

Towards the Isomer-Specific Synthesis of Higher Fullerenes and Buckybowls by the Surface-Catalyzed Cyclodehydrogenation of Aromatic Precursors**

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Carbon-based materials, such as fullerenes, carbon nanotubes, and graphene, are attracting increasing interest because of their remarkable properties and potential applications.^[1,2] Fullerenes are a unique family of cage molecules with a variety of sizes and shapes. Most effort thus far has focused on the study of C₆₀ fullerene, for which superconducting properties have been demonstrated, along with high mechanical and heat resistance.^[3] The investigation of properties of higher fullerenes requires their production in macroscopic quantities. Whereas the synthesis of the most-familiar members of the fullerene family—C₆₀ and C₇₀—in such amounts by graphite vaporization in an inert atmosphere is well-established, the synthesis of higher fullerenes remains a challenge because of the low yield of the evaporation technique and accompanying purification issues. For example, the two major isomers of C₈₄ obtained with this method (out of 24 possible structures satisfying the isolated-pentagon rule),^[4] cannot be fully separated even after 20 rounds of recycling high-performance liquid chromatography.^[5] Therefore, synthetic methods are needed for the production of a single isomer of a desired fullerene, free from impurities of other isomers or fullerenes of different sizes.

A promising route for the selective synthesis of fullerenes is based on planar polycyclic aromatic hydrocarbon precursor molecules that already contain the carbon framework required for the formation of the target fullerene cage. Such an unfolded fullerene can be stitched up through an intramolecular cyclodehydrogenation to form the desired fullerene isomer. Flash vacuum pyrolysis has been found to be an effective technique for such intramolecular cyclization. Many small curved fullerene fragments have been obtained by this method.^[6–9] However, the yield of the target fullerenes is still too low for preparative synthesis. C₆₀, for example, has been

obtained in 0.1–1% yield,^[10] whereas higher fullerenes were only detected in trace amounts by mass spectrometry.^[11,12]

The first step towards the controlled synthesis of non-planar carbon nanostructures on a surface was made by Rim et al.,^[13] who demonstrated the formation of carbon half-spheres (so called buckybowls) from planar precursor molecules on a Ru(0001) surface. The method used—surface-catalyzed cyclodehydrogenation (SCCDH)—exhibits high dehydrogenation selectivity as a result of the catalytic activity of the surface and a high conversion ratio of the deposited precursors into nonplanar cap structures.

Otero et al.^[14] recently demonstrated the efficiency of this SCCDH method for the synthesis of C₆₀ fullerene cages. In their study, the precursor molecules C₆₀H₃₀ and C₅₇N₃H₃₀ were deposited onto a Pt(111) surface under ultrahigh-vacuum conditions and annealed at 750 K. The surface acts as a support for the precursors and final products and thus enables the use of scanning tunneling microscopy (STM) investigations at the single-molecule level. Importantly, the surface also serves as a catalyst for the SCCDH reaction. A simple annealing step led to the formation of the corresponding C₆₀ and C₅₇N₃ cages with an unprecedented high relative yield. Despite the variety of experimental and theoretical methods employed to characterize the process, the particular stability of the C₆₀ target molecule prevented demonstration of the selectivity of the C–C bond-formation process. In this case, it cannot be excluded that C–C bonds rearrange to form the most stable compound, the C₆₀ I_h isomer.

Herein we address this important question by studying the SCCDH process of specifically designed precursor molecules. We provide strong evidence that the reaction indeed occurs in a selective manner and that only correctly programmed precursors yield the desired molecule. That is, we show that the SCCDH process does not involve C–C bond rearrangement, and that cage formation proceeds through dehydrogenation and the zipping of newly formed bonds at preselected positions only. On the basis of this result, we proceeded to the synthesis of the higher fullerene C₈₄. The production of fullerenes by means of surface-assisted cyclodehydrogenation is an efficient and controlled method, as the isomeric identity of the fullerene can already be built in at the stage of precursor synthesis.

