

Adsorption of 1,3,5-Triphenylbenzene Molecules and Growth of Graphene Nanoflakes on Cu(100) Surface *

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Adsorption of 1,3,5-triphenylbenzene (TPB) molecules on Cu(100) surface is studied using ultraviolet photoelectron spectroscopy (UPS) and density functional theory (DFT) calculations. Researches on the bottom-up fabrication of graphene nanoflakes (GNFs) with TPB as a precursor on the Cu(100) surface are carried out based on UPS and DFT calculations. Three emission features *d*, *e* and *f* originating from the TPB molecules are located at 3.095, 7.326 and 9.349 eV below the Fermi level, respectively. With the increase of TPB coverage on the Cu(100) substrate, the work function decreases due to the formation of interfacial dipoles and charge (electron) rearrangement at the TPB/Cu(100) interface. Upon the formation of GNFs, five emission characteristic peaks of *g*, *h*, *i*, *j* and *k* originating from the GNFs are located at 1.100, 3.529, 6.984, 8.465 and 9.606 eV below the Fermi level, respectively. Angle resolved ultraviolet photoelectron spectroscopy (ARUPS) and DFT calculations indicate that TPB molecules adopt a lying-down configuration with their molecular plane nearly parallel to the Cu(100) substrate at the monolayer stage. At the same time, the lying-down configuration for the GNFs on the Cu(100) surface is also unveiled by ARUPS and DFT calculations.

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Graphene was firstly discovered by physicists from Manchester University with the method of micro-mechanical cleavage in 2004.^[1–6] Graphene is an ideal one-atom-thick two-dimensional material.^[7] Due to its outstanding electronic, magnetic and thermal properties,^[4,8–16] graphene has potential applications including solar cells,^[16] energy storage,^[12] etc. Graphene-based nanostructures possess unique properties^[17–22] of electricity, magnetism and spintronics, thus they are ideal materials for nanodevice manufacturing, such as sensors,^[17,19] nanoscale ferromagnet,^[21,22] and nanoelectronic devices.^[18,20]

However, for practical applications, the large-scale production of graphene is of vital importance. The preparation of graphene typically is based on four methods.^[1,23–28] Among these methods, the bottom-up fabrication of graphene, namely carbonizing some special organic precursors on metal substrates (especially those highly active transition metals) by thermal treatment, is the most ideal approach for precise control over the morphology and the size.^[29] Recently, Tian *et al.* reported the mechanism of CVD synthesis of CNTs.^[30] Graphene has been extensively grown on substrates with *C3V* symmetry^[31–41] and rarely grown on substrates with other symmetries, for example, Ru(10 $\bar{1}$ 0), Cu(100)^[42–44] with a rectangular lattice. Graphene growth on these *C2V* symmetric substrates may produce intriguing physics and their special growth mechanisms can also be well

learned.^[42–45]

Cu is an especially important substrate due to its low cost, industrial scalability and efficient processing,^[42] and the fact that graphene films grown on Cu substrate are predominantly one monolayer.^[31] The TPB molecule is an ideal precursor due to its low cost. Therefore, we report on the bottom-up fabrication of GNFs on Cu(100) surface by molecular self-assembly using TPB as the precursor. The adsorption configurations of TPB molecules, along with the growth mechanism of GNFs on the Cu(100) substrate were studied by UPS and DFT. The experiments were performed in an ultra-high vacuum system (VG ADES-400 angle-resolved electron energy spectrometer) with a base pressure better than 3×10^{-8} mbar. The system is described in detail elsewhere.^[46–50]

The Cu(100) single crystal substrate ($10 \times 10 \times 1.0$ mm³) was cleaned with several cycles of argon ion sputtering for 30 min (the electron-beam energy gradually decreased from 1500 eV to 1000 eV, 500 eV) and annealing up to 550°C in the substrate-preparation chamber.^[45–48] The cleanness of the substrate was checked by low-energy electron diffraction and UPS.^[46–48] The evaporation source TPB powder was purchased from Alfa Aesar company (purity up to 99+%), and it was loaded in a homemade tantalum boat, carefully being degassed overnight before the deposition on the Cu(100) substrate.^[45] Evaporation was conducted by heating the tantalum boat

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under circumstance of a constant current. The coverage of the adsorbate was monitored by a quartz crystal microbalance.^[46–48] Subsequent annealing of the surface with different coverages induced the dehydrogenation of the TPB molecules on the Cu(100) substrate and resulted in the formation of graphene. To obtain the low-energy secondary electron cutoff clearly, a -5.0 V bias was applied to the sample during UPS measurements.^[47,48] During the measurements, the binding energy of all UPS spectra was calibrated based on the Fermi level of a clean Cu(100) substrate in electrical contact with the samples.^[48,51] All spectra were measured at room temperature. The temperature of the substrate was monitored with a thermocouple on the substrate. To study adsorption of TPB on the Cu(100) substrate, and growth of GNFs on the Cu(100) substrate, the isolated TPB molecule and GNF were calculated using the DMOL3 package integrated in the materials studio (MS) program of Accelrys Inc.^[47,48] This package employs density functional Hamiltonian for molecules and three-dimensional periodic solid and approximate true wave functions through an expansion of crystalline orbitals as a linear combination of atomic orbitals.^[47] A $1 \times 1 \times 1$ k -point sampling obtained from the Monkhorst-Pack scheme was used during the calculations.^[45]

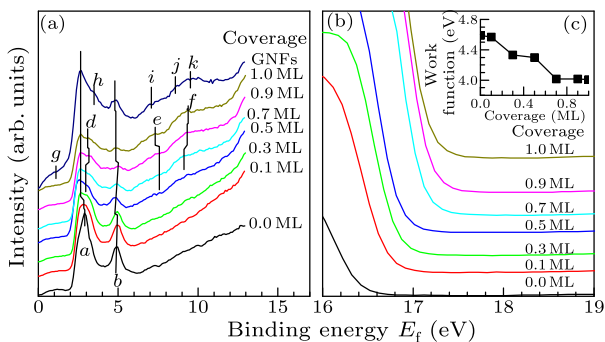


Fig. 1. (a) UPS spectra of valence electron parts with different coverages. (b) UPS spectra of secondary electron cutoff parts with different coverages. (c) Work function of TPB molecules with different coverages.

UPS spectra of the clean Cu(100) surface, TPB overlayer on the Cu(100) substrate for different coverages, and GNFs on the Cu(100) substrate are shown in Fig. 1. The photoelectrons were collected at the incidence angle of 30° and the outgoing angle of 40° . The bottom spectrum (0.0 ML) in Fig. 1(a) exhibits the characteristic valence structure of the clean Cu(100) substrate with two feature peaks at 2.906 eV (a) and 4.929 eV (b) below the Fermi level corresponding to the 3d band of the metal Cu substrate,^[52–54] indicating that the clean Cu(100) surface was obtained before TPB deposition. Due to the large photoionization cross section of the outmost 3d subshell of the Cu atom, the 3d peak of the Cu atom is clearly visible, which is the sign of a pure Cu(100) substrate.

After the deposition of TPB molecules, three new

spectral peaks d , e and f derived from the electronic states of the TPB molecule emerge. With the increase of coverage, relatively notable shifts for both feature peaks a and b originating from the Cu(100) substrate and characteristic peaks d , e and f originating from TPB molecules, can be observed. Such a phenomenon indicates that the interfacial charge (electron) is transferred from the Cu(100) substrate to TPB molecules,^[47] and illustrates the relatively strong interaction between the TPB molecules and the Cu(100) substrate. With further increasing the TPB molecular coverage to higher than 1.0 ML, features a , b , d , e and f were located at 2.654 eV, 4.866 eV, 3.095 eV, 7.326 eV, and 9.349 eV below the Fermi level, respectively. With increasing the coverage of TPB molecules, peak intensities of a and b decrease, while peak intensities of d , e and f increase. This can be attributed to some overlapping between valence band peaks of TPB molecules and spectrum peaks of the 3d orbital electron of the Cu atom.

Annealing of the sample at 550°C induces the dehydrogenation of the TPB molecules on the Cu(100) substrate, resulting in the formation of GNFs. The enhancement of intensity of peaks a and b of the Cu(100) substrate in Fig. 1(a) denotes the formation of GNFs rather than monolayer graphene. Upon the formation of GNFs, the peaks a and b shift to 2.654 eV and 4.803 eV below the Fermi level, respectively, suggesting the interfacial charge (electron) rearrangement at the GNFs/Cu(100) interface and the interaction between GNFs and the Cu(100) substrate. At the same time, five new characteristic peaks deriving from GNFs emerged, located at 1.100 eV, 3.529 eV, 6.984 eV, 8.465 eV and 9.606 eV below the Fermi level, respectively,^[55–57] which are labeled as g , h , i , j and k in Fig. 1(a). The five peaks are parts of the occupied orbits of the graphene. Peak g is considered to be spectroscopic evidence for the hybridization of the C π network with Cu d -orbitals;^[55] peak h is the GNFs C $2p$ π bands; peak i is defined as the mixture of the GNFs C $2p$ π and $2p$ σ bands; peak j is the GNFs C $2p$ σ bands; and peak k is associated with the GNFs C $2s$ and $2p$ hybridized states.^[56,57]

The nominal coverages of the TPB film of each spectrum are 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 ML near the secondary electron cutoff energy in Fig. 1(b). The secondary electron cutoff energies are located at 16.610 eV, 16.630 eV, 16.870 eV, 16.904 eV, 17.183 eV, 17.186 eV and 17.195 eV, respectively, in Fig. 1(b). Their work functions can be determined by

$$\phi = h\nu - (E_{\text{cutoff}} - E_f), \quad (1)$$

where $h\nu$ is the ultraviolet photoelectron energy of He-I with the energy of 21.2 eV, ϕ represents the work function, E_f denotes the Fermi level, and all spectra have been calibrated with reference to the Fermi level of the Cu(100) substrate,^[53] in other words, shifted with the Fermi level of the Cu(100) substrate aligned to 0 eV, and E_{cutoff} is the energy of the secondary elec-

tron cutoff. We can calculate the corresponding work functions with different coverages by the above equation, which are 4.590 eV, 4.570 eV, 4.330 eV, 4.296 eV, 4.017 eV, 4.014 eV and 4.005 eV, respectively. The spectrum in Fig. 1(c) shows the corresponding change of work function in different coverages. When the coverage increases, the work function representing the difference between vacuum energy level/Fermi level decreases resulting from the formation of interfacial dipoles and charge (electron) rearrangement at the TPB/Cu(100) interface.^[58]

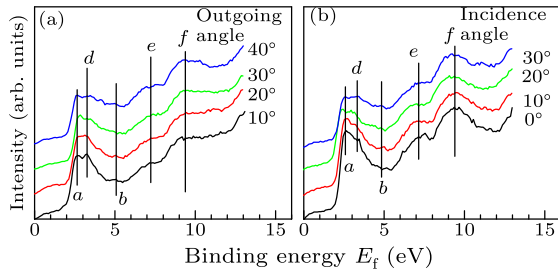


Fig. 2. ARUPS spectra of 1.0 monolayer TPB molecules on Cu(100) surface: (a) the incidence angle maintained 30°, and (b) the outgoing angle maintained 30°.

The intensity of the spectral peak is associated with the photoionization cross section. According to quantum mechanics, the photoionization cross section can be given by

$$\sigma = |\langle i | \mathbf{A} \cdot \mathbf{P} | f \rangle|^2, \quad (2)$$

where σ is the photoionization cross section, $\langle i |$ is the initial state of the photoelectron, $|f\rangle$ denotes the final state, \mathbf{A} denotes the vector potential of the incidence light, and \mathbf{P} denotes the polarization vector of the molecular orbital.^[46,47,49] With increasing the incidence angle, the photoionization cross section σ gradually becomes smaller, for the polarization directions of the orbitals are parallel to the substrate. In contrast, if the orbitals polarized are perpendicular to the substrate, the photoionization cross section σ would become larger. Therefore, based on the aforementioned principle, the adsorption geometry of TPB molecules on the Cu(100) substrate with the variation of the emission peaks could be inferred.

Figure 2 shows the ARUPS spectra of TPB molecules on the Cu(100) substrate with 1.0 ML coverage. The spectra in Fig. 2(a) were collected at the incidence angle of 30°, while with varying outgoing angle from 10° to 40°, as marked on the curve. With the increase of the outgoing angle, the binding energies and peak intensities of d , e and f peaks do not show an obvious change. The spectra in Fig. 2(b) were collected at the outgoing angle of 30°, while with varying incidence angle from 0° to 30°. There is no apparent binding energy change of these features with the increasing incidence angle, either. As described in Fig. 2(b), the attenuation of the peak intensities with the increased incidence angle for peaks d , e and f (dominated by

σ orbitals as described in the following) is recognizable in ARUPS measurements, indicating that the polarization directions of TPB molecular σ orbitals are parallel to the substrate surface. It signifies that the TPB molecule plane is parallel to the Cu(100) surface. In other words, TPB molecules for monolayer on the Cu(100) substrate adopt a lying-down configuration, which is in accordance with the precious STM results of the monolayer TPB overlayer on the Ru(0001) substrate reported by Song *et al.*,^[45] suggesting a strong interaction between TPB molecules and the Cu(100) substrate.^[47] The adsorption of other aromatic compounds on metal substrates such as the adsorption of FePc on the Cu(110) substrate,^[47] the adsorption of CoPc on the Au(111) substrate,^[46] and perylene adsorbed on the Ag (110) surface,^[59] also reach the same conclusion.

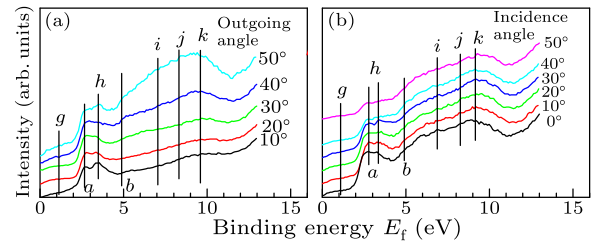


Fig. 3. ARUPS spectra of GNFs after annealing 1 ML TPB overlayer on the Cu(100) surface at 550°C: (a) recorded with a fixed incidence angle at 30°; and (b) recorded with a fixed outgoing angle at 40°.

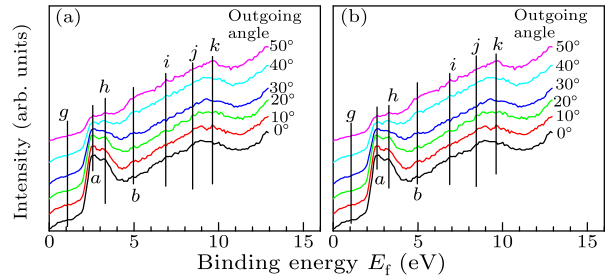


Fig. 4. Recorded with a fixed outgoing angle at 40°: (a) ARUPS spectra of GNFs after annealing 0.5 ML TPB overlayer on the Cu(100) surface at 400°C; and (b) ARUPS spectra of GNFs after annealing 0.1 ML TPB overlayer on the Cu(100) surface at 350°C.

ARUPS spectra of GNFs shown in Figs. 3 and 4 were collected after annealing at 550°C for 1.0 ML TPB overlayer, annealing at 400°C for 0.5 ML, and annealing at 350°C for 0.1 ML on Cu(100) surface, respectively. Five new feature peaks (g , h , i , j and k) in Fig. 4 can be observed after annealing the 0.5 ML TPB overlayer at 400°C, while the characteristic peaks of the Cu substrate do not disappear, suggesting the formation of GNFs, which is similar to the 0.1 ML TPB on the Cu(100) substrate after annealing at 350°C. With the increase of coverage, the annealing temperature for generating GNFs gradually increases.

No obvious change in binding energy and peak intensities of g , h , i , j and k peak with the increase of

outgoing angle from 10° to 40° could be observed in Fig. 3(a). There is no apparent binding energy change of these features with increasing the incidence angle in Figs. 3(b) and 4, either. However, the decrease of the peak intensities with increasing the incidence angle for these features is discernable in ARUPS spectra, manifesting that the corresponding polarization directions of GNFs are parallel to the substrate surface, and namely the GNF plane is parallel to the Cu(100) surface. Furthermore, GNFs on the Cu(100) substrate adopting the flat-lying growth mode were also demonstrated by STM, SEM and other techniques,^[42,43] being attributed to a strong interaction between GNFs and the Cu(100) substrate.^[59]

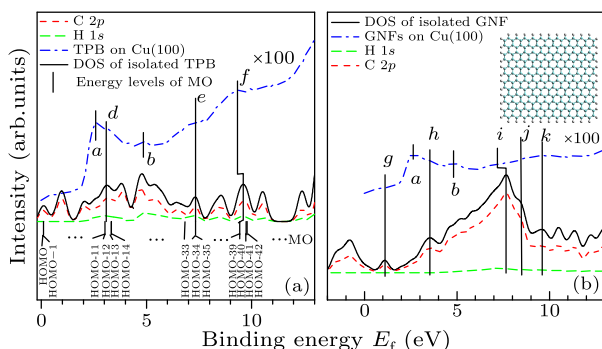


Fig. 5. (a) A comparison between the experimental UPS spectrum for monolayer TPB molecules on the Cu(100) substrate with a factor of 100 and the calculated density of states (DOS) and molecular orbitals (MOs) of isolated TPB molecules. (b) A comparison between the experimental UPS spectrum for GNFs on the Cu(100) substrate with a factor of 100 and the calculated DOS of GNF. The top right inset shows the structure of GNF (the natter blue spheres belong to the carbon atoms and the gray spheres belong to the hydrogen atoms) used in the calculation.

To further characterize the origin of TPB related features (as mentioned above) in UPS spectra, a DFT calculation for a free TPB molecule was carried out. Simulation calculations according to plane and non-planar TPB molecules are performed using DMOL3 integrated in the MS program of Accelrys inc, and the calculation results suggest the most ideal state shown in Fig. 6. Figure 5(a) shows a comparison between the experimental UPS spectrum for monolayer TPB molecules (Fig. 6 state) on the Cu(100) surface (multiplied by 100 to make it more comparable) and the calculated DOS and MOs of the isolated TPB molecule. For a better comparison, the theoretical energy scale was aligned to the experimental scale (by a shift of 0.11 eV towards higher binding energy), and the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are aligned to 0.11 eV and -3.185 eV, respectively, thus the theoretical results correspond to the experimental data well for the energy positions of features of *d*, *e* and *f* in the UPS spectrum.^[47,48] Obviously, the feature *f* of a free TPB molecule, located at 9.596 eV in binding energy, shifts to 9.349 eV for

TPB absorbed on the Cu(100) surface. This discrepancy should be ascribed to the interaction between TPB and the Cu(100) substrate. The main contribution to the MOs in the valence band is ascribed to the partial DOS's of two atomic orbitals (C 2*p*, H 1*s*) below the total DOS. Among these atomic orbitals, the contribution of C 2*p* atomic orbitals is the most important. As presented in Fig. 5(a), the HOMO of the TPB molecule derives from the C 2*p* orbital. Compared with the UPS spectrum of the 1.0 ML TPB molecule, peak *d* is formed by HOMO-11 and HOMO-12, peak *e* is formed mainly by HOMO-34 and HOMO-35, while peak *f* is formed mainly by HOMO-39 and HOMO-40. On the basis of our DFT calculations, the LUMO and HOMO, HOMO-11, HOMO-12, HOMO-34, HOMO-35, HOMO-39 and HOMO-40 of the free TPB molecule are portrayed in Fig. 6. Those MOs contributing to the peaks *d*, *e* and *f*, all of them have basic characteristics of σ orbitals, which suggests that the polarization directions of the TPB molecule are parallel to the substrate surface, and again backs up that the monolayer of TPB molecule on the Cu(100) surface is a flat-lying adsorption. The HOMO and LUMO orbitals of the TPB molecule are dominated by the π character and the electron clouds of HOMO and LUMO are primarily distributed on the benzene rings of the molecule with its polarization perpendicular to the molecular plane.

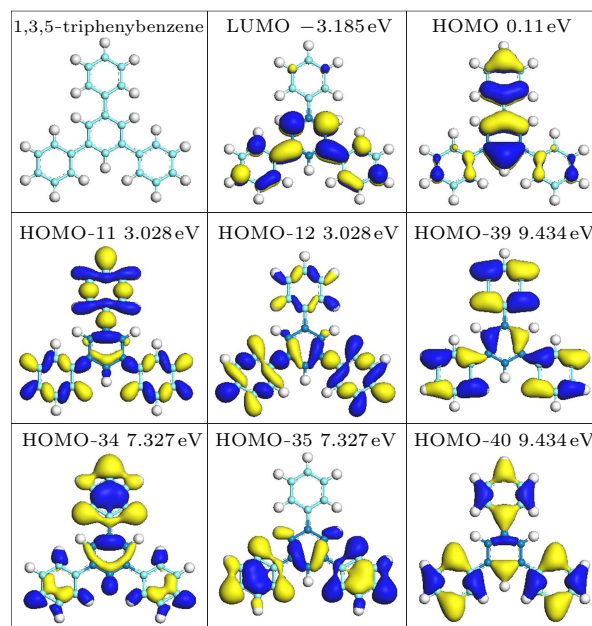


Fig. 6. TPB molecule (the natter blue spheres belong to the carbon atoms and the gray spheres belong to the hydrogen atoms) and the schematic diagrams of some typical MOs in free TPB molecules by DFT calculation.

To figure out the origin of GNFs' features (as described above) in UPS spectra, a DFT calculation for a free GNF in Fig. 6(b) was carried out. The experimental UPS spectrum for GNFs on the Cu(100) surface is exhibited with a factor of 100 to make it more comparable with the calculated DOS of GNFs. The HOMO

level of GNFs was aligned to the first emission peak (g) in the UPS spectrum (by a shift of 1.1 eV toward higher binding energy), which makes the accordance between the theoretical DOS and experimental UPS data pretty well, allowing the assignment of the contribution from the specific molecular orbitals to the UPS peaks.^[47,48] The partial DOS of two atomic orbitals (C 2*p*, H 1*s*) below the total DOS, which is predominantly conducive to the MOs in the valence band. The contribution of C 2*p* atomic orbitals in these atomic orbitals is most important.

In summary, based on UPS and DFT, we have investigated the adsorption of TPB molecules on the Cu(100) surface, and the bottom-up fabrication of GNFs with TPB as a precursor on the Cu(100) surface. Three emission peaks originating from TPB molecular orbitals are observed at 3.095, 7.326 and 9.349 eV in binding energy, respectively. The five emission features g , h , i , j and k originating from the GNFs are located at 1.100, 3.529, 6.984, 8.465 and 9.606 eV in binding energy, respectively. The formation of interfacial dipoles^[58] and charge (electron) rearrangement at the TPB/Cu(100) interface result in the decrease of work function with the increase of TPB molecular coverage. It is found that TPB molecules for monolayer on a Cu(100) substrate and GNFs on Cu(100) adopt a lying-down configuration by ARUPS and DFT.

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