Functional Single-Layer Graphene Sheets from Aromatic Monolayers


After the first experimental studies of the exciting electronic properties of individual graphene sheets,[1-3] the research landscape in physics, chemistry and materials science has been strongly dominated by two-dimensional (2D) carbon materials in particular due to their promises for novel applications in nanotechnology.[4-6] Despite recent progress in fabrication of graphene by various techniques (e.g., via chemical exfoliation of graphite,[7] CVD growth on metals[8] or thermal graphitization of silicon carbide[9]), technologically efficient tailoring of this truly 2D material with specific application-dependent properties is still a demanding task. The main challenges include large-scale fabrication of homogeneous graphene sheets with well-controlled thickness and crystallinity, chemical functionalization of graphene without impairing the electronic structure, direct graphene growth on technologically relevant substrates, fabrication of functional graphene nanostructures and lowering the production costs.[10] Methods towards graphene based on molecular self-assembly[11,12] possess high potential for addressing these challenges, however, they have been comparably little investigated.[11-16]

Here we demonstrate how self-assembled monolayers (SAMs) of aromatic molecules on copper substrates can be converted into monolayer graphene using low-energy electron irradiation (50 eV) and subsequent annealing (~800 °C). We characterize this 2D solid state reaction on the atomic scale and study the physical and chemical properties of the formed graphene sheets by complementary microscopic and spectroscopic techniques and by electrical transport measurements. As substrates we successfully used Cu(111) single crystals and the technologically relevant polycrystalline copper foils. Because SAMs can easily be prepared on chemically diverse substrates (metals, semiconductors, insulators) of various sizes and shapes,[17] and the areas converted into graphene are simply defined by the electron irradiated regions, we expect that our findings will strongly facilitate the fabrication of graphene with tunable properties both for the wafer-scale and for the nanoscale applications using defocused and focused electron beams, respectively.

Our route to graphene from organic self-assembled monolayers[17] (SAMs) is schematically presented in Figure 1. It consists of three consecutive production steps: (i) formation of an aromatic SAM with a well-defined surface density of the carbon atoms on a solid substrate; (ii) electron-irradiation-induced crosslinking of the SAM into a dielectric carbon nanomembrane (CNM) with high thermal stability;[18] (iii) temperature-induced conversion of CNM into graphene via annealing in vacuum or under protective atmosphere. In the following we characterize in detail each of the steps of this conversion on catalytically active copper substrates, and we discuss advantages of our approach for technological applications of graphene.

The first step in the fabrication of graphene sheets from organic monolayers is the self-assembly of aromatic molecules on a solid substrate, Figures 1a, b. To this end, we employed vacuum vapor deposition of 1,1′-biphenyl-4-thiols (BPTs) on the atomically clean copper substrates at room temperature (details in Supporting Information (SI)). Figure 2a presents a scanning tunneling microscopy (STM) image of a BPT SAM on the Cu(111) single crystal surface directly after vapor deposition. As can be seen, the BPT molecules form a highly ordered monolayer on Cu(111) that exhibits various rotational domains of the same densely packed structure. One of these domains, imaged by high-resolution STM is presented as an inset in Figure 2a (see also SI Figure 1). Low energy electron diffraction (LEED) patterns obtained from the BPT SAM, like the one displayed in Figure 2a, indicate that the molecular structure is incommensurate to the substrate. An approximate unit cell that satisfies both the STM and LEED data is characterized by the vectors with the lengths of 5.00 Å and 5.35 Å and an angle of 122.5°. This unit cell is rotated with respect to Cu(111) by an angle of 16.5° (see SI Figure 2a) and shows twelve rotational domains due to the hexagonal symmetry of the substrate. In agreement with the STM and LEED results the formation of a densely packed BPT SAM is confirmed by X-ray photoelectron spectroscopy (XPS) measurements, shown in Figure 3a. The Cls signal has a binding energy (BE) of 284.6 eV (green) with a full width at half maximum (FWHM) of 1.1 eV and is accompanied by a shoulder at 285.5 eV (red) due to C-S bonds. The S2p signal consists of two doublets demonstrating the
The presence of two sulfur species on Cu(111) with a branching ratio between the S2p\(^{3/2}\) and S2p\(^{1/2}\) components of 2:1 due to the spin-orbit coupling. A species with the BE of the S2p\(^{3/2}\) component at 162.7 eV (red) contributes to ∼80% of the total intensity showing the formation of thiolates.\(^{19}\) The second doublet with the lower BE of 161.2 eV (blue) is characteristic for the formation of copper sulfides,\(^{20}\) which may result from the partial decomposition of BPT molecules during their vapor deposition.

