

Self-assembly of trimetallic nitride template fullerenes on surfaces studied by STM

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Abstract

Trimetallic nitride template fullerenes have been deposited onto a variety of substrates in order to elucidate the substrate–fullerene interactions. We have investigated self-assembled island formation and molecular detail of $\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ on $\text{Ag}/\text{Si}(111)$, $\text{Au}(111)/\text{mica}$, $\text{Si}(111)$, and $\text{Si}(001)$ using variable temperature scanning tunnelling microscopy (STM). At room temperature, the fullerenes self-assemble into monolayer-high hexagonal close-packed islands on Ag-passivated $\text{Si}(111)$ whereas annealing at elevated temperatures (250–300 °C) is necessary for the self-assembly of close-packed islands on $\text{Au}(111)$. Intra-molecular resolution of the fullerenes has been achieved at liquid nitrogen temperature on $\text{Ag}/\text{Si}(111)$ and already at room temperature on $\text{Si}(001)$, when the rotation of the fullerenes is frozen. Whereas the bonding between the fullerenes and Si surfaces is mainly covalent, it appears to be mainly van der-Waals on the other surfaces.

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1. Introduction

Trimetallic nitride template (TNT) fullerenes were discovered in 1999 [1]. Typical representatives of this new class of endohedral metallofullerenes are the stable $\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ containing a trimetal nitride cluster encapsulated in a C_{80} cage (Fig. 1). The otherwise unstable C_{80} cage is stabilized by charge transfer from the planar nitride cluster, with a total of six electrons being donated to the carbon cage [1], hence the description of the trinitride cluster

acting as a template for the carbon cage. TNT fullerenes are expected to be less reactive than other metallofullerenes because they have six electrons transferred to the carbon cage compared to most metallofullerenes, where usually three electrons are donated from the incarcerated ion to the cage. This means a weaker substrate–fullerene interaction resulting in enhanced mobility of the molecules on inert surfaces such as HOPG, $\text{Au}(111)$ or $\text{Ag}/\text{Si}(111)$, leading to self-assembled island formation.

Trimetallic nitride containing fullerenes are of potential use in the field of optoelectronics and quantum information processing. The great advantage is that there is no cage absorption at the frequencies where some clusters are optically active, allowing direct and selective optical interaction with an ion encapsulated within the fullerene cage [2,3].

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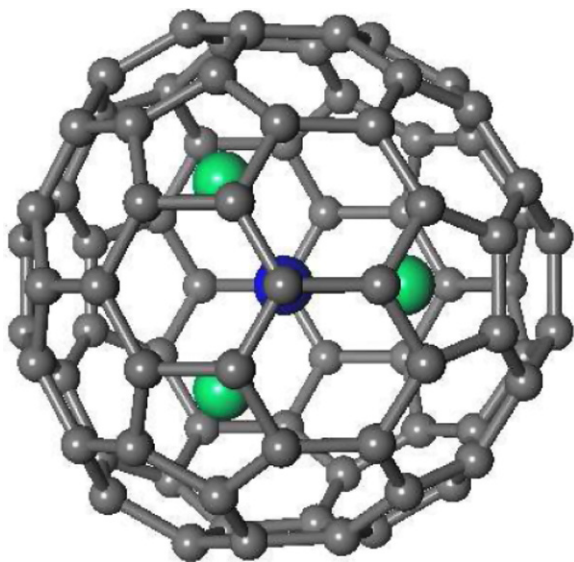


Fig. 1. Ball and stick model of an $\text{Er}_3\text{N}@C_{80}$ molecule. The planar Er_3N cluster is lying in an equatorial plane of the C_{80} cage with the metal atoms pointing towards pentagonal rings.

Direct optical excitation resulting in luminescence may provide a possible way for the realization of fullerene-based quantum computation schemes based on optical readout methods of endohedral spin qubits [4]. The practical implementation of such schemes requires the controlled fabrication of well-ordered one-dimensional or two-dimensional arrays of endohedral fullerenes on suitable substrates. Encapsulation of fullerenes in a carbon nanotube provides a means for producing one-dimensional arrays, whilst direct deposition onto a surface can create two-dimensional networks. Custom-made two-dimensional networks with controlled spacings between fullerenes may be created using supramolecular [5–7] or structural [8,9] templates. Regular arrays of qubits open the door for global addressing schemes for quantum information processing, and two-dimensional networks have the advantage of being able to employ much more powerful error correction techniques [10].

