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A photochemical approach for a fast and self-limited covalent modification of surface supported graphene with photoactive dyes

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Abstract

Herein, we report a simple method for a covalent modification of surface-supported graphene with photoactive dyes. Graphene was fabricated on cubic-SiC/Si(001) wafers due to their low cost and suitability for mass-production of continuous graphene fit for electronic applications on millimetre scale. Functionalisation of the graphene surface was carried out in solution via white light-induced photochemical generation of phenazine radicals from phenazine diazonium salt. The resulting covalently bonded phenazine-graphene hybrid structure was characterised by scanning tunnelling microscopy (STM) and spectroscopy (STS), Raman spectroscopy and density functional theory (DFT) calculations. It was found that phenazine molecules form an overlayer, which exhibit a short range order with a rectangular unit cell on the graphene surface. DFT calculations based on STM results reveal that molecules are standing up in the overlayer with the maximum coverage of 0.25 molecules per graphene unit cell. Raman spectroscopy and STM results show that the growth is limited to one monolayer of standing molecules. STS reveals that the phenazine-graphene hybrid structure has a band gap of 0.8 eV.

Keywords: graphene, covalent functionalisation, dyes, photochemistry, scanning tunnelling microscopy, density functional theory

1. Introduction

Graphene is a single-atom thick carbon allotrope arranged in a two-dimensional honeycomb-like lattice. Being a zero band gap material with a large specific surface area, it has a wide range of unique mechanical, electronic and physical properties [1-3]. Since the first isolation of a graphene single-layer by the so-called "Scotch-tape" method by mechanical exfoliation of graphite [1], many methodologies of graphene synthesis have been developed [4]. There are top-down exfoliation and bottom-up approaches to produce various qualities aiming at either mass or high quality production [4-9]. Chemical vapour deposition and epitaxial growth are two bottom-up techniques to produce graphene on substrates [4-13]. In this way mono- or multilayered graphene films of a high quality with a relatively small number of defects can be created.

Gaining control over the band structure is considered to be a bottleneck to uncover the true potential of graphene. One of the pathways for band gap modification is the chemical modification of graphene through covalent or non-covalent chemical functionalisation [14-23]. In turn, covalent functionalisation of graphene represents an important and challenging field of modern graphene science [19-26]. Technological advances in this area can lead to a controllable band structure modification of graphene, allow a combination of its unique properties with those of photo-/electroactive compounds, as well as significantly improve the solubility and processability of graphene [21-23].

One of the technological challenges in covalent functionalisation of graphene is to find a simple yet effective method for a high degree, homogeneous modification, available ex situ, without the use of ultra-high vacuum. Photochemical methods overcome this issue due to their simplicity and the mild conditions needed for generation of highly reactive intermediates through the absorption of light [27]. Recently, we have reported a versatile method for the covalent modification of graphene nanoplatelets by photochemically generated phenazine radicals resulting in a hybrid material with enhanced optical properties and improved solubility [28].

In this study, we show the applicability of this method to the covalent modification of graphene grown on the technologically important silicon carbide surface. The choice to use cubic-SiC/Si(001) wafers is governed by their low cost and suitability as a substrate in the mass-production of continuous graphene on millimetre scale fit for electronic applications [9, 29]. To take full advantage of this functionalisation strategy, a deep understanding of the effect of covalent modification on the surface morphology and electronic structure of graphene is required. To elucidate these phenomena we have studied the hybrid phenazine-graphene material using scanning tunnelling microscopy (STM) and spectroscopy (STS), Raman spectroscopy and density functional theory (DFT) calculations.

2. Experimental

Graphene layers were fabricated on cubic-SiC(001) films grown on on-axis Si(001) wafers using Si-atom sublimation followed by surface layer graphitisation at high temperatures [9, 29]. 3-Methyl-7-dimethylaminophenazine 2-diazonium tetrafluoroborate (phenazine diazonium salt) was synthesised according to a published procedure [28]. During functionalisation, graphene/SiC(001) samples were placed into a solution of phenazine diazonium salt (10 mg) in EtOH (100 mL). The samples were illuminated for 20-120 min with a white LED light (Prevac, 400 Lumens) placed at a distance of 5 cm from the sample. After illumination, the samples were washed and then sonicated in EtOH for 5 min to remove physisorbed species. After that the samples were transferred to the load-lock of an ultra-high vacuum (UHV) chamber.

The STM experiments were performed at 78 K in UHV conditions. Electrochemically etched [111] and [100]-oriented single crystalline W tips [30], sharpened in UHV by electron beam heating and ion sputtering, were used to record STM images in constant-current mode. Due to the high stability of the single crystalline tips [31] 90% of the STM images recorded were similar to the ones shown in this work. STM topographic images were processed using WSxM software [32]. No drift corrections have been applied to any of the STM images presented. Scanning tunnelling spectra (dI/dV) were obtained by numerical differentiation of the I(V) spectra. Each spectrum is the result of averaging over a few hundred spectra taken within an STM image using a grid of specified points. Before and after I(V) spectra acquisition the quality of the surface was verified by STM imaging to ensure that the molecular layer remained intact and no damage was caused during STS measurements.

DFT calculations were performed using the PWscf (Plane-Wave Self-Consistent Field) package from the Quantum ESPRESSO software distribution [33]. The electron exchange and correlation were treated within the local density approximation with the Perdew-Zunger parametrisation [34]. A single k-point (Γ) was used for all calculations to sample the Brillouin zone. The applied energy cut-off was 120 Ry. The global break condition for the electronic self-consistent loops was set to a total energy change of less than 1×10^{-5} eV. In the calculations, the four phenazine molecules of 32 atoms each were placed on top of a graphene layer of 100 atoms and allowed to relax. The graphene atoms involved in bonding with the molecules and their nearest neighbours were allowed to relax. The graphene atoms on the model's periphery were constrained for simplicity. A vacuum slab of 10 Å was used to separate the 228-atom system from its translational images in the z-direction. The relaxed model was visualised using the VMD package [35].

3. Results and discussion

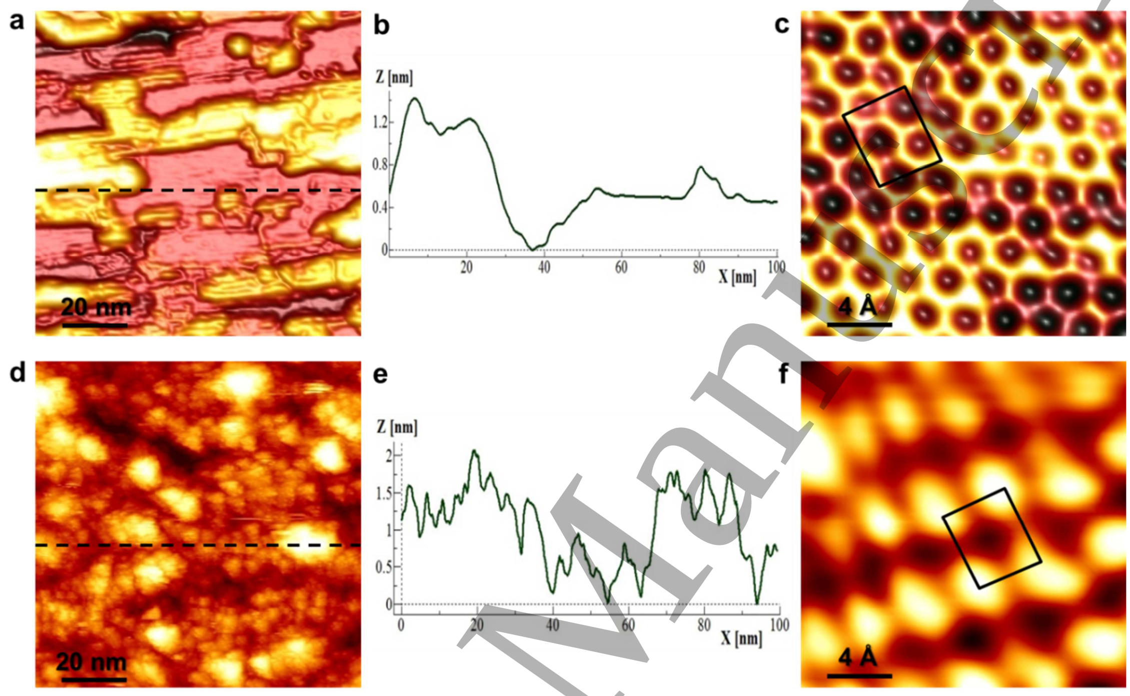

Figure 1. STM images from pristine graphene/SiC(001) (**a**, V_{sample} = -0.8 V, I = 60 pA, 100 nm x 100 nm and **c**, V_{sample} = 10 mV, I = 150 pA, 2 nm x 2 nm) and phenazine/graphene/SiC(001) (**d**, V_{sample} = -2.5 V, I = 60 pA, 100 nm x 100 nm and **f**, V_{sample} = -2.5 V, I = 50 pA, 2 nm x 2 nm) samples. (**b**), (**e**) Line profiles measured along the dashed lines shown in STM images in (**a**) and (**d**), respectively. The unit cell of the molecular overlayer is highlighted by the solid line (**c** and **f**).

Figure 1(a) shows a typical STM image of graphene grown on cubic-SiC(001) by surface layer graphitisation at high temperatures. Previous experiments have shown that graphene fabricated under similar preparation conditions grows on this surface as a few layer graphene with two preferential nanodomain boundary directions [29, 36, 37]. Individual graphene nanodomains are typically elongated in either the [110] or [1-10] direction of the SiC lattice, have widths in the range of 5–30 nm and their lengths vary from 20 to 200 nm [36]. These graphene nanodomains possess a rippled morphology and connect to each other through domain boundaries, forming a continuous graphene layer (see line profile in figure 1(b)). Atomically resolved STM images of individual nanodomains reveal graphene's honeycomb lattice (figure 1(c)).

After a 20 min long functionalisation of graphene by phenazine molecules the surface images reveal dramatic changes. Figure 1(d) presents a typical STM image of the molecule/graphene hybrid system on cubic-SiC(001) showing the "cloudy" appearance of the surface, which is usual for graphene surfaces modified by organic molecules [15, 20]. The line profile (figure 1(e)) exhibits fine structure due to molecular formations on the surface. However, the overall height changes observed are comparable with those found for the pure graphene grown on cubic-SiC(001). This suggests rather uniform coverage of the graphene surface by phenazine molecules where the molecular overlayer adapts the graphene's surface topology.

Small area STM images of the molecule/graphene hybrid system reveal elongated bright protrusions which have a length of approximately 3.5 Å and represent individual phenazine molecules (figure 1(f)). Such length corresponds to the top part of the molecule (which will be discussed after introducing the DFT model); therefore, the molecules are standing up on the graphene surface. Furthermore, the molecular layer exhibits a short range order with a rectangular unit cell (highlighted by solid lines in figures 1(c) and (f)) within the individual graphene nanodomain. The unit cell parameters are found to be 4 Å by 5 Å. The density of the molecular overlayer is 0.25 molecules per graphene unit cell which corresponds to one molecule attached to every eighth carbon atom of the individual graphene nanodomain. Therefore, every eighth graphene atom changes its hybridisation from sp^2 to sp^3.

The high density of the molecular overlayer on graphene/SiC(001), its adapted topology of graphene surface and the stability of the layer during imaging suggest that the molecules are covalently bonded to the graphene surface. The presence of physisorbed molecular species on the surface can be excluded due to specific preparation conditions [28]: after white light induced reaction between phenazine diazonium salt and graphene on SiC(001) the samples were sonicated for 5 min in EtOH several times. Furthermore, an anneal of the phenazine/graphene/SiC(001) system to 200 °C does not change the molecular composition on the surface, confirming covalent bonding between phenazine and graphene. Such a medium temperature annealing usually leads to a complete desorption of similar organic molecules physisorbed on the surface [38].

Recently, experiments involving a white light induced covalent modification of graphene using a phenazine dye have been performed on graphene nanoplatelets [28]. The reaction mechanism proposed includes a photoactivation of graphene that leads to a transfer of a generated hot electron from graphene to a phenazine molecule, which is followed by immediate reaction between the molecule and graphene [28]. Furthermore, an illumination of phenazine diazonium salt solution (without graphene) by white light does not lead to any reaction or immediate decomposition of the molecules. This emphasises the significance of the graphene surface and its electrons for the photochemical reaction process. Previously it has been shown that a photogenerated hot-electron can be transferred from the photoactivated graphene to benzoyl peroxide forming free phenyl radicals, despite the lifetime of the