![Figure 1. Schematic of the fabrication route to graphene from aromatic self-assembled monolayers (SAMs) on copper substrates: a) Deposition of molecules on a substrate; here, vapor deposition of biphenylthiols (BPT) on copper. b) Formation of a SAM. c) Electron-irradiation-induced crosslinking of the BPT SAM into a carbon nanomembrane (CNM). d) Conversion of a CNM into graphene via annealing.](image)

![Figure 2. Characterization by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) of the conversion of BPT SAMs into graphene on Cu(111): Simulated LEED patterns are presented below the experimental ones as insets. a) Pristine BPT SAM prepared by vapor deposition on Cu(111) (substrate at RT, evaporation of BPT at 60 °C for 2 h). Lower inset demonstrates a high magnification STM image of one of the structural domains of the BPT SAM. b) The same substrate after electron-irradiation (50 eV) with a dose of 50 mC/cm\(^2\) leading to the formation of a CNM. The inset shows a high-resolution STM image of the CNM/Cu substrate. c) Formation of graphene islands within the CNM after UHV annealing for 15 min at 730 °C. The lower inset shows a superstructure of graphene with Cu(111) imaged within these islands. d) Complete conversion of the CNM into graphene after annealing for 2 h at 800 °C (for details see text). The lower inset shows a superstructure of graphene with Cu(111), the atomic structure of graphene is shown in (e). f) Raman spectrum (λ = 633 nm) of the formed graphene sheet on Cu(111).](image)
Au(111), although on the latter surface only thiolate species quality of the formed SAM in comparison to the BPT SAM on Figure 2a, which is reflected in a much higher structural deposition on the reactive copper substrate (see also discussion below). Note that this additional sulfur species does not impair the self-assembly of the intact BPT molecules on Cu(111) (see Figure 2a), which is reflected in a much higher structural quality of the formed SAM in comparison to the BPT SAM on Au(111), although on the latter surface only thiolate species are observed by XPS. An effective thickness of the monolayer obtained from the attenuation of the Cu2p signal is ∼0.4 Å, which corresponds well to a nearly vertical arrangement of BPT molecules in the SAM.

The next step in the fabrication of graphene is the electron-irradiation-induced crosslinking of the BPT SAM, resulting in the dehydrogenation of BPT molecules and formation of the CNM (see Figure 1c) with an extremely high thermal stability. An STM image in Figure 2b shows topographical changes induced in the BPT SAM on Cu(111) (compare with Figure 2a) via irradiation with 50 eV electrons and a dose of 50 mC/cm² (~3000 electrons per 1 nm²). To a large extent the initially well-ordered alignment of the BPT SAM is lost. As obtained from the STM scans, the root-mean-square (RMS) roughness of the surface increases from 0.3 Å for the BPT SAM to more than 1 Å for the CNM. Thereby, the long-range order disappears, evidenced by vanishing LEED patterns from the sample. However, a short-range order persists across the surface. Periodicities of 5.5 Å are detected by STM resembling the structural features in the pristine SAM (see inset in Figure 2b). Upon crosslinking the amount of copper sulfides increases to ~60%, as observed from the XPS measurements (see Figure 3b), indicating the decomposition of the C-S bonds. Also the C1s signal experiences changes in accord with the introduced structural modifications. Thus, the BE of the main peak shifts to 284.3 eV and the FWHM increases by 0.1 eV (1.2 eV) in comparison to the pristine BPT SAM, whereas the intensity decreases by ~5% showing some desorption of carbon; the shoulder due to the C-S species shifts to 285.2 eV and its intensity increases by ~30%.