In this paper, we have studied the self-assembled formation of two-dimensional islands and molecular detail of $\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ on a variety of substrates including $\text{Au}(111)$ layers on mica, silver-terminated as well as clean $\text{Si}(111)$ and $\text{Si}(001)$. *In situ* variable-voltage STM imaging at ambient and liquid nitrogen temperature has been used to investigate the bias dependence of the fullerene contrast and to examine substrate–fullerene interactions.

2. Experimental methods

$\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ were supplied by Luna Innovations, Blacksburg, VA, USA and purified using high-performance liquid chromatography (HPLC). They were evaporated *in situ* from separate Knudsen cells at 480–

530 °C in a variable-temperature (VT) UHV STM system (JEOL 4500S) in Oxford, as well as in Omicron VT STM/AFM systems in Swansea and Milano. The $\text{Ag}/\text{Si}(111)$ substrates were prepared by depositing a monolayer of silver from an Oxford Applied Research EGN4 e-beam evaporator onto a freshly cleaned $\text{Si}(111)$ (7×7) substrate at 550 °C. The adsorbed silver atoms covalently bond to the silicon atoms, saturating all the dangling bonds and thereby passivating the silicon surface. The typical $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction of the silver has been observed with STM prior to the deposition of fullerenes. $\text{Au}(111)/\text{mica}$ Molecular Imaging PicoSubstrates™ purchased from the Molecular Imaging Corporation were sputtered with 1 keV Ar^+ ions and annealed in UHV (base pressure 10^{-11} mbar) at 550 °C for 20 min. The resulting surfaces are atomically flat with terrace widths of 100–300 nm, showing the $(23 \times \sqrt{3})$ herringbone reconstruction. Atomically clean $\text{Si}(001)$ (2×1) and $\text{Si}(111)$ (7×7) surfaces were prepared by flashing the samples in UHV repeatedly to 1150 °C for a few seconds until this caused only a small pressure rise. Sample temperatures were measured using optical pyrometers with an accuracy of ± 20 °C. STM images were taken at room temperature as well as liquid nitrogen temperature using chemically etched tungsten tips.

3. Results and discussion

3.1. TNT fullerenes on $\text{Ag}/\text{Si}(111)$

The deposition of $\text{Er}_3\text{N}@C_{80}$ or $\text{Sc}_3\text{N}@C_{80}$ onto $\text{Ag}/\text{Si}(111)$ substrates at room temperature leads to the formation of small close-packed islands (10–30 nm diameter) on step edges of the $\text{Ag}/\text{Si}(111)$ surface (Fig. 2a). An angle of $30^\circ \pm 1^\circ$ is measured between the lattice directions of the fullerene island and the underlying $\text{Ag}/\text{Si}(111)$ ($\sqrt{3} \times \sqrt{3})R30^\circ$ surface (Fig. 2b). This so-called A-type orientation with an inter-fullerene spacing of 1.15 nm has also been reported for a number of other endohedral metallofullerenes [11,12]. It is the preferred arrangement of these fullerenes as it is lattice matched with the substrate, forming a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with respect to the underlying monolayer of silver and a (3×3) lattice match with respect to the $\text{Si}(111)$ substrate.

Bias-dependent STM reveals interesting contrast effects within the $\text{Er}_3\text{N}@C_{80}$ islands. Fig. 3 shows two images of the same island at different sample bias voltages. In the filled states image (Fig. 3a), taken at -1.5 V, some fullerenes appear distinctly brighter than the others, whilst in the empty states image (Fig. 3b), taken at $+1.2$ V, the effect is reversed and these same molecules now appear much darker than the rest. The molecules that go dark at -1.4 V are bright in empty states down to around $+0.5$ V, while those that are dark in empty states at 1.2 V are bright in filled states down to around -0.6 V. The bias range over which both types appear dark is around 1.8–1.9 V, which suggests that only the relative position of

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