The cyclodehydrogenation process used in this study consists of the following steps: first, the designated precursor molecules are deposited by organic molecular beam epitaxy onto the surface; second, the sample is annealed to induce the surface-assisted reaction, which results in the aforementioned

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partially and fully closed cage molecules. Besides the C_{60} precursor **1** with the molecular formula $C_{60}H_{30}$, which was also used by Otero et al.,^[14] we synthesized a modified $C_{60}H_{30}$ precursor **2** to verify the selectivity of the reaction (Figure 1). We also prepared compound **3** ($C_{84}H_{42}$) as the precursor for $C_{84}(20)$ fullerene.

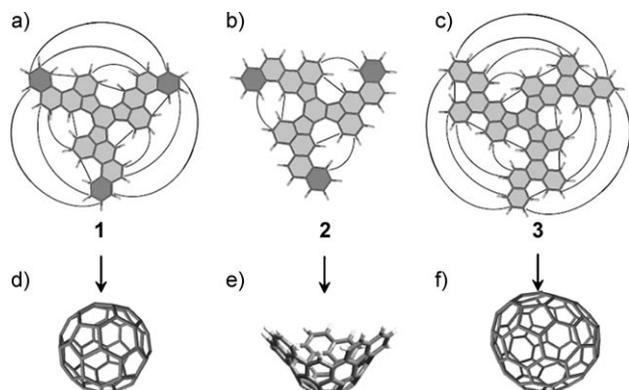


Figure 1. Structures of the precursor molecules and their condensation products. a) C_{60} precursor **1** ($C_{60}H_{30}$); b) modified $C_{60}H_{30}$ precursor **2**; c) $C_{84}H_{42}$ precursor **3**. The dark lines indicate the C–C bonds that form upon cyclodehydrogenation to give the expected products: d) C_{60} fullerene; e) nanotetrahedron; f) C_{84} fullerene.

The molecules in Figure 1 a–c are composed of hexagonal and pentagonal rings terminated by hydrogen atoms at the periphery. The dark lines connecting the outer carbon atoms show the C–C bonds to be formed upon dehydrogenation. Figure 1 d–f shows the desired products, in which all possible C–C bonds have been formed as indicated in Figure 1 a–c without further C–C bond rearrangements.

Figure 2 summarizes the results of our STM investigations for precursors **1** and **2**. We monitored C_{60} formation from precursor **1** to be able to directly compare the results with those for the modified $C_{60}H_{30}$ isomer **2**. Upon deposition on Pt(111), precursor **1** was imaged as a triangular protrusion (Figure 1 a). After annealing at 480°C , the SCCDH reaction was complete, and all molecules had been transformed into round C_{60} fullerenes with an apparent height and width of 0.4 and 1.5 nm, respectively (Figure 2 b). These dimensions are in accordance with the results of Otero et al.^[14] and previously reported values for C_{60} on Pt(110) and Pd(110).^[15] Although these observations indirectly pointed to C_{60} formation, it remained to be demonstrated that bond formation follows the selective zipping mechanism, in which only preselected C–C bonds are formed.

To show the selectivity of the SCCDH and rule out the possibility of C–C bond rearrangement, we synthesized the precursor molecule **2** (Figure 1 b), which has the same chemical formula as **1** and a very similar structure; however, three of its benzene rings have been shifted to a different position, as indicated in Figure 1 a,b by the shaded hexagons. The possible folding paths are shown in Figure 1 a,b by the dark lines. The repositioning of the benzene rings prevents some folding steps essential to fullerene formation; thus,