Finally, Figures 2c-e show the conversion of the CNM (Figure 2b) into graphene upon annealing in vacuum. The presented STM and LEED measurements were conducted at room temperature after the preceding annealing steps. Figure 2c demonstrates an intermediate stage of this 2D solid state transformation after annealing the sample for 15 minutes at 730 °C. It can be seen by STM that most of the surface is still rough showing the same structure as for the non-annealed sample (Figure 2b). However, a few islands with flat areas, indicated with arrows, have been formed. In comparison to the rest of the surface their corrugation is very low with a RMS value of only 0.4 Å. High-resolution STM imaging shows a regular hexagonal structure within these areas, which results in the formation of a LEED pattern (see inset of Figure 2c). From STM and LEED data we conclude that the unit cell of this LEED pattern has a length of 6.75 Å and a rotational angle with respect to the substrate of 19.1° (see SI Figure 2b). As seen from the insets of Figure 2c, the simulated LEED pattern matches the experimental one very well. We assign the observed structure to the formation of a superstructure between the graphene lattice and the Cu(111) substrate. Such a phenomenon, often referred to as the formation of moiré patterns, is routinely observed in the growth of graphene on metal substrates. In this example the superstructure has a unit cell that is only about three times larger than the unit cell of graphene, making it difficult to directly resolve the atomic structure in STM.

The STM and LEED data for the complete conversion of the CNM into graphene are presented in Figure 2d. Here, the same sample as in Figure 2c was subsequently annealed for two hours at 800 °C. This treatment causes a drastic change in the topology. A very smooth surface has been formed across the sample resulting in the appearance of a new LEED pattern. High-resolution STM imaging reveals the presence of a hexagonal structure on this surface (see inset of Figure 2d); by increasing the resolution, the honeycomb lattice of a graphene monolayer is clearly imaged by STM (see Figure 2e). Its lattice is rotated with respect to the Cu(111) substrate by ~38°, resulting in the formation of a hexagonal superstructure. In comparison to the superstructure presented in Figure 2c, its unit cell is much larger and has a lattice constant of 2.2 nm and a rotational angle of 23.4° with respect to the substrate (see SI Figure 2c). The simulated LEED pattern, presented in the inset of Figure 2d, reflects most but not all experimentally observed diffraction spots, indicating that also other superstructures with different lattice constants can be present. The hexagonal superstructure discussed in this paragraph was also occasionally imaged by STM after annealing at 730 °C, but its surface density was not sufficient to contribute to the LEED pattern. These observations strongly suggest that during the nucleation and growth of graphene, the crystallites may undergo structural reorientations with respect to the substrate.

Figure 3c shows the XPS spectra for the CNM sample after its complete conversion into graphene (see Figures 2d-e). As a result of this conversion, the FWHM of the C1s signal (BE = 284.5 eV) significantly decreases to a value of 0.9 eV, which corresponds to the resolution of our spectrometer. The signal.
intensity decreases to ~70% of the initial value for a pristine BPT SAM showing desorption of carbon from the CNM upon the conversion into graphene. Also the S2p signal experiences significant changes, its intensity reduces to ~60% of the initial value and the shape shows only the presence of a copper sulfide species (BE Sp3/2 = 161.5 eV). The desorption of this species from the copper substrate is hindered by the intrinsic stability of copper sulfides and by the presence of the graphene layer, which acts as a diffusion barrier for sulfur atoms. Even much longer annealing times (~12 h) do not reduce the intensity of the copper sulfide peak substantially.

From the surface density of the BPT SAM on Cu(111) obtained by STM and LEED and taking into account desorption of carbon during the crosslinking and annealing, the thickness of the graphene can be estimated (see SI p.6). The calculation shows that after the conversion precisely a single-layer of graphene is formed on the copper substrate. To further support this result, we characterized the graphene formed on Cu(111) by Raman spectroscopy. A typical Raman spectrum is shown in Figure 2f. The G- and 2D-peaks are located at 1583 cm⁻¹ and 2672 cm⁻¹. The Lorentzian-shape of the 2D peak with the FWHM of 37 cm⁻¹, in combination with the low-intensity D-peak at 1340 cm⁻¹, clearly confirm the formation of single-layer graphene with high structural quality. Note that annealing of the pristine (non-cross-linked) BPT SAM results in desorption of the monolayer at temperatures above 120 °C. After annealing at ~800 °C only a small amount of the sulfide species are detected by XPS on the copper substrate. Thus, the high thermal stability of CNMs is of key importance for their conversion into graphene via annealing.

