanosystems. For this reason, scientists curiously search for efficient alternatives for demands of future technologies. One of the possible strategies consists in trying to reverse the prevalent top-down to bottom-up approaches, in order to build nanosystems starting from single molecules. Among a limited number of bottom-up procedures, self-assembly has demonstrated tremendous potential, thus opening new promising horizons in nanofabrication [1-4]. Molecular

self-assembly can be generally described as spontaneous and reversible organization of building blocks into long-range ordered networks as a consequence of locally specific non-covalent interplays (such as van der Waals interactions or hydrogen bonds) among the precursors. However, despite the versatile potential of the self-assembled materials, one of the impediments for their effective engineering in real applications can be their low stability to external stimuli whether mechanical, thermal, physical or chemical, due to the weak coupling among the molecules. To obviate this drawback, scientists proposed the possibility of establishing covalent bonds among the building units after self-assembly to properly entangle them to each other [5-8]. Although both organic and inorganic building units can produce self-assembled layers, the former, with carbon atoms as their backbones, have attracted much more attention. Scientists have tried to obtain several two-dimensional meta-materials made of carbon atoms that cannot be naturally found in nature to exploit their sophisticated physical, chemical, electrical and mechanical properties [9-12]. Within this trend, one of the recent hot research topics is the formation of one- and two-dimensional on-surface structures by starting from rationally selected single hydrocarbon molecules and extending to nanowires and nanomeshes of carbon allotropes by exploiting the benefits of self-assembly followed by surface-assisted covalent bonding [13-18]. For electronics applications, carbon-based nanowires and nanoribbons, among all others, are the most significant nanostructures because they possess electronic properties that the two-dimensional nanomaterials such as graphene sheets do not. These properties can be attributed to the tunable band gap in their electronic band structures that does not show up in graphene, thus limiting its applications in semiconductor technology [19-20]. Hence, in this study we contribute to addressing this issue through the on-surface synthesis of largely ordered diphenylacetylene based nanowires on Ag(110) and their characterization by scanning tunneling microscopy (STM). Fig. 1 illustrates schematically the one-dimensional on-surface polymerization steps starting from 1,2-bis(4-bromophenyl) ethyne (DBPE) molecules.

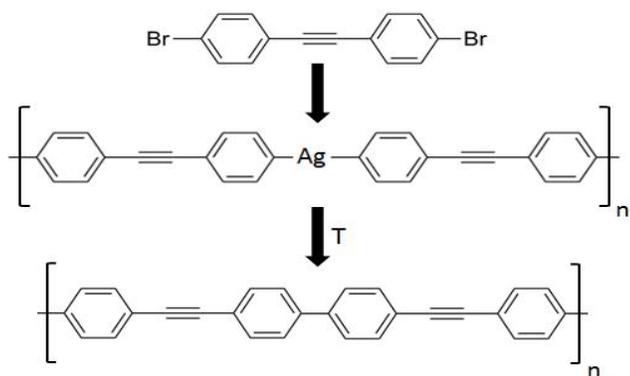


Fig. 1. Schematic representation of the polymerization of DBPE molecules.

2 EXPERIMENT

The Ag(110) substrate was cleaned by repeated cycles of 1 keV Ar⁺ sputtering and annealing in ultra-high vacuum (UHV) conditions. The DBPA precursors were deposited from a pyrolytic boron nitride crucible to reach a fraction (usually ~ 0.7) of a monolayer (ML). The coverage was evaluated by C 1s X-ray photoelectron spectroscopy (not shown here). During deposition, the surface was held at room temperature (RT), and the polymerization was activated by subsequent thermal annealing. The UHV STM experiments were performed at a base pressure of 2×10^{-10} mbar with an Omicron VT-STM. The STM measurements were carried out at RT in constant-current mode using an electrochemically etched Pt-Ir tip. The images were processed by WSXM software [21].

3 RESULTS AND DISCUSSION

The relatively large scale image of the as-deposited surface of Ag (110) in Fig. 2 reveals a surface fully covered by the DBPE molecules.