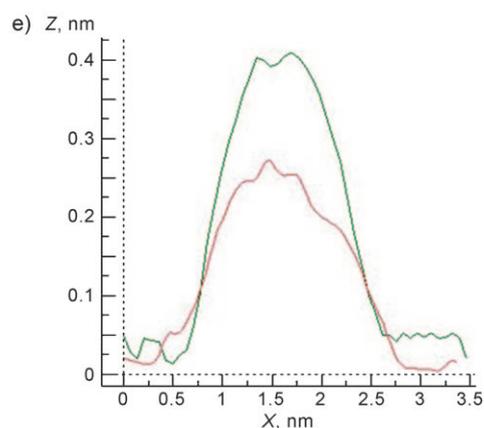
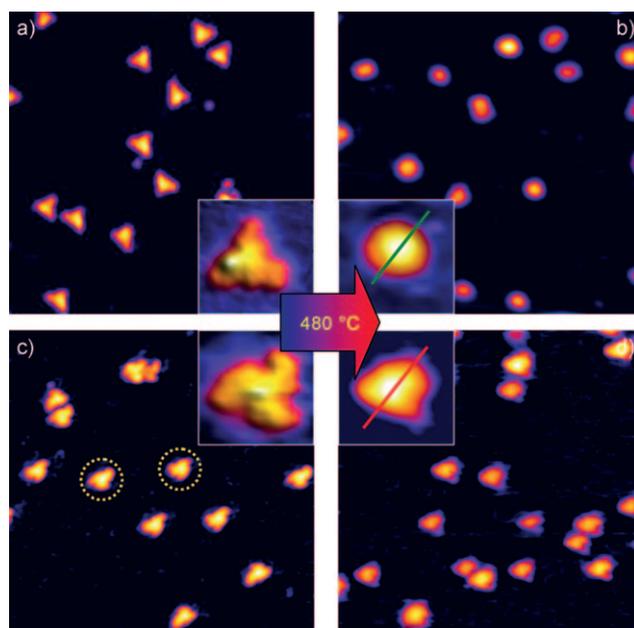


Figure 2. STM images ($25 \times 25 \text{ nm}^2$) of the C_{60} cyclization process: a) Precursor **1** as deposited on Pt(111); b) product of the annealing of **1** at 480°C ; c) precursor **2** as deposited on Pt(111) (the circles highlight two 2D enantiomers of **2**); d) product of the annealing of **2** at 480°C for 10 min. The insets ($3 \times 3 \text{ nm}^2$) show magnified adsorbates. e) Superposition of the line scans indicated in the insets of (b) and (d) (green and red line, respectively): upon annealing, the modified precursor **2** yielded species of lower apparent height than that of species derived from precursor **1**.

folding should lead to structurally different species. The folding of **2** was expected to yield an open-cage structure, which we refer to as the nanotetrahedron (Figure 1 e).

STM analysis of a partially covered surface (ca. 0.2 monolayer) clearly showed that individual planar molecules exhibit a three-blade-propeller shape with a width of approximately 2.1 nm and an apparent height of 0.14 nm (Figure 2 c). The molecule is prochiral, and STM images showed that there were in fact two 2D enantiomers on the surface (Figure 2 c, yellow dashed circles). The shape and size of the molecules with three distinct lobes confirmed that the molecules remained intact during the thermal evaporation process. The structure of this precursor molecule was designed in such

a way that upon folding it would form a tetrahedral molecule which should be readily distinguishable by STM, as such molecules are lower and wider than C_{60} . Upon annealing at 480°C for 2 min, the shape of the molecules changed, and STM revealed various species that we ascribe to intermediate states of the partially dehydrogenated and folded molecules (see Figure S5 in the Supporting Information). After annealing at 480°C for 10 min, the cyclization process was complete, as evidenced by STM, which showed full conversion into triangular species, all with a similar size and shape (Figure 2d).

