

I. INTRODUCTION

Graphdiyne and graphyne as well as their derivatives are 2D semiconducting allotropes of carbon with non-zero band gaps [1], which make a distinct advantage over graphene for transistors with high on-off ratios [2]. The 1D limit of graphyne and graphdiyne consists of repeating units of phenylene and ethynylene or butadiynylene, respectively [3, 4]. The ultimate small width (0.5 nm) and moderate band gap (~1.5 eV) of graphdiyne make it a promising candidate for miniature nanoelectronics and optoelectronic devices [5-7]. More interestingly, the band structure of the 1D graphdiyne wire can be further tuned by extending the numbers of phenylene unit [8], which can be regarded as an extended graphdiyne molecular wires. Recently, graphdiyne wires have been successfully synthesized on surfaces of noble metals by dehydrogenative homocoupling of terminal alkynes [9] and dehalogenative homocoupling of terminal alkynyl bromides [10]. Both methods are based on the mechanism of terminal acetylenic coupling [11, 12]. However, due to the high reactivity of the terminal alkynyl groups in presence of noble metal atoms, unwanted side reactions of the alkyn homocoupling are always there and lead to branched graphdiyne wires with very short length or cross-linked 2D polymeric networks [13, 14]. So far, guided growth of long graphdiyne wires with regioselective reaction pathway can only be obtained by surface templating at the vicinity of surface step edges [7, 15]. A facile approach to synthesizing high-quality graphdiyne wires with long length and high yield is desired.

In this work, we present a new approach to the synthesis of isolated graphdiyne nanowires [−C≡C-Ph2−C≡C−]n (PYP) via on-surface Ullmann coupling on Au(111) instead of acetylenic coupling. We show that isolated long graphdiyne nanowires can be readily synthesized without the assistance of surface templating. This is realized by simply depositing 1,4-bis(4-bromophenyl)-1,3-butadiyne (DBYP) molecules on Au(111) surface held at elevated temperatures, i.e., via a chemical vapor deposition (CVD) method. The butadiynylene units are encapsulated by the terminal aryl groups in the precursor molecules, which significantly reduces the probability of unwanted side reactions and leads to high-yield of the polymerization via terminal aryl-aryl coupling. High-resolution atomic force microscopy (AFM) based on qPlus technique clearly identified the chemical bonds of both biphenylene and butadiynylene units in the polymeric structures, confirming the formation of 1D graphdiyne nanowires. The semiconductor band gap of the ultralong graphdiyne wires was characterized by scanning tunneling spectroscopy, which agrees well with first-principles calculations. More importantly, the CVD method enables the formation of Au-π ligand bonds [16, 17] between Au adatoms and butadiynylene units.
Scheme 1 On-surface polymerization of DBYP molecules. The reaction routes for both CVD method and annealing method are shown.

which was evidenced by qPlus-AFM images. Compared with a controlled experiment with annealing method, we found that the Au-π ligand bonding stabilizes the butadiynylene units and dramatically prevents possible unwanted side reactions of branched coupling (Scheme 1). That is to say, the single Au adatoms act as effective protecting groups for on-surface synthesis of graphdiyne nanowires. Our results demonstrated the first example of on-surface single-atom protecting group may stimulate further investigation on the role of various surface adatoms in protecting on-surface reactions.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

All sample preparation procedures were performed in ultra-high vacuum with a base pressure of $5 \times 10^{-10}$ mbar. Single crystal Au(111) surface was cleaned by cycles of Ar$^+$ sputtering and annealing to get atomically flat surface. DBYP powder was purchased from TCI Company. DBYP molecules were sublimated from a ceramic crucible heated to 380 K for deposition. For CVD experiments, the molecules were deposited on clean Au(111) kept at three temperatures of 393, 423, and 483 K. For controlled experiment with annealing method, we deposited DBYP molecules on clean Au(111) surface held at room temperature then we annealed the sample from room temperature to 483 K. The samples were then cooled down to room temperature and transferred to an Omicron STM/qPlus-AFM operated at 4.3 K. The STM images were taken in the constant-current mode while the qPlus-AFM measurements were carried out in constant-height mode with a CO-functionalized tungsten tip [18] (resonance frequency $f_0=26$ kHz, oscillation amplitude $A\sim 100$ pm, quality factor $Q>7000$). The CO decorated tip was made by picking up a single CO molecule with the AFM tip. CO molecules were dosed on the samples held at ~10 K.

