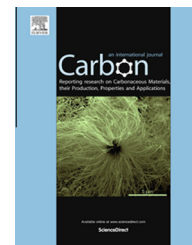


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Bottom up fabrication of (9, 0) zigzag and (6, 6) armchair carbon nanotube end-caps on the Rh(111) surface



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ABSTRACT

The exploration and wide application of single walled carbon nanotubes (SWCNTs) require the development of new synthetic approaches enabling facile and fully rational CNT fabrication. In this communication the conversion of two precursors yielding the potential CNT seeds of (9, 0) zigzag and (6, 6) armchair nanotubes using surface-assisted cyclodehydrogenation on the Rh(111) single-crystal surface is reported. The conversion efficiency found is nearly 100% and the CNT-caps remain thermally stable on the Rh surface up to 820 K which is high enough for subsequent SWCNT growth. It is shown that Rh is a suitable catalyst for the controllable synthesis of SWCNTs by the surface assisted bottom-up strategy.

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1. Main text

Single-walled carbon nanotubes (SWCNTs) attract considerable attention due to their extraordinary electronic, thermal and mechanical properties, that have stimulated their incorporation into a wide range of applications [1]. The large number of possible isomeric nanotube structures allows for the tuning of the required properties for specific purposes. For instance, the electronic structure of SWCNTs strongly depends on the orientation of the hexagonal lattice relative to the tube axis and on the diameter of the CNT and can exhibit either metallic or semi-conducting characteristics [1]. In order to fully exploit this structural variety isomerically pure CNT samples are needed, which may be achieved by chirality specific growth of SWCNTs, one of the long standing challenges in this field. Among several suggested approaches

for controllable SWCNT fabrication, a very promising route is based on the synthesis of hemispherical buckybowls that could serve as seeds for the growth of SWCNTs with predefined chirality [2–4]. The corresponding buckybowl molecules can be obtained from planar polycyclic aromatic hydrocarbon (PAH) precursors by surface-assisted cyclodehydrogenation (SACDH), which was found to be a very effective and highly selective process [5–7]. Recently we have demonstrated that the uncontrolled nucleation of an end-cap can be avoided by introducing a hemispherical buckybowl with predefined structure and subsequent growth on Pt(111) surface yielding isomerically pure SWCNTs [8]. Based on this discovery a one-pot synthesis strategy appears to be very attractive for the preparative synthesis of isomerically pure SWCNTs. For the successful application of this method, both formation of the end-cap as well as subsequent growth of the CNTs have

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to be performed on the same catalytic surface. Big efforts have been dedicated in the past towards the exploration of catalytically active elements for Chemical Vapor Deposition (CVD) growth of CNTs. However, there is very little experimental data concerning catalytically active substrates for the selective cyclodehydrogenation, and so far only Pt and Ru single-crystal surfaces were shown to be suitable for an efficient conversion of planar PAHs to buckybowls [5–8]. Since CNT growth on known catalyst such as of Fe, Ni or Co under the CNT synthesis conditions proceeds via complete dissolution of the carbon in the catalyst nanoparticle [9], these metals cannot be used for the SACDH method discussed here. Therefore, the choice is limited to the Pt group metals for which carbon dissolution does not take place [6]. In this work we present the surface catalyzed cyclodehydrogenation of two CNT precursors (compound I and II) to the corresponding CNT end-caps of a (9, 0) zigzag and a (6, 6) armchair SWCNT on a Rh(111) surface with nearly 100% conversion efficiency. Furthermore it is shown that the CNT end-caps formed are thermally stable on the Rh(111) surface at least up to the required growth temperature for CNT synthesis.

All STM measurements were carried out at room temperature. The single crystal Rh(111) sample was cleaned with repeated cycles of Ar⁺ sputtering and annealing to 1200 K, leading to atomically flat, ca. 100 nm wide, clean terraces as evidenced by STM. Precursors I and II were synthesized according a previously reported procedure [2]. Both molecules were additionally purified by gradient sublimation in vacuo (750 K, 10⁻³ mbar). The high purity of both molecules was confirmed by LDI-MS analysis (for details see [Supporting information](#)). The employed precursor molecules and their expected reaction products after the SACDH process are shown in Fig. 1. The Precursor I-C₅₄H₂₄ is expected to lead to a (9, 0) nanotube cap with the diameter of 0.73 nm and a

zig-zag structure, and precursor II-C₆₀H₃₀ was designed to yield a cap for an (6, 6) armchair nanotube with the diameter of 0.77 nm. When deposited onto the substrate at room temperature, both precursors I and II are imaged as trefoil-shaped protrusions (Fig. 2a and b). The molecules remain intact despite the relatively high evaporation temperatures of 740 K and 780 K for precursor I and II, respectively. The random distribution of the molecules and the absence of step-edge decoration points to a strong molecule–substrate interaction, which is one of the key conditions for successful SACDH reactions. The base size of the molecules as determined from the STM images amounts to 1.8 nm and 2 nm with an apparent height of 0.15 nm and 0.12 nm for precursors I and II respectively. After annealing the sample to 730 K and 750 K for 5 min for I and II respectively, a complete transformation of all the trefoil species into the round molecules was observed. Previously we have demonstrated that similar transformation to the ultra-short nanotubes which can be grown to isomer pure SWCNTs by epitaxial elongation can be realized on the Pt(111) surface [8]. Although this work proves the feasibility of the approach for fully controlled synthesis of chirality pure SWCNTs, the yield obtained was hampered already by the precursor molecule itself. Due to presence of single C–C bonds in the structure of the precursor used, undesired adsorption conformations result when the molecule is deposited on the catalyst surface thus leading to the formation of irregular buckybowls upon cyclodehydrogenation. Thus only 50% of all deposited precursors end up with the desired cap connectivity. In contrast the formation of only one type of the CNT caps was observed in present study due to utilizing of rigid and robust CNTs precursors which do not have any weak bonds in the structure and can accept only one single conformation on a surface. Importantly no formation of species of other geometries was detected upon annealing, pointing out that no C–C rearrangements take place under SACDH condition and the condensation is highly selective in nature. This indicates that the cap formation is a result of regioselective intramolecular cyclization leading to the desired CNT caps exclusively as it is “programmed” by the molecular structure of the precursors. Virtually only hemispherical caps of the same dimension can be identified on the surface after annealing whereas the density of undefined defect structures is very low, thus showing that the conversion efficiency is close to unity (Fig. 2). The apparent height and width of newly formed species was found to be 0.25 nm and 0.9 nm for precursor I and 0.3 nm and 1.2 nm for precursor II, additionally suggesting that the desired CNT caps have successfully formed. The notably lower, as would be expected, height of the caps (Fig. 2e) indicates strong adsorbate–substrate interactions leading to the reconstruction of the underlying Rh surface. This effect was observed previously for buckybowls and fullerenes where a similar in magnitude reduction of their apparent height was observed after annealing on the metallic surface [5–8]. This effect seems to be responsible for slight inhomogeneity in height, which was also observed previously [7,8]. A strong molecule–substrate interaction is one of the key conditions for successful SACDH reactions which prevents the fusion of the precursor molecules. Nevertheless it is not possible to exclude completely close proximity of two molecules on the

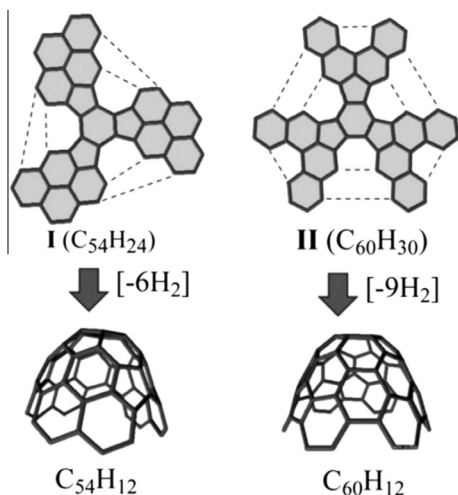


Fig. 1 – SWCNT-cap precursors and corresponding reaction products C₅₄H₁₂ and C₆₀H₁₂ after intramolecular cyclodehydrogenation: I C₅₄H₂₄ and II C₆₀H₃₀. Dashed lines indicate the formation of new C–C bonds upon SACDH. Hydrogen atoms are omitted for clarity.