The molecules are imaged as triangular protrusions, thus suggesting that the rim is in contact with the platinum surface. Such a configuration would be in favor considering the formation of strong C–Pt bonds. The apparent height of the final product is approximately 0.28 nm, and the base width is about 1.8 nm, as opposed to 0.4 and 1.5 nm for C_{60} produced from precursor **1** after annealing at 480°C (Figure 2e). These parameters indicate that although the nanotetrahedral precursor has all the necessary C atoms to form C_{60} and a similar structure to that formed from precursor **1**, annealing at 480°C resulted in the formation of a structurally different species, as no C–C bond rearrangement occurred during the annealing. Furthermore, the observation of intermediate products along with final products supports the zipper mechanism of the reaction, whereby only preselected bonds are formed. Therefore, we conclude that the SCCDH process is selective in nature and can be used to produce specifically designed carbon-based nanostructures.

Once the possibility of C–C rearrangement has been ruled out, the SCCDH method opens up new horizons in the synthesis of carbon nanostructures. An example is the efficient synthesis of the higher fullerene C_{84} .

The structure of the $C_{84}H_{42}$ precursor molecule is shown in Figure 1c. The molecule was imaged as three distinct bright lobes with a width of 2.4 nm and a height of 0.14 nm. This image confirmed that the molecule does not decompose during evaporation (Figure 3a,c). The model of $C_{84}H_{42}$ (Figure 1c) shows that the molecule is prochiral; adsorption on the surface led to two distinct chiral forms (Figure 3a, yellow dashed circles). However, chirality does not affect the reaction path, as the zipping mechanism for both of these forms is the same (Figure 1c, dark lines).

Upon annealing at 550°C , the shape of all the molecules changed. The molecules became spherical with a lateral size of about 1.7 nm and an apparent height of 0.42 nm, as evidenced by STM (Figure 3b,d). The lateral size of the newly formed molecules was larger and the apparent height lower than those of the free C_{84} fullerene (the van der Waals diameter obtained from DFT calculations was approximately 1.2 nm). This difference in size might be due to the imaging process but could also indicate that the molecules on the surface undergo relaxations as a result of strong adsorbate–substrate interactions; that is, they maximize the number of bonds with the surface by deformation of the cage. Furthermore, these interactions could lead to the modification of the underlying surface. These effects were observed for C_{60} after annealing on various substrates, including Pt(111),^[15,16] as well as for an isomeric mixture of C_{84} on Si(111)- 7×7 (apparent

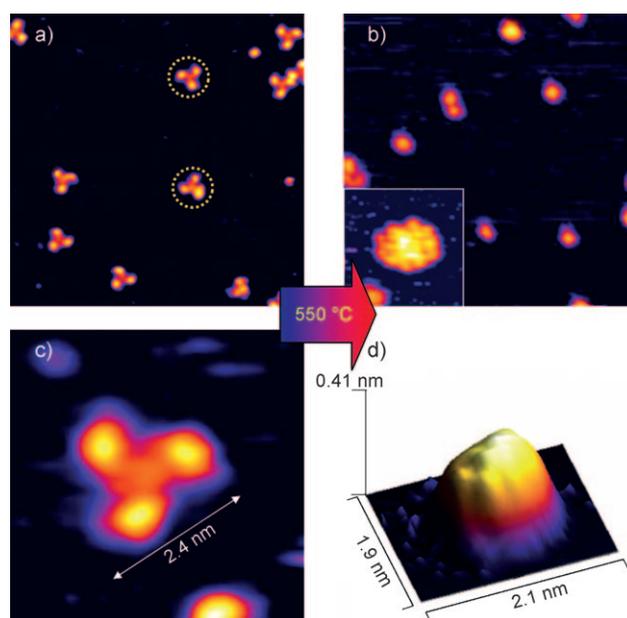


Figure 3. STM images of the C_{84} cyclization process: a) $25\times 25\text{ nm}^2$ and c) $4\times 4\text{ nm}^2$ images of Pt(111) after the deposition of $C_{84}H_{42}$; b,d) images of the surface after annealing of the $C_{84}H_{42}$ precursor at 550°C . The inset in (b) shows a $3\times 3\text{ nm}^2$ image of C_{84} with submolecular resolution.

