Synthesizing Highly Regular Single-Layer Alkynyl–Silver Networks at the Micrometer Scale via Gas-Mediated Surface Reaction

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Supporting Information

ABSTRACT: Extended organometallic honeycomb alkynyl-silver networks have been synthesized on a noble metal surface under ultrahigh vacuum conditions via a gasmediated surface reaction protocol. Specifically, the controlled exposure to molecular oxygen efficiently deprotonates terminal alkyne moieties of 1,3,5-tris(4ethynylphenyl)benzene (Ext-TEB) precursors adsorbed on Ag(111). At $T_{sub} = 200$ K, this O₂-mediated reaction pathway features high chemoselectivity without poisoning the surface. Through mild annealing to 375 K, long-range ordered alkynyl-silver networks incorporating substrate atoms evolve, featuring Ag-bis-acetylide motifs, high structural quality and a regular arrangement of nanopores with a van der Waals cavity of $\approx 8.3 \text{ nm}^2$.

n-surface synthesis¹⁻³ under ultrahigh vacuum (UHV) conditions opens new avenues toward preparing novel light-element-based two-dimensional (2D) materials with oneatom-thickness, such as graphene,⁴ hexagonal boron nitride,^{5,6} graphyne and graphdiyne-related materials,⁷⁻¹⁰ via the bottom-up construction route.¹¹ In this field, a commonly adopted approach is to trigger reactions among preadsorbed species on a substrate by thermal treatment, whereby the adsorbates are in equilibrium with the substrate. In contrast, research into chemical transformations involving gas-phase species, in analogy to the Eley-Rideal type reactions,¹ received less attention.^{13,14}

Creating extended covalent or organometallic 2D architectures through interfacial molecular engineering remains challenging and is mainly limited by the simultaneous opening of multiple reaction channels causing undesired side reactions at elevated temperatures.^{15,16} It has recently been shown that the carbon-halogen bond dissociation at metal surfaces frequently yields carbon-metal-carbon (C-M-C) inter-mediates,¹⁷⁻²⁰ which could potentially afford regular C-C coupled structures after further chemical conversions. Intriguingly, the C-M-C bond itself was found to be of covalent nature²¹ and represents a key ingredient for hypothesized 2D organic topological insulators.^{22,23} However, the formation of regular C-M-C structures at large scales (e.g., micrometer) via dehalogenation reactions proved difficult.¹⁹

Herein, employing complementary scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) coupled with density functional theory (DFT) modeling, we report the fabrication of alkynyl-silver-alkynyl bonded honeycomb networks (alkynyl-Ag networks in brief) at the micrometer scale via a novel synthetic protocol. The employed gas-mediated approach includes a low-temperature deprotonation step and is free from halogens. Specifically, we found that molecular O2 efficiently deprotonates terminal alkyne groups of 1,3,5-tris(4-ethynylphenyl)benzene (Ext-TEB) precursors adsorbed on Ag(111) at low substrate temperature (T_{sub} = 200 K). The thorough deprotonation and the concomitant desorption of the reaction byproducts prepare the system in a state favoring the formation of alkynyl-Agalkynyl bonds via incorporation of thermally released silver substrate atoms with high chemoselectivity upon thermal activation (cf. also Scheme 1). In sharp contrast, when the reactions started with coadsorbed oxygen and Ext-TEB molecules on Ag(111), irregular structures as well as a heavily modified surface were observed.

After exposing a submonolayer of intact Ext-TEB covered Ag(111) surface held at 200 K to O_2 (≈ 6000 L), dense-packed molecular islands evolve with distinct order (Figure 1a), differing from the nanoporous structures of self-assembled intact molecules (cf. Figure S1).^{25,26} Figure 1b displays highresolution STM data, revealing (i) individual molecules appearing as triangular protrusions; (ii) a molecular arrangement reminiscent of ionic hydrogen bonding networks previously observed for the Ext-TEB/Cu(111) system²⁷ (cf. also Figure S2); (iii) characteristic electron depletion in the vicinity of the terminal groups^{27,28} discernible at the island edges (cf. black arrow in Figure 1b). These features are fully consistent with a terminal alkyne deprotonation scenario.²

XPS measurements were carried out to assess O2-induced chemical changes. In comparison with the intact Ext-TEB species, after O_2 exposure ($T_{sub} = 200$ K), the C 1s main corelevel line shifts by ≈ 0.3 eV toward lower binding energies

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Scheme 1. Two-Step Formation of Extended Alkynyl-Silver-Networks via Oxygen Gas Mediated Deprotonation on the Ag(111) Surface

Step i (O₂-mediated terminal alkyne deprotonation):

 $\left[\mathbf{R} - \mathbf{H} \right]_{ad} + \mathbf{O}_2 \bigvee \left[\begin{array}{c} 200 \text{ K} \\ -Ag(111) \end{array} \right]_{ad} + by \text{-products} \right]_{ad}$

Step ii (on-surface alkynyl-Ag-alkynyl bond formation):



(Figure 1c). A similar tendency has been observed for onsurface dehalogenation²⁹ as well as CH activation reactions,³¹ which can be ascribed to the slight negative charging of the molecular species upon chemically bonding to the metal surface.^{27,28} Furthermore, a signal contribution developed at 283.6 eV (Figure 1c, red component), usually observed upon C-M-C bond formation.^{29,31,32} Since the STM data shows that under the employed conditions alkynyl-Ag-alkynyl linkages have not yet formed (cf. also Figure S3), this peak evidences the strong chemical interaction³³ between the alkynyl groups and the substrates.^{27,30} This low binding energy component contributes \approx 19% of the total area, indicating a thorough deprotonation close to the ideal value of 20% (cf. Figure S4).²⁵ Importantly, the absence of an O 1s signature in the XPS spectrum of the same sample (red dotted O 1s curve in Figure 1c) excludes adsorbed oxygen species³⁰ or oxygencontaining reaction intermediates or byproducts (Figure S5).

Upon annealing this sample to 250 K, organometallic dimers, trimers, and oligomers including closed hexagons evolve (Figure 1d). These structures can be rationalized as alkynyl–Ag–alkynyl species (Figure S6), frequently encountered on the Ag surfaces when terminal alkynes have been deprotonated.^{29,34} Further annealing to 300 K entails two types of molecular domains (cf. Figure 1e): (i) the alkynyl–Ag networks (denoted as phase I); and (ii) noncovalent structures comprising mainly the hexagonal Ag-*bis*-acetylide macrocycles (denoted as phase II). Apparently, the energy barrier for direct C–C coupling between alkynyl groups is higher than that for forming an alkynyl–Ag–alkynyl linkage by incorporating a silver adatom.

Finally, following moderate annealing at 375 K, XPS reveals that the main peak in the C 1s spectrum shifts by ≈ 0.1 eV back



Figure 1. (a) Overview STM image of deprotonated Ext-TEB molecular islands on Ag(111) prepared by dosing O₂ gas at $T_{sub} = 200$ K ($I_t = 0.1$ nA, $U_b = -0.5$ V). (b) Zoomed-in image of an area in panel a, featuring ionic hydrogen bonding ($I_t = 0.1$ nA, $U_b = -0.2$ V). (c) C 1s and O 1s XPS spectra of a submonolayer sample subjected to the O₂ exposure, followed by subsequent annealing steps. Percentages correspond to relative contributions from different carbon species (cf. Figure S4). (d) Formation of alkynyl–silver dimers, trimers, and hexamers after annealing at 250 K ($I_t = 0.1$ nA, $U_b = -0.1$ V). (e) STM overview image of the same sample after annealing at 300 K. Phase I and II represent the alkynyl–silver network and the noncovalent alkynyl–silver hexamer domain, respectively ($I_t = 0.1$ nA, $U_b = -0.5$ V).

to the high energy side, whereas the low binding energy component remains at 283.6 eV with similar intensity (Figure 1c), as verified by DFT calculations (Figure S4). The corresponding STM imaging shows that regular alkynyl–Ag networks extend to the micrometer scale, as depicted in Figure 2a. The bright protrusions in the networks correspond to impurities as well as trapped molecules (Figure S7). Their atomistic modeling supported by DFT calculations (Figure 2c) is consistent with the alkynyl–Ag–alkynyl bridging motifs. The networks terminate with zigzag edges (Figure S8) and do not continue when crossing the steps, indicating that only the width of the Ag(111) terrace limits the network size.