As shown in Fig. 3, the DBPE precursors deposited on the Ag(110) substrate create organo-metallic nanowires. In fact, the bromine atoms detach from the molecules at RT and adsorb on the surface, whereas silver adatoms replace them forming organometallic wires stabilized by C-Ag-C bonds. Annealing the deposited surface at higher temperatures results in the release of the bridging silver atoms and in the synthesis of organic nanowires through direct C-C bond formation between adjacent molecular precursors. Fig. 3 (a) and (b) show the high resolution STM images of as-deposited and annealed phases, respectively, of the molecules and nanowires and their corresponding models. As shown in Fig. 3 (a), the silver atoms (blue spots) replace the bromine atoms (red spots) on two ends of the DBPE molecule and originate the organo-metallic nanowires. Concomitantly, dissociated bromine atoms form the parallel “rails” between the organometallic wires and occupy two different sets of positions: (a) between two adjacent silver adatoms and (b) in free space between the triple bonds belonging to adjacent nanowires. Such bromine

atoms rows play a crucial role in the process by limiting the access of adjacent triple bonds to each other, thereby inhibiting their transverse polymerization.

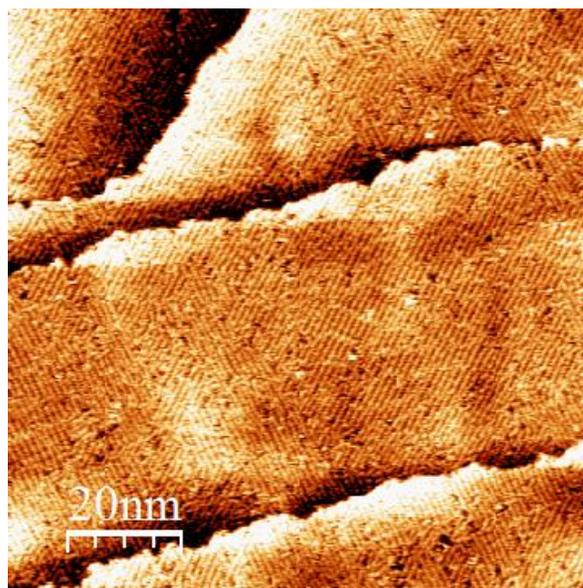


Fig. 2. Ag (100) surface after deposition of the DBPE molecules.

Fig. 3 (b) shows that the organo-metallic nanowires release the silver adatoms after annealing, resulting in the production of continuous organic nanowires characterized by the alternation of two phenyl rings and one triple bond.

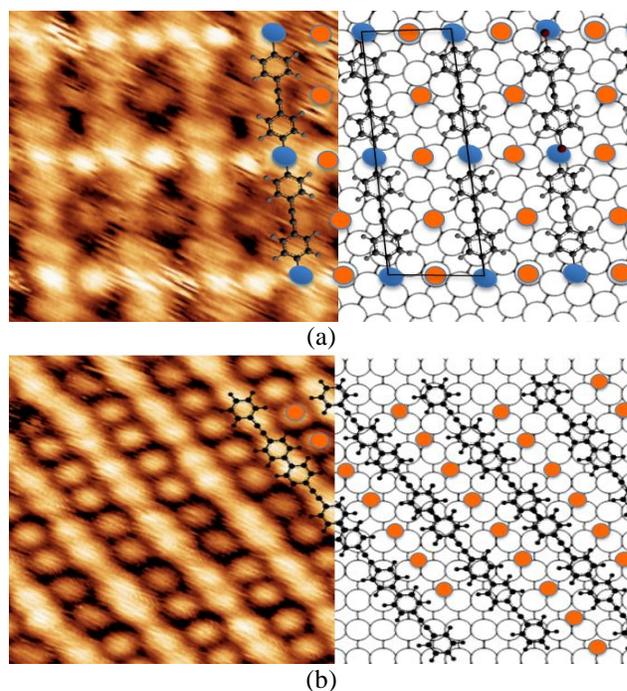


Fig. 3. STM images and models of the organometallic and organic nanowires, red spots: Br, blue spots: Ag.

4 CONCLUSION

We report on the fabrication of a novel polymeric nanowire starting from DBPE building blocks on the Ag(110) surface. The STM images of the organometallic wires forming by self-assembly at room temperature after the precursor evaporation are shown and the formation of organic nanowires after annealing the substrate is demonstrated. The provided images and the corresponding models describe the process very well. The next step to this work will be the electronic structure characterization of the nanowires by means of angle-resolved photoemission, in order to obtain their electronic band structures.

