Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2013

Chemistry and Temperature-assisted Dehydrogenation of $C_{60}H_{30}$ Molecules on $TiO_2(110)$ surfaces

Carlos Sánchez-Sánchez[1,2], José Ignacio Martínez[1], Valeria Lanzilotto[3,4], Giulio Biddau[5,6], , Berta Gómez-Lor[1], Rubén Pérez[5], Luca Floreano[3], María Francisca López[1], José Ángel Martín-Gago[1,8]

(1) Instituto de Ciencia de Materiales de Madrid (CSIC), Sor Juana Ines de la Cruz 3, 28049 Madrid, Spain

(2) EMPA, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland.

(3) CNR-IOM, Laboratorio TASC, Basovizza SS-14, Km 163.5, I-34149 Trieste, Italy

(4) Department of Physics, University of Trieste, Via A. Valerio, 2 - 34127 Trieste, Italy

(5) Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain

(6) Theoretische Festkörperphysik, Institüt fur Physik, Humboldt Universität zu Berlin, Newtonstrasse 15, 12489 Berlin, Germany

(7) Research Center for Integrated Science, Japan Advanced Institute of Science and Technology (JAIST)1--1 Asahidai, Nomi, Ishikawa 923-1292, Japan

(8) Centro de Astrobiología INTA-CSIC. Torrejón de Ardoz, 28850 Madrid, Spain

THEORETICAL METHODOLOGY

Computational Details

For the *ab-initio* atomistic and molecular dynamics simulations of the different adsorbate/$TiO_2(110)$ configurations analysed in this study, Density Functional Theory (DFT) was used effectively combining the localized-basis-set and plane-wave schemes as implemented in the FIREBALL[S1] and PWSCF[S2] simulation packages, respectively. A perturbative van der Waals (vdW) correction was used to check the reliability of the physisorbed configuration.[S2] The exchange-correlation (XC) effects have been accounted by using the local density PW91 parametrization[S3] and norm-conserving scalar-relativistic pseudopotentials[S4] have been considered to model the ion-electron interaction. For the localized-basis-set code FIREBALL, a $sp^3d^5d^{*5}$ basis set of single and double numerical atomic orbitals (one *s*, three *p*, and a double set of five *d* orbitals) was employed for Ti, a double numerical $sp^3s^*p^{*3}$ basis set for O, an extended sp^3d^5 basis set for C. and an optimized single *s* basis set for H – successfully validated in previous calculations of PAHs.[S5] For the plane-wave code PWSCF, a plane-wave basis set with kinetic energy cutoff as high as 30 Ry was used. In all the calculations the Brillouin zones (BZ) were sampled by means of a [2×2×1] Monkhorst-Pack grid,[S6] guaranteeing a full convergence in energy and electronic density. The $TiO_2(110)$ surface was modelled in a repeated slab geometry: i) a slab of four physical $TiO_2(110)$ layers with a distance ~ 25 Å of vacuum between neighbouring cells along the axis perpendicular to the surface; as well as ii) full periodic boundary conditions representing an infinite $TiO_2(110)$ surface. Each substrate physical layer contained 96 atoms with perfectly balanced stoichiometry in order to avoid polarization effects, and the size of the unit cell in the direction parallel to the surface was 24.1 x 26.6 $Å^2$, large enough to minimize any possible inter-molecular interaction between neighbouring cells. To define the equilibrium properties of the different structural configurations involved along the (cyclo)dehydrogenation process we carried out full geometry optimizations, and only the two bottom TiO_2 physical layers were kept fixed. Two additional oxide layers were accounted for the calculations of the energetics, density of states profiles, and theoretical STM imaging.

Electronic Structure and Energy Level Alignment

For the calculation of the electronic properties of the system, as well as the theoretical STM images, once the optimized structures of the different configurations were fully established by the molecular dynamics calculations, the electronic levels of the adsorbates were properly aligned with respect the levels of the TiO_2 substrate by using an efficient scissor operator – implemented in the FIREBALL code – according to the experimental evidence.

The computational details underlying this technique have been deeply explained elsewhere (see Refs. S7-S9 and references therein). This approach has been successfully employed previously for improving the electronic structure description in organic / (metal/oxide) systems given by conventional DFT calculations, which, sometimes, fails at providing important physical magnitudes such as charge transfer rates, density of states, and theoretical STM images – among others – mainly due to an incorrect alignment between the energy levels of the adsorbate and the subtrate. [S7-S9] This formalism dramatically improves the description of quantities of paramount importance in this study, which are the density of states, and the STM images. In this particular case, accounting the existing experimental electronic spectroscopy information, the

Fermi energy obtained from the conventional calculation has been properly aligned with the Ti^{+3} level of the TiO_2, around 0.5 eV below the TiO_2 conduction band. On the other hand, experiments identify the HOMO level of the molecule to be located at around 1.2 eV below the Ti^{+3} level. Thus, previous considerations permit to fully establish a suitable starting point for the electronic structure calculations. Nevertheless, it is important to address that the starting point for the electronic structure calculations is self-consistent adjusted when the electronic charge convergence is solved through the implementation of the DFT equations. This approach, particularly important for large-scale atomic systems (which is the case), shall allow us to obtain a realistic density of states profiles, and STM-scan at practically the same voltages than in the experimental realization.[S7-S9]

Theoretical STM Imaging

In our STM approach, tunnelling currents for the STM images have been calculated using a Keldysh–Green function formalism, together with the first-principles tight-binding Hamiltonian obtained from the local-orbital DFT-FIREBALL method (as explained in detail elsewhere[S1,S10,S11]). Some examples of the application of this approach can be found in references S7-S9; in particular, reference S7 is a good example of how the accurate theoretical simulation of STM images, and its comparison with high-quality experimental STM images, can guide us towards the correct atomic structure of an organic molecule on a metal substrate. Within this formalism, the tip – a standard pyramidal clean W-tip in our case – and the sample – adsorbate/TiO_2(110) – are calculated independently providing independent subsystem Hamiltonians. Thus, the overlapping Hamiltonian is obtained by using a dimer approximation: a dimer formed by one W atom (corresponding to the tip) and another one (H, C, O or Ti coming from the sample) is calculated for different atom–atom distances and for all the non-zero interactions, using the Keldish-Green formalism to propagate the tunnel current between both subsystems. The details are widely explained by Blanco *et al.* in Refs. S10,S11 (and references therein). The theoretical STM images have been obtained at constant-current scanning conditions, moving the W-tip perpendicularly to the sample in each scanning stage to search a pre-selected fix value of the tunnel current. The theoretical scanning parameters used here were I_{tunnel} = 0.2 nA, with $V_{substrate}$ varying up to +2 V above the Fermi energy, in order to mimic the experimental procedure.

EXPERIMENTAL STATISTICAL ANALYSIS

Upon annealing at 750K, a dramatic change in the molecular morphology is observed (see Fig. 3). As explained in the main text, a transition from flat triangular to round features takes place. The obtained features present an increase of the width together with a decrease of the apparent height, as it can be observed in the statistical analysis presented in Fig. S1. This modification of the molecular structures is rationalized as being the consequence of dehydrogenation plus on-surface addition processes. Dehydrogenated molecules can diffuse and form new C-C bonds with neighboring molecules giving rise to macromolecules with some curvature induced by the presence of pentagons in the precursors. This so-formed structures can be considered nanodomes.

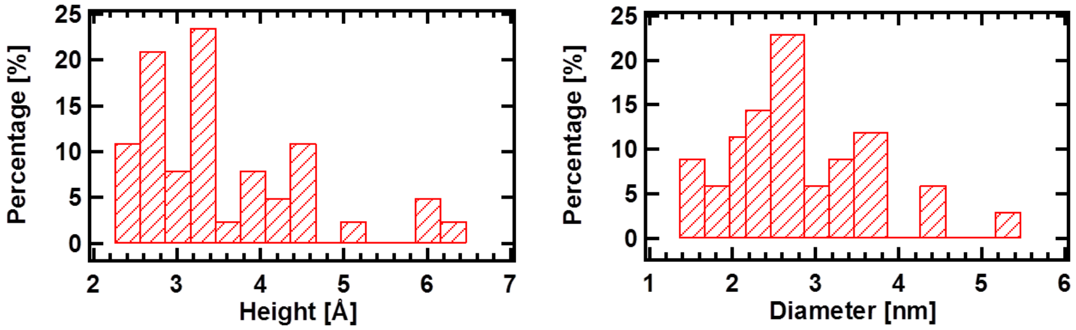

Figure S1.- Statistical analysis of the molecular features formed upon annealing at 750K. Left panel: bargraph for the molecular heights. Right panel: bargraph for molecular diameter.

REFERENCES

S1.- J. P. Lewis *et al.*, *Phys. Stat. Solidi B* **2011**, *248*, 1989.

S2.- P. Giannozzi *et al.*, *J. Phys.: Condens. Matter* **2009**, *21*, 395502.

S3.- J. P. Perdew *et al.*, *Phys. Rev. B* **1992**, *46*, 6671.

S4.- D. Vanderbilt, *Phys. Rev. B* **1986**, *25*, 4228.

S5.- G. Otero, G. Biddau, T. Ozaki, B. Gomez-Lor, J. Mendez, R. Perez, J.A. Martin-Gago, *Chem. Eur. J.* **2010**, 16, 13920.

S6.- D. J. Chadi, and M. L. Cohen, *Phys. Rev. B* **1973**, *8*, 5747.

S7.- J. I. Martínez *et al.*, *Phys. Rev. Lett.* **2012**, *108*, 246102.

S8.- J. I. Martínez *et al.*, *Phys. Stat. Sol. B* **2011**, *248*, 2044.

S9.- E. Abad *et al.*, *J. Chem. Phys.* **2011**, *134*, 044701.

S10.- J. M. Blanco *et al. Phys. Rev. B* **2004**, *70*, 085405.

S11.- J. M. Blanco *et al.*, *Prog. Surf. Sci.* **2006**, *81*, 2403.