height 0.59–0.69 nm),^[17,18] in which the molecule–substrate interaction is considered to be weaker than that with the Pt(111) surface (see Ref. [18] and references therein). The molecules were imaged as featureless spherical species (Figure 3b); however, under certain conditions, for example, with an adsorbate on the probe tip, the intramolecular structure was resolved (Figure 3b, inset). The structure was similar to that observed for a C_{84} isomeric mixture^[18] and suggests a π -electron system decoupled from the substrate. Since the possibility of C–C bond rearrangement was excluded by the experiments with precursor **2**, we assume that the newly formed molecule is the $C_{84}(20)$ fullerene. The required annealing temperature for the synthesis of C_{84} is higher than that for C_{60} . We ascribe this difference to the larger precursor size, which does require the breaking of more C–Pt bonds during the cyclization.

The structure of the products cannot be inferred directly from the STM images. Furthermore, the minute amount of material (ca. 10^{12} molecules/ cm^2) and strong surface bonding prevent further analysis by other standard structure-sensitive methods. However, the formation of nanotetrahedra from the modified $C_{60}H_{30}$ precursors is strong evidence against C–C rearrangements in such systems. Theoretical studies showed that Stone–Wales defects and C–C rearrangements in fullerenes and carbon nanotubes would require a temperature of 1250°C even in the presence of a catalyst, which would usually lower the activation temperature significantly.^[19,20] Under the conditions used, it is therefore very unlikely that these processes accompany the folding on Pt(111) (the conversion of buckybowl into a planar carbon layer is observed only upon annealing at 720°C). The surface selectively catalyzes the dehydrogenation reaction, and

together with the demonstrated selectivity of C–C bond formation, the only possibility left is the formation of a single product, the structure of which is defined by the precursor molecules; thus, isomer-specific species are very likely formed.

Our STM experiments show that the conversion ratio of the planar precursor molecules **1**, **2**, and **3** into the corresponding fullerene and open-cage structures is nearly 100% (that is, no desorption occurs during the annealing) and that all precursors are transformed into nonplanar structures. The variation in the shape and size distribution of the products is related to many different possible adsorption geometries and potential surface modification below the products. Our findings demonstrate that the SCCDH method is a very efficient approach towards the synthesis of fullerenes, open-cage structures, heterofullerenes, and endofullerenes. There is essentially no limitation to the variety of organic nonplanar target molecules that could be accessed on the basis of this retrosynthetic strategy.^[21] The procedure could be extended to the fabrication of carbon nanotubes of well-defined diameter and chirality, since the buckybowls can be viewed as a seed for carbon-nanotube growth by chemical vapor deposition (CVD).

Besides the clear advantages of the SCCDH synthesis method, there are some limitations. First, it can only be applied in a well-defined temperature interval. Our results show that the annealing temperature required for the completion of SCCDH increases with the number of C atoms in the precursor molecule (480 °C for **1** and **2**, and 550 °C for **3**). On the other hand, annealing at higher temperatures of about 720 °C leads to complete C–C rearrangement and subsequent decomposition of all the carbon structures into a planar adlayer similar to that grown by CVD on different substrates.^[22] These results indicate that only a small temperature window exists for each specimen for the application of SCCDH, and that the SCCDH process on Pt(111) for the synthesis of high-mass fullerenes might be difficult. Therefore, appropriate substrates have to be explored for the efficient conversion of precursor molecules into the desired carbon nanostructures. Such substrates could be based on platinum-group metals (Ru, Rh, Pd, Os, Ir, and Pt), since these metals are good catalysts for hydrogenation or dehydrogenation reactions.^[23] Control measurements by Otero et al.^[14] for the C₆₀ cyclization on an Au(111) surface showed only very little fullerene formation.