All experiments described in the previous paragraphs were conducted inside...
an ultra-high vacuum chamber, except Raman spectroscopy, employing a Cu(111) single crystal as a substrate. In the following we demonstrate that high quality graphene can also be grown on copper foils, which is relevant for a wide spectrum of technological applications. Graphene sheets grown on copper foils were then transferred onto Si-wafers with a 300 nm thick SiO$_2$ layer for Raman spectroscopy, XPS, and electrical transport measurements, or onto transmission electron microscope (TEM) grids for characterization with a 80 kV aberration corrected TEM (AC-TEM). The Raman spectroscopy data (see Figure 4a) show an evolution of the D, G and 2D peaks as a function of temperature. A gradual conversion of a CNM into graphene with temperature is clearly seen from these data. For the highest annealing temperature (830 °C) the same features as known for single-layer graphene prepared by mechanical exfoliation with the G-peak at 1587 cm$^{-1}$ and narrow Lorentzian-shape 2D-peak at 2680 cm$^{-1}$ (FWHM $= 24$ cm$^{-1}$)[12,28] are observed after the conversion. The low-intensity D-peak at 1342 cm$^{-1}$ indicates defects, which may result from graphene grain boundaries observed by STM (see S1 Figure 4) and TEM (see following). Complementary to these results, XPS shows that the graphene transferred onto a silicon wafer consists only of carbon species, Figure 3d. The sulfur species detected directly after the growth on copper substrates (see Figure 3c) is no longer detected, confirming its assignment to copper sulfides.

To further characterize the grown graphene sheets we employed AC-TEM, which proved to be an extremely powerful tool for investigating the structure of graphene from the monolayer (via dark-field imaging[30]) down to the single atom scale (via high-resolution (HR)-TEM imaging[31]) scale. Figure 4b and Figure 4c present an AC-HRTEM image of the suspended graphene sheet at 80 kV and a diffraction pattern obtained from a much wider region than shown in Figure 4b, respectively. The intensity distribution of the diffraction pattern unambiguously proves the single-layer nature of the sheet.[13] Complementary to the STM on Cu(111) (see Figure 2e), which probes the electron charge density, in TEM the atomic potential scale (via high-resolution (HR)-TEM imaging[31]) scale. Figure 4b and Figure 4c present an AC-HRTEM image of the suspended graphene sheet at 80 kV and a diffraction pattern obtained from a much wider region than shown in Figure 4b, respectively. The intensity distribution of the diffraction pattern unambiguously proves the single-layer nature of the sheet.[13] Complementary to the STM on Cu(111) (see Figure 2e), which probes the electron charge density, in TEM the atomic potential

**Figure 4**

The electrical transport properties of the graphene films synthesized on copper foils were studied by four point measurements in the Hall bar geometry (see inset in Figure 4g). Figure 4f presents the ambipolar electric field effect, which was observed in the samples. The room temperature charge carrier mobility, extracted from the data at a hole concentration of $1 \times 10^{12}$ cm$^{-2}$, has a high value of $-1600$ cm$^2$/Vs. We further characterized the transport properties at low temperatures ($T = 0.3$ K) in a magnetic field of 15 T. By varying the charge density with the back-gate voltage of the devices, Shubnikov - de Haas oscillations and resistivity plateaus of the quantum Hall effect specific for a single-layer graphene[2] were clearly observed, Figure 4h. These results unambiguously confirm the high electronic quality of the grown graphene single-layers making them attractive for applications.

In summary, we have demonstrated that self-assembled monolayers of biphenylthiols on Cu(111) single crystals and copper foils can be converted into high quality graphene with attractive technological properties simply via the electron irradiation and subsequent annealing. This 2D solid state reaction can be tuned by temperature, which enables adjusting the crystallinity of the formed graphene monolayers. Since only the electron-beam irradiated areas undergo this conversion, we expect that both large-area graphene sheets and graphene nanostructures of various architectures (e.g., nano-ribbon, dot, antidot patterns) can be generated from SAMs employing either electron flood guns (as in this work) or focused electron beams, respectively. The lateral resolution of the generated nanostructures is defined by the resolution of electron-beam lithography, which has been shown to be 7 nm for SAMs[13]. Although this study addresses one molecular precursor only, diverse aromatic molecules[31] can be used for the described route as well. In this way tuning the thickness of graphene layers or introducing well-defined concentrations of dopants by employing dopant-containing molecules should now be possible. Moreover, molecular self-assembly can be conducted on non-planar surfaces, thus it is also feasible to create graphene structures of any three-dimensional shape. Since SAMs can be formed also on insulating substrates, it is promising to directly grow graphene sheets on these substrates for use in electronic or optical devices. We expect that our route to graphene from well-defined aromatic SAMs will strongly facilitate applications of this material in nanotechnology.

**Supporting Information**

This material contains the detailed description of techniques and methods, a video file of dark field TEM measurements, model calculations, additional STM, LEED and XPS data.

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