5 REFERENCES

- [1] Hunt, S.T. et al., "Self-assembly of noble metal monolayers on transition metal carbide nanoparticle catalysts," *Science*, 352 (6288), pp.974–978, 2016.
- [2] Timonen, J.V. et al. "Switchable static and dynamic self-assembly of magnetic droplets on superhydrophobic surfaces," *Science*, 341 (6143), pp.253–257, 2013.
- [3] Qiu, H. et al., "Multidimensional hierarchical self-assembly of amphiphilic cylindrical block composites," *Science*, 347(6228), pp.1329–1332, 2015.
- [4] Luo, C. et al., "General strategy for self-assembly of highly oriented nanocrystalline semiconducting polymers with high mobility," *Nano letters*, 14(5), pp.2764–2771, 2014.
- [5] Colazzo, L. et al., "Metal-Free on-Surface Photochemical Homocoupling of Terminal Alkynes," *Journal of the American Chemical Society*, 138(32), pp.10151–10156, 2016.
- [6] Basagni, A. et al., "Tunable Band Alignment with Unperturbed Carrier Mobility of On-Surface Synthesized Organic Semiconducting Wires," *ACS nano*, 10(2), pp.2644–2651, 2016.
- [7] Baek, K. et al., "Free-standing, single-monomer-thick two-dimensional polymers through covalent self-assembly in solution," *Journal of the American Chemical Society*, 135(17), pp.6523–6528, 2013.
- [8] Bjork, J., Hanke, F. & Stafstrom, S., "Mechanisms of halogen-based covalent self-assembly on metal surfaces," *Journal of the American Chemical Society*, 135(15), pp.5768–5775, 2013.
- [9] Cai, J. et al., "Atomically precise bottom-up fabrication of graphene nanoribbons," *Nature*, 466(7305), pp.470–473, 2010.
- [10] Cai, J. et al., "Graphene nanoribbon heterojunctions," *Nature nanotechnology*, 9(11), pp.896–900, 2014.
- [11] Fan, Q. et al., "Surface-Assisted Organic Synthesis of Hyperbenzene Nanotroughs," *Angewandte Chemie International Edition*, 52(17), pp.4668–4672, 2013.
- [12] Fan, Q. et al., "Surface-assisted formation, assembly, and dynamics of planar organometallic macrocycles and zigzag shaped polymer chains with C–Cu–C bonds," *ACS nano*, 8(1), pp.709–718, 2013.
- [13] Bieri, M. et al., "Two-dimensional polymer formation on surfaces: insight into the roles of precursor mobility and reactivity," *Journal of the American Chemical Society*, 132(46), pp.16669–16676, 2010.
- [14] Fan, Q. et al., "Covalent, organometallic, and halogen-bonded nanomeshes from tetrabromo-terphenyl by surface-assisted synthesis on Cu (111)," *The Journal of Physical Chemistry C*, 118(24), pp.13018–13025, 2014.
- [15] Blunt, M.O. et al., "Templating molecular adsorption using a covalent organic framework," *Chemical Communications*, 46(38), pp.7157–7159, 2010.
- [16] Fan, Q. et al., "Tribromobenzene on Cu (111): Temperature-dependent formation of halogen-bonded, organometallic, and covalent nanostructures," *The Journal of chemical physics*, 142(10), p.101906, 2015.
- [17] Chen, M. et al., "Combined photoemission and scanning tunneling microscopy study of the surface-assisted Ullmann coupling reaction," *The Journal of Physical Chemistry C*, 118(13), pp.6820–6830, 2014.
- [18] Liu, J. et al., "Cyclotrimerization of arylalkynes on Au (111)," *Chemical communications*, 50(76), pp.11200–11203, 2014.
- [19] Li, X. et al., "Chemically derived, ultrasoft graphene nanoribbon semiconductors" *Science*, 319(5867), pp.1229–1232, 2008.
- [20] Son, Y. W., Cohen, M.L. & Louie, S.G., "Half-metallic graphene nanoribbons". *Nature*, 444(7117), pp.347–349, 2006.
- [21] Horcas, I. et al., "WSXM: a software for scanning probe microscopy and a tool for nanotechnology," *Review of Scientific Instruments*, 78(1), p.013705, 2007.