To elucidate the role of the catalytic properties of the substrate, we performed measurements on Cu(100), on which the molecule–substrate interaction is stronger than on Au(111) but significantly weaker than on Pt(111).^[17,24] The STM measurements demonstrated that the molecules were mobile on the Cu(100) surface. After annealing at 380 °C, stable islands of randomly merged triangular-shaped molecules evolved (see Figure S6 in the Supporting Information). Annealing at 480 °C yielded fuzzy mobile features, but no fullerene formation was observed. These observations contrast with the results on the Pt(111) surface, on which the molecules did not form islands at similar temperatures. They indicate that thermally induced diffusion prevents closing of the cage: it is likely that the formation of C–C bonds between

adjacent molecules stabilizes the random aggregates. Thus, a low coverage of precursor molecules is necessary also on the Pt(111) surface to avoid the interlinking of neighboring molecules. On the other hand, the strong molecule–substrate interaction is required for the successful completion of the SCCDH process. Indeed, our STM observations of immobile molecules and time-of-flight secondary-ion mass spectrometry (ToF-SIMS; see the Supporting Information) data indicate that this is the case for Pt(111) substrate.

To conclude, we have shown that the SCCDH process is highly selective in nature. Therefore, the final structure of any kind of carbon-based nanostructure, such as a fullerene or nanotube, can be programmed or built in at the precursor-synthesis stage. Our findings enabled us to produce C₈₄ fullerene for the first time. Although the quantities of the final products are too small to permit direct confirmation of the structural uniformity of the fullerene formed, we believe that SCCDH is an efficient approach to the production of various isomerically pure higher fullerenes and open-cage fullerenes once the respective precursors have been synthesized. SCCDH has been successfully conducted so far on Pt(111) and Ru(0001)^[13] substrates only. Therefore, other substrates have to be explored with regard to whether the SCCDH process can be carried out with optimal efficiency for the desired carbon nanostructure. Furthermore, these findings go even beyond SCCDH reactions. They prove the principle suitability of prefabricated planar precursors for the synthesis of bulk fullerenes.

Experimental Section

The C₆₀H₃₀ fullerene precursor **1** was prepared according to a previously described procedure.^[25] The synthesis of the C₈₄H₄₂ precursor **3** is described elsewhere^[11] (see the Supporting Information for details). Precursor **2** was obtained by the reaction of 1-methylbromo-2-bromonaphthalene with truxene trianion. Subsequent palladium-catalyzed intramolecular arylation gives compound **2** (see the Supporting Information). All precursors were purified by gradient sublimation.

Samples were prepared in an ultrahigh-vacuum (UHV) chamber with a base pressure of 3×10^{-10} mbar. The single-crystal Pt(111) substrate was cleaned by repeated cycles of sputtering with Ar⁺ ions at a sample temperature of 600 °C and annealing at 960 °C. Precursor molecules were deposited on the clean Pt(111) surface by organic molecular beam epitaxy from a Knudsen cell type evaporator with the sample kept at room temperature. Precursors **1** and **2** were sublimed at 540 °C; precursor **3** was sublimed at 590 °C.

Evaporators were degassed for at least 14 h before deposition at 20 °C below the indicated evaporation temperature to avoid any contamination. After deposition, the sample was imaged by variable-temperature STM (Omicron GmbH). After the molecular coverage and integrity of the precursor had been confirmed, the sample was annealed for 2–15 min and then imaged with STM at room temperature. Tunneling parameters of 0.1–0.5 nA and 0.5–1.1 V were used for imaging. To determine the required annealing temperatures for complete SCCDH, the temperature was increased stepwise in the interval 420–720 °C, and the surface was imaged with STM after each annealing step. STM images were analyzed by using WSxM software.^[26]