The periodic density functional theory (DFT) calculations were performed by using VASP software [19] with the projected augmented wave method [20] and the Perdew-Burke-Ernzerhof exchange-correlation functional [21]. The plane wave basis set was expanded to a kinetic energy cut-off of 520 eV. Structural optimizations were performed until the forces acting on all atoms were smaller than 0.01 eV/Å. Iterative method of energy calculation is Davidson blocked iteration scheme. We generated $5 \times 1 \times 1$ k points by using the automatic k-mesh generation method. Band structure calculation was done non-self-consistently, making use of the converged self-consistent electron density. We generated k points by using the line mode. The simulated AFM images were performed using a routine method [22, 23].

III. RESULTS AND DISCUSSION

FIG. 1(a) is a schematic view of the CVD method we employed in this study. DBYP molecules were evaporated from a ceramic crucible and deposited on the Au(111) substrate held at 483 K. The CVD method with a hot Au surface generates considerable numbers of diusive Au atoms that will provide sufficient Au adatoms during the dehalogenative homocoupling reactions of the DBYP molecules once they reached the surface. A typical STM image of the wires synthesized by CVD method is shown in FIG. 1(b). The ratios of precursor molecules polymerized into PYP wires is shown in FIG. 1(c). We found that more than 60% of the precursors were polymerized into PYP wires longer than 50 nm and the yield of aryl-aryl Ullmann reaction is counted to be high than 95%. For a comparison, we made a controlled sample by depositing DBYP molecules on Au(111) held at room temperature, followed by an annealing procedure to the same temperature of 483 K. FIG. 1(d) shows the STM image of the self-assembled domains of DBYP along [11 2] direction of Au(111) surface with grain boundaries along the herringbone structure attributed to surface reconstruction of Au(111). A zoomed-in STM image of the molecular assembly is shown in the inset with the molecular structures superimposed on it. The closely packed structure of the assembled molecular island indicates that no Au adatoms could exist between neighboring molecules. The sample was then annealed to 483 K and the corresponding STM image is shown in FIG. 1(e). Although all the DBYP molecules were also polymerized into wires, there are lots of junctions in the wires with cross-linking and branched coupling. These junctions strongly limit the length of the branchless parts of the wires. Only 3% of the precursors can be polymerized into PYP wires longer than 20 nm. Moreover, the PYP wires are cross-linked into a polymeric network, and hence are extremely hard to be isolated for any further practical devices.

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FIG. 1 PYP wires synthesized by CVD and annealing methods. (a) Schematic sample preparation set-up. (b) STM image of PYP wires synthesized by CVD method with substrate temperature of 483 K. (c) Ratios of precursor molecules polymerized into PYP wires in the sample of (b). (d) STM image of DBYP deposited on the Au(111) at room temperature. Inset, close-up STM image near the edge of a DBYP self-assembled domain shows a parallelly close-packed structure. (e) STM image of the sample in (d) annealed to 483 K. (f) Ratios of precursor molecules polymerized into PYP wires in the sample of (e). All the scale bars are 10 nm.

To reveal the origin of the high yield of terminal homocoupling reactions and inhibit branched coupling in the on-surface synthesis of PYP wires in the CVD method, we performed a set of experiments at different substrate temperatures. STM images in FIG. 2 show the oligomers and the wires on-surface synthesized by CVD method with different substrate temperatures. For the sample prepared at 393 K, most DBYP molecules were polymerized into dimers by dehalogenative homocoupling (FIG. 2(a)). For the sample prepared at 423 K, tetramers were observed along with dimers (FIG. 2(c)). For the sample prepared at 483 K, most molecules were polymerized into long PYP wires and only very few oligomers can be found (FIG. 2(d)). The interesting thing is that for all three samples branched coupling was scarcely observed. If we take a close look at the assembled structure in FIG. 2(a), we found that the polymerized dimers are not closely packed but separated with adatoms (FIG. 2(b)). The line profile in FIG. 2(b) shows that the distance between the two Br atoms from two neighboring dimers is \(0.94\) nm and an atomic protrusion shows up in the middle. These adatoms look dimmer than the DBYP dimers in STM images and cannot be assigned to dissociated Br atoms since Br adatoms typically have a much higher apparent height \([24]\). We therefore attribute these interstitial adatoms to single Au atoms trapped in the molecular assembly during the on-surface reaction.