The mesoscopic extension of the alkynyl-Ag network is confirmed by low-energy electron diffraction (LEED). The LEED patterns show sharp spots corresponding to the network on the entire crystal surface (cf. inset of Figure 2a and Figure

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Figure 2. (a) Large-scale STM image of sample annealed at 375 K, featuring a uniform, regular alkynyl–Ag domain extending at the micrometer scale ($I_t = 0.1 \text{ nA}$, $U_b = -2.0 \text{ V}$). Inset: zoomed-in image of a small area with both phases I and II coexisting ($I_t = 0.1 \text{ nA}$, $U_b = -0.1 \text{ V}$); LEED pattern of the alkynyl–Ag network prepared on a different Ag(111) crystal ($T_{\text{meas}} = 100 \text{ K}$, $E_{\text{electron}} = 39 \text{ eV}$). The yellow and red circles indicate the first order diffraction spots of the network and the Ag(111), respectively. (b) High-resolution STM image of the alkynyl–Ag network ($I_t = 0.1 \text{ nA}$, $U_b = -1.0 \text{ V}$). Inset: FFT of an area (150 nm × 150 nm) where b is embedded. (c) DFT calculated unit cell and the molecular registry of the alkynyl–Ag network superposed with a scaled STM image. Orange dashed lines indicate the distorted kagome lattice defined by the intercalated silver atoms coded in blue.

S9b) and remain stable up to room temperature (Figure S9c), further proving the robustness of the network.

We tested the possibility of converting the organometallic network into a covalent sheet through further thermal treatment. After annealing to $T_{\rm ann}$ = 450 K, we did not observe the conversion of alkynyl–Ag–alkynyl bridges into a C–C linkage; rather, irregular structures appeared (cf. Figure S10). This observation again points to the fact that high-temperature annealing is not an optimal choice for the construction of 2D covalent networks.

A zoomed-in image of the alkynyl-Ag network shows that the pores in the network are not perfect hexagons; however, their shape remains the same along one direction (cf. the [112] direction in Figure 2b,c), whereas the neighboring columns display a glide symmetry. Notably, the silver atoms in the organometallic network generate a distorted kagome lattice (Figure 2c). The adsorption registries of the Ext-TEB backbone as well as the alkynyl-Ag-alkynyl bridges (Figure 2c) span a commensurate rectangular unit cell ($a_1 = 63.6$ Å, a_2 = 35.0 Å), which is nicely reproduced by means of extensive DFT calculations. The 2D fast Fourier transform (2D-FFT) of a large domain (inset of Figure 2b), where the magnified area is embedded, also shows a rectangular reciprocal lattice, consistent with the real-space analysis and the DFT modeling (Figure 2c). Note that in the LEED pattern the slight distortion of the honeycomb network induced by moleculesubstrate interaction cannot be recognized straightforwardly (cf. also Figure S9).

In order to gain further insight into the alkyne deprotonation scenario, similar doses of O_2 gas were applied at $T_{sub} =$ 90–100 K, leading to surface decoration with oxygen (cf. Figure S11a). XPS characterization of this sample shows that both molecular as well as atomic oxygen species coexist (Figure S12b), being consistent with earlier studies.^{35,36} Annealing this sample to 200 K yielded reaction products other than purely deprotonated Ext-TEBs as well as a heavily modified surface (Figure S11). However, the reactions among coadsorbed oxygen species and Ext-TEBs on Ag(111) do not afford regular architectures after annealing to higher temperatures. Noteworthy, direct annealing of intact Ext-TEB on the Ag(111) surface without additional gas species triggers homocoupling of terminal alkynes.²⁵ The marked differences of the products depending on the recipes highlights the importance of carefully tuning the reaction conditions and the distinction of our approach.

In addition, we explored whether other gas molecules could trigger a similar deprotonation reaction. It was found that neither CO nor H_2O molecules are able to deprotonate Ext-TEBs on Ag(111). We also examined Ext-TEB layer on the more noble Au(111) surface, and found that the system remain unchanged after O_2 and CO exposure. These results indicate that both the gas phase species and the surface play a crucial role for the particular deprotonation reaction.

To summarize, we introduced a potentially versatile fabrication procedure for extended interfacial nanoporous molecular networks reaching micrometer domain size. Our method may have general implications in the field of interfacial synthesis and molecular engineering and demonstrates the promise of combining both gas-mediated chemical conversions as well as UHV on-surface reactions for achieving novel carbon-based 2D-sheet materials with extensive regularity and long-range order.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b13547.

Experimental details, modeling for molecular selfassemblies and organometallic structures, additional STM, XPS, TPD, LEED data and DFT-XPS simulations (PDF)

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Notes

The authors declare no competing financial interest.

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