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- [1] *Carbon Nanomaterials* (Ed.: Y. Gogotsi), Taylor & Francis Group, Boca Raton, **2006**.
- [2] M. Burghard, H. Klauk, K. Kern, *Adv. Mater.* **2009**, *21*, 2586.
- [3] *Fullerenes: Chemistry, Physics, and Technology*. (Eds.: K. M. Kadish, R. S. Ruoff), Wiley-VCH, Weinheim, **2000**.
- [4] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, **1995**.
- [5] T. J. S. Dennis, T. Kai, T. Tomiyama, T. H. Shinohara, *J. Phys. Chem. A* **1999**, *103*, 8747.
- [6] G. Mehta, H. S. P. Rao, *Tetrahedron Lett.* **1998**, *54*, 13325.
- [7] M. J. Plater, M. Praveen, D. M. Schmidt, *Fullerene Sci. Technol.* **1997**, *5*, 781.
- [8] L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291.
- [9] L. T. Scott, *Angew. Chem.* **2004**, *116*, 5102; *Angew. Chem. Int. Ed.* **2004**, *43*, 4994.
- [10] L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. A. de Meijere, *Science* **2002**, *295*, 1500.
- [11] K. Y. Amsharov, M. Jansen, *Chem. Commun.* **2009**, *19*, 2691.
- [12] K. Y. Amsharov, M. Jansen, *J. Org. Chem.* **2008**, *73*, 2931.
- [13] K. T. Rim, M. Sij, S. Xiao, M. Myers, V. D. Carpentier, L. Liu, C. Su, M. L. Steigerwald, M. S. Hybertsen, P. H. McBreen, G. W. Flynn, C. Nuckolls, *Angew. Chem.* **2007**, *119*, 8037; *Angew. Chem. Int. Ed.* **2007**, *46*, 7891.
- [14] G. Otero, G. Biddau, C. Sánchez-Sánchez, R. Caillard, M.-F. López, C. Rogero, F. J. Palomares, N. Cabello, M. A. Basanta, J. Ortega, J. Méndez, A. M. Echavarren, R. Pérez, B. Gómez-Lor, J. A. Martín-Gago, *Nature* **2008**, *454*, 865.
- [15] a) T. Orzali, M. Petukhov, M. Samb, E. Tondello, *Appl. Surf. Sci.* **2006**, *252*, 5534; b) J. Weckesser, J. V. Barth, K. Kern, *Phys. Rev. B* **2001**, *64*, 161403.
- [16] R. Felici, M. Pedio, F. Borgatti, S. Iannotta, M. Capozzi, G. Ciullo, A. Stierle, *Nat. Mater.* **2005**, *4*, 688.
- [17] L. Gavioli, C. Cepek, in *Applied Scanning Probe Methods IX* (Eds.: M. Tomitori, B. Bhushan, H. Fuchs), Springer, Heidelberg, **2008**, pp. 1–20.
- [18] C.-P. Huang, C.-C. Su, M.-S. Ho, *Appl. Surf. Sci.* **2008**, *254*, 7712.
- [19] H. Su, R. J. Nielsen, A. C. T. van Duin, W. A. Goddard III, *Phys. Rev. B* **2007**, *75*, 134107.
- [20] R. Pfeiffer, M. Holzweber, H. Peterlik, H. Kuzmany, Z. Liu, K. Suenaga, H. Kataura, *Nano Lett.* **2007**, *7*, 2428.
- [21] T. N. Hoheisel, S. Schrett, R. Szilluweit, H. Frauenrath, *Angew. Chem.* **2010**, *122*, 6644; *Angew. Chem. Int. Ed.* **2010**, *49*, 6496.
- [22] J. Coraux, A. T. N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie, F.-J. Meyer zu Heringdorf, R. van Gastel, B. Poelsema, T. Michely, *New J. Phys.* **2009**, *11*, 023006.
- [23] P. N. Rylander, *Organic syntheses with noble metal catalysts*, Academic Press, New York, **1987**.
- [24] G. Schull, N. Néel, M. Becker, J. Kröger, R. Berndt, *New J. Phys.* **2008**, *10*, 065012.
- [25] B. Gómez-Lor, Ó. de Frutos, A. M. Echavarren, *Chem. Commun.* **1999**, 2431.
- [26] L. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, A. M. Baro, *Rev. Sci. Instrum.* **2007**, *78*, 013705.
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