Although FIG. 2(a, b) indicates the presence of Au adatoms on the heated surface during the dimer formation \([25, 26]\), it is hard to identify the role of the Au adatoms in the formation of long PYP wires simply from STM images like FIG. 2(d). To solve the problem, non-contact AFM experiment with single-bond resolution was performed on the CVD sample prepared

FIG. 2 STM images of samples acquired by CVD method with different substrate temperatures. (a, c, d) are STM images of samples prepared by CVD with the substrate temperatures of 393 K, 423 K, and 483 K respectively. All scale bars are 1 nm. (b) A close-up STM image of the dimers in (a). The corresponding structural model is shown below. The line profile along the black line is also shown to highlight the presence of Au adatoms.
FIG. 3 Imaging of Au-PYP system. Close-up STM image (a), corresponding structure model (b) and AFM image (c) of PYP wires synthesized by CVD method. (d) Line profile along the blue line in (c) and corresponding STM topograph line profile along the orange line in (a). The profiles were taken from Au(111) surface and across the PYP wires. Each peak in gray zones indicates a C–C bond between alkyne pairs, while the peak at STM curve and the protrusion at nc-AFM curve in the yellow zone indicate a gold adatom. (e) Close-up AFM image of a repeat unit of PYP wire with a gold adatom. (f) Simulated AFM image for (e). Scanning parameters are $V = 1.0\ \text{V}$, $I = 300\ \text{pA}$ in (a), $V = 0\ \text{V}$, $\Delta z = 0.15\ \text{nm}$ in (c), $V = 0\ \text{V}$, $\Delta z = 0.10\ \text{nm}$ in (e).

FIG. 4 Band structure and tunneling spectra of PYP wires. (a) Band structure of a PYP wire of infinite length. The occupied bands and unoccupied bands are illustrated in red and blue lines respectively. (b) Conductance ($dI/dV$) spectra taken at a biphenylene unit (green) and a butadiynylene unit (purple) of a PYP wire shown in the inset. Red and blue arrows mark the maximum of valance band (VBM) and the minimum of conduction band (CBM), respectively. The background conductance is denoted by the dashed line.

dance to the Dewar-Chatt-Duncanson model [28] which explains the type of chemical bonding between unsaturated ligands and a metal forming a $\pi$ complex. The distance between the Au adatom and each of the alkyne units is determined to be $\sim 3.1\ \text{Å}$ from the AFM image, corresponding to moderate Au-$\pi$ interaction. The simulated AFM image of this complex structure is shown in FIG. 3(f) which perfectly reproduces all the main characters in the experimental AFM image, including the enhanced frequency shift between Au and butadiynylene. In the controlled sample prepared with annealing method, we cannot find any signature of the presence of Au adatoms at the vicinity of the molecular wires. The only difference between the CVD method and the annealing method is that the former provides much more diffusive Au adatoms than the latter during the on-surface reaction. Therefore, we conclude that the Au adatoms must act as protecting groups that effectively stabilize the butadiynylene parts in the PYP wires, forming steric effects at side of butadiynylene and impeding the addition reactions of coupling with other dehalogenative radicals. In this way, the PYP wires can only be extended via terminal dehalogenative Ullmann coupling and hence long graphdiyne wires were finally obtained.

The above analysis demonstrates the protected synthesis of long isolated graphdiyne nanowires in presence of Au adatoms. The as-grown long nanowires are perfect examples of 1D infinite semiconductors. First-principles calculations show that the graphdiyne nanowire is a semiconductor with a band gap of $\sim 1.5\ \text{eV}$ (FIG. 4(a)). We performed STS measurements on our synthesized PYP wires, the results are shown in FIG. 4(b). The conductance ($dI/dV$) spectra obtained at the butadiynylene units (green line) and the bipheny-
ylene units (purple line) are nearly identical, indicating a delocalized electronic property owing to the fully π-conjugated molecular structure. Both spectra show conductance onsets at −0.7 and +0.8 V, corresponding to the maximum of valance band and the minimum of conduction band. This gap agrees very well with the theoretical calculations, suggesting that the unsaturated triple bonds are not disturbed upon bonding with Au adatoms.

IV. CONCLUSION

In summary, we report a new approach to the on-surface synthesis of long and branchless graphdiyne nanowires by CVD method. The main finding of this work is that we identified that single Au adatoms act as protecting groups in this on-surface polymerization with the aid of high-resolution AFM characterization. The butadiynylene units in the graphdiyne wires are stabilized by Au adatoms by forming Au–π bonding, which significantly reduces the probability of unwanted side reactions, leading to the high-yield of terminal aryl-aryl coupling. Our results demonstrated for the first time on-surface reactions can be in-situ protected with high selectivity and may stimulate further investigation on the role of various surface adatoms in protecting on-surface reactions.

V. ACKNOWLEDGMENTS

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