

FULLERENES FORMATION FROM AROMATIC PRECURSORS BY A SURFACE CATALYSED CYCLODEHYDROGENATION PROCESS

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Controlled synthesis of fullerenes and heterofullerenes on surfaces is a preceding step towards the development of a true fullerene-based molecular electronics. New methods are required for the rational, size-controlled synthesis of fullerenes, heterofullerenes, and endohedral fullerenes that cannot be accessed by the current method of graphite vaporization. Recently, pioneering experiments have shown that C₆₀ fullerene can be formed by flash vacuum pyrolysis of a trichlorinated precursor C₆₀H₅₇Cl₃. However, this precursor was prepared in 11 steps from commercially available materials and the final dehydrogenation/dehydrochlorination proceeds in the gas phase in ca. 0.1-1.0% yield¹.

Here we report a highly efficient (<100%) dehydrogenation mechanism leading to the formation of fullerene C₆₀ and for the first time triazafullerene C₅₇N₃ in a one-step from their corresponding planar polycyclic aromatic precursors by a surface catalysed process². We have visualized the whole process by in-situ Scanning Tunneling Microscopy (STM) and X-Ray Photoemission spectroscopy (XPS). The cyclodehydrogenation has been confirmed by the thermal desorption of HD and D₂ from hexadeuterated 1-d₆ precursors, by the mass-spectrometric detection of C₆₀ in the platinum-catalysed dehydrogenation, and the whole process followed by first principles DFT calculations.

The process is catalysed by reactive substrates, as Pt, which favours strong surface-molecule interactions. We have deeply studied by STM and DFT the interaction of the polycyclic planar precursors with different surfaces. The number of established bonds between the substrate and molecule seems to play a key-role in the catalytic properties of the system.

The mechanism we describe opens the door to size-controlled production of fullerenes and heterofullerenes, it could allow the encapsulation of different atomic and molecular species to form endohedral fullerenes and to the formation of different carbon-based nanostructures, such as graphene or doped graphene, which nowadays are not readily available on surfaces by other methods.

References:

[1] Scott, L.T. *Science* **295**, (2002)1500.

[2] G. Otero, G. Biddau, C. Sánchez-Sánchez, et al. *Nature*, 454 (2008) 865

Figures:

