Bottom-Up Synthesis of Metalated Carbyne

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S *Supporting Information*

ABSTRACT: Because of stability issues, carbyne, a one-dimensional chain of carbon atoms, has been much less investigated than other recent carbon allotropes such as graphene. Beyond that, metalation of such a linear carbon nanostructure with regularly distributed metal atoms is even more challenging. Here we report a successful on-surface synthesis of metalated carbyne chains by dehydrogenative coupling of ethyne molecules and copper atoms on a Cu(110) surface under ultrahigh-vacuum conditions. The length of the fabricated metalated carbyne chains was found to extend to the submicron scale (with the longest ones up to ∼120 nm). We expect that the herein-developed on-surface synthesis strategy for the efficient synthesis of organometallic carbon-based nanostructures will inspire more extensive experimental investigations of their physicochemical properties and explorations of their potential with respect to technological applications.

For a long time, carbon-based materials have received tremendous attention, fueled also by the successive discoveries of novel carbon allotropes such as fullerenes, carbon nanotubes, and graphene, which exhibit extraordinary properties rendering potential scientific and industrial applications.[1] Another carbon allotrope, carbyne, a linear, one-dimensional chain of carbon atoms, is also expected to have interesting properties such as extreme mechanical behaviors among known materials (i.e., ultrahigh stiffness and Young's modulus),[2] room-temperature superconductivity,[3,4] intriguing nonlinear optical properties,[5] and high hydrogen storage capability.[6] Although the structure of carbyne was proposed long ago, scientific advances made on carbyne are limited in comparison with those on other carbon allotropes, and the main challenge lies in synthesizing the elusive carbyne with a well-defined structure.[7−9] Beyond that, metalation of such a carbon nanostructure with well-distributed metal atoms is even more challenging and of great interest because it may allow regulation of the intrinsic physicochemical properties of the carbon nanostructure/nanomaterial.[10,11]

Recently, on-surface synthesis has emerged as a rapidly developing research field because of its fascinating potential for the fabrication of novel nanostructures/nanomaterials. Among others, carbon nanomaterials such as fullerenes,[12] graphene,[13,14] graphene nanoribbons,[15] and single-chirality carbon nanotubes[16] have been achieved by such a method. Inspired by recent investigations of dehydrogenative/dehalogenative coupling of terminal alkynes/alkynyl bromides with metal atoms on surfaces,[17,18] here we chose the ethyne molecule (the simplest alkyne with two terminal alkynyl groups) as a precursor with the aim of forming linear metalated carbon chains through on-surface dehydrogenative coupling, as sketched in Figure 1. The anisotropic Cu(110) surface was selected because of its relatively high chemical activity and the well-known one-dimensional (1-D) templating effect that facilitates the formation of 1-D carbon-based nanomaterials. Herein we present our successful synthesis of metalated carbyne by a facile and highly efficient surface chemistry
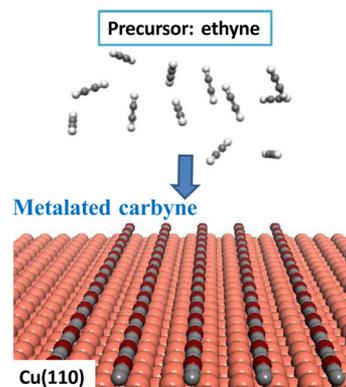
Figure 1. Illustration of the bottom-up synthesis of metalated carbyne on Cu(110) through dehydrogenative coupling of ethyne precursors and copper adatoms on Cu(110) under UHV conditions. Gray, carbon; white, hydrogen; brown, copper substrate atom; red, copper adatom.

method and report characterization of the products by high-resolution scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), and X-ray photoelectron spectroscopy (XPS) combined with density functional theory (DFT) calculations. We have found that the length of the obtained metalated carbyne chains extends into the submicron range.

After deposition of ethyne on Cu(110) at low temperature (~220 K) under ultrahigh-vacuum (UHV) conditions, we mainly found the formation of bright protrusions that desorbed from the surface after gentle annealing of the sample to ~330 K (Figure S1). These observations are in agreement with a previous study showing that ethyne can be cyclized into benzene on Cu(110), as determined by temperature-programmed desorption.[19] After deposition of ethyne at temperatures between room temperature and 400 K, we observed complicated structures whose nature could not be unambiguously determined (Figure S2). Some of them could be assigned to polyacetylene with the help of high-resolution nc-AFM imaging. Detailed structural and spectroscopic analyses to elucidate these structures are underway (the corresponding results will be reported elsewhere). Next, we tried to optimize the experimental conditions by substrate temperature regulation to avoid undesired side reactions and to facilitate the dehydrogenative coupling reaction.

As shown in Figure 2a, after deposition of ethyne (at a base pressure of 1×10^{-8} mbar for 10 min) on the surface held at
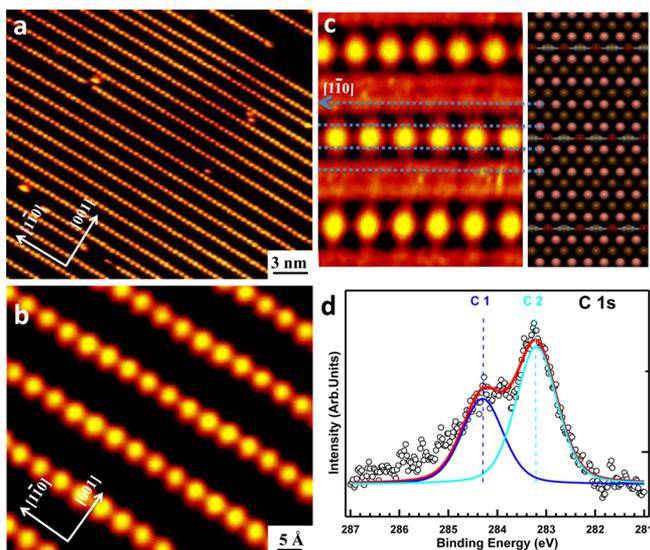
Figure 2. (a) Large-scale and (b) close-up STM images showing the formation of metalated carbyne chains. (c) High-resolution STM image resolving the metalated carbyne and the substrate lattice simultaneously. The underlying copper rows along the $[1\bar{1}0]$ direction are indicated by blue dashed lines. The corresponding DFT-optimized structure model of metalated carbyne is presented aside for comparison. (d) C 1s core-level XP spectrum showing the major peak C2 located at a binding energy of 283.2 eV (cyan curve).

~450 K, 1-D chains along the close-packed $[1\bar{1}0]$ direction of the substrate were formed. This chain structure is characterized by periodic protrusions in close-up STM images (Figure 2b). To get further insight, we performed an XPS analysis. As depicted in Figure 2d, the C 1s spectrum showed a minor peak at ~284.3 eV (marked as C1) and a major peak at ~283.2 eV (marked as C2). According to previous experimental and

theoretical studies, the peak at ~284.3 eV is characteristic of unsaturated carbon atoms on surfaces,[15,20,21] and the lower-binding-energy (~283.2 eV) C 1s peak is attributed to carbon atoms bound to metal (copper atoms in this case).[20−23] It is known that copper adatoms are often involved in dehydrogenative/dehalogenative coupling reactions by the formation of organometallic species.[17,24−26] Therefore, we attribute this chain structure to metalated carbyne, i.e. $[-Cu-C-C-]_n$ 1-D organometallic carbon chains. The high-resolution STM image shown in Figure 2c allowed us to identify the registry between the metalated carbyne and the substrate lattice. We found that the metalated carbyne prefers to be located at the bridge sites of copper rows along the $[1\bar{1}0]$ direction, which is in good agreement with its theoretically optimized most stable structure (cf. right panel of Figure 2c). Since the two carbon atoms within the metalated carbyne structure are equivalent, the C1 peak must be related to some other (undetermined) byproduct, as indicated in Figure S3. It is noteworthy that we could easily fabricate well-defined metalated carbyne on the Cu(110) surface at different coverages. At relatively high coverage (~0.8 monolayer), the surface was predominately covered by metalated carbyne chains, the longest of which reached ~120 nm (Figure S4).

We believe that the substrate temperature plays a crucial role in facilitating the formation of metalated carbyne on Cu(110) on the basis of the following considerations: (i) the relatively high substrate temperature (450 K in this case) provides enough thermal energy for dehydrogenation of ethyne on the surface; (ii) enough free copper adatoms exist at such a substrate temperature; and (iii) a specific temperature window may prohibit unwanted side reactions and allow selective triggering of the metal-assisted dehydrogenative coupling reaction. It has also been reported that upon postannealing the Cu atoms can be released from C−Cu−C structures to give purely C−C-bonded structures.[24] We thus also postannealed our metalated carbyne samples to 500, 550, and 600 K gradually. Rather than the formation of C−C bonds, however, we found a gradual decrease in the coverage of metalated carbyne and finally the degradation of all carbon atoms. We performed similar experiments on Ag(110) and Au(110) surfaces but found that ethyne molecules would hardly stick on either of these surfaces over a wide temperature range ($T_{substrate}$ from 180 to 600 K), indicating relatively weak interactions between ethyne and these two surfaces.

To further verify the formation of metalated carbyne and unravel its atomic-scale structure, we resorted to nc-AFM imaging in conjunction with extensive DFT calculations. As shown in Figure 3a,b, the simultaneously acquired nc-AFM frequency shift and current images show the same characteristic chain structure as in Figure 2, which undoubtedly confirms the proposed metalated carbyne structure on the surface. From a comparison of the equally scaled high-resolution nc-AFM frequency shift image, STM image (i.e., the current image), DFT-optimized model, and STM simulation and line-scan profile of a metalated carbyne chain on Cu(110), as shown in Figure 3c, we determine that (i) the experimental periodicity of the metalated carbyne chain is 5.2 ± 0.2 Å, which corresponds to two copper lattice spacings along the $[1\bar{1}0]$ direction; (ii) the periodic protrusions of the chain seen in the STM images are due to the incorporated copper atoms; and (iii) the copper atoms are not imaged in the nc-AFM imaging, but instead the carbon−carbon bonds are resolved.
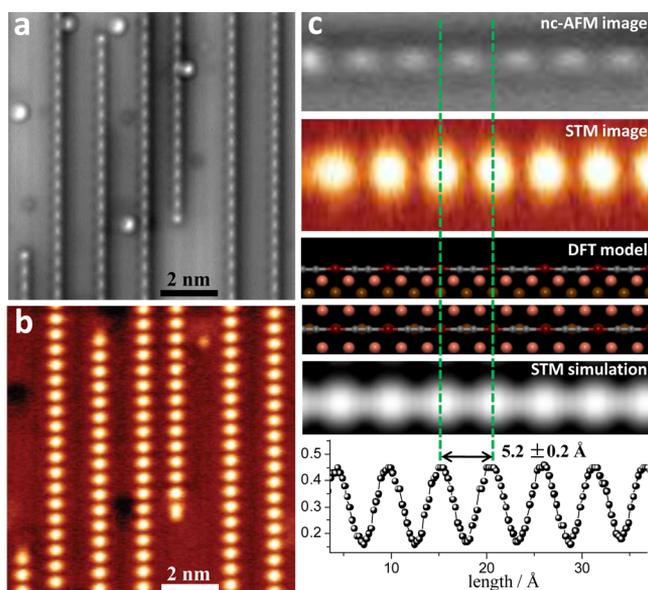
Figure 3. (a) Large-scale nc-AFM frequency shift image, taken in constant-height mode using a CO-terminated tip at a small bias voltage of 5 mV. (b) Current image acquired simultaneously with the frequency shift image in (a). (c) Equally scaled high-resolution nc-AFM frequency shift image, current image, DFT-optimized model, and STM simulation and line-scan profile of a single metalated carbyne chain on Cu(110).

To elucidate this at first sight unexpected phenomenon, we performed further DFT calculations to analyze the electronic properties of a metalated carbyne chain on Cu(110). As shown in Figure 4, the corresponding electron density and bond length analyses clearly revealed the alternating carbon−carbon

(1.310 Å) and carbon−copper (1.902 Å) bonds. Moreover, it is clearly seen that high electron densities are mainly located along the carbon−carbon bonds, which accounts for the bright protrusions being the carbon−carbon bonds reflected in the nc-AFM imaging. The projected density of states (PDOS) of the carbon atoms demonstrates the sp hybridization characteristics, as reflected by the overlap of the electronic features of the s and p_x orbitals, and the interaction between carbon and copper atoms is reflected in a broadening of the electronic features of the p_y and p_z orbitals.

The synthesis of well-defined metalated carbon nanostructures has remained a major experimental challenge because of the difficulty in incorporating metal atoms into carbon scaffolds. To the best of our knowledge, metalated carbyne structures have not been achieved previously. In our study, the anisotropic Cu(110) substrate not only served as a catalytically active template for directing the growth of unidirectional metalated carbyne chains but also separated them from each other because of their energetically favorable bridge adsorption sites, inhibiting the occurrence of cross-linking.

The present on-surface chemistry strategy is a facile and highly efficient method to fabricate metalated carbyne that paves the way to further explorations of its properties and potential applications. The involvement of metal atoms provides a versatile manner for modulating the intrinsic electronic properties of carbon nanostructures, which will perspectively enrich their potential applications in diverse fields. For example, metal-doped carbon nanomaterials could be promising for organic superconductors.[10,11] A further challenging objective will be to explore the feasibility of transferring the synthesized metalated carbyne outside UHV conditions by methods similar to the ones developed for epitaxial graphene.[27]

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10725.

Experimental details and additional STM images (PDF)

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Notes

The authors declare no competing financial interest.

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Figure 4. (top) DFT-optimized model of metalated carbyne on Cu(110) and its electron densities (shown in yellow) at an isosurface value of 0.4 e Å^{-3}. The lengths of the carbon−carbon and carbon−copper bonds are indicated. (bottom) Corresponding PDOS for the s, p_x, p_y, and p_z orbitals of the carbon atoms of metalated carbyne on Cu(110).

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