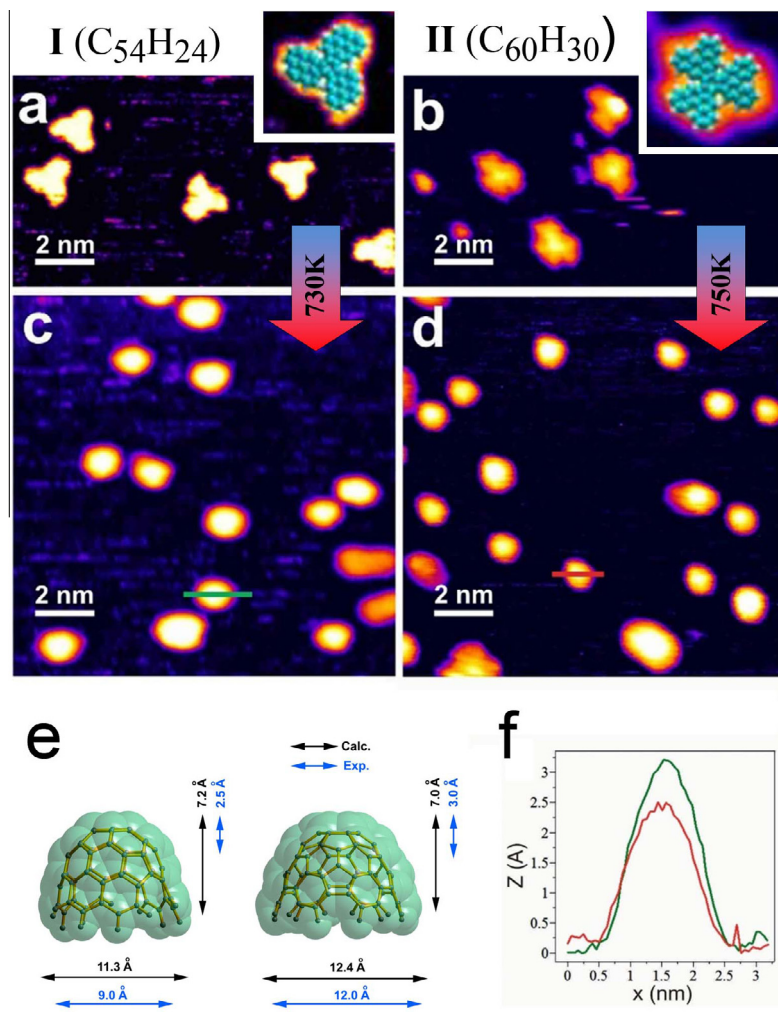


Fig. 2 – STM images of the CNT cap formation from precursors. Precursors (a) I and (b) II as deposited onto the Rh(111) surface (image size $13 \times 8 \text{ nm}^2$). Cap formation from the precursor (c) I after annealing to 730 K for 5 min and (d) II after annealing to 750 K for 5 min (image size $13 \times 13 \text{ nm}^2$). (e) The geometries of $\text{C}_{54}\text{H}_{12}$ and $\text{C}_{60}\text{H}_{12}$ buckybowls. Experimentally observed (blue) and calculated on DFT 6-311 basis set (black). (f) Scan profiles along the lines shown in (c) and (d). Comparison of STM observed and theoretically estimated heights and widths of CNT caps: $\text{C}_{54}\text{H}_{12}$ (left) and $\text{C}_{60}\text{H}_{12}$ (right). (A color version of this figure can be viewed online.)

surface after deposition even at very low surface coverage. In such a case, the possibility of the merging of two precursor molecules and formation of undesired nanostructures during SACDH cannot be excluded. Fortunately, as it has been shown experimentally, such irregular geodesic species are not able to provoke a SWCNT growing [8], since further elongation of these structures to the nanotube by only hexagons construction is not possible. Thus this side reaction will not affect the quality of SWCNTs fabricated by the suggested strategy. To test the stability of the newly formed caps, higher annealing temperatures in the range of 780–930 K were explored with an increment of 10 K. For precursor I no change in the structure was found up to 820 K, after which the shape and the height of the caps started to transform. The full transformation into graphene-like structures took place at about 875 K, where small islands with a typical moiré-pattern were found. For precursor II, the stability threshold is somewhat higher,

approximately 850 K, and the nanographene formation was completed at about 900 K. Although the threshold temperatures are lower than the temperatures typically used in the conventional CVD process [9], they are high enough in order to achieve epitaxial nanotube elongation. Recently we have demonstrated that an effective CNT growth from CNT seeds can be realized at very low temperatures, even below 670 K [8]. Since the caps for carbon nanotubes are already formed on the Rh surface which is catalytically active for CNT growth [10], they might be used as seeds for the fully controllable growth of CNTs.

In conclusion, we have shown that specially designed planar aromatic precursors can be effectively converted into hemispherical buckybowls using SACDH approach on Rh(111) surface. The threshold temperatures for the degradation of CNT caps on the Rh surface were found to be high enough in order to conduct subsequent CNT growth and

Rh(111) surface therefore appears to be suitable for the controllable synthesis of SWCNT by one-pot bottom-up strategy [8]. Since the approach mimics the fabrication of SWCNTs under conventional CVD condition we strongly believe that nanotubes of all chiralities, at least those which can be grown by CVD method, can be fabricated in fully controllable manner in isomer pure form by utilizing a proper catalyst surface and respective SWCNT precursors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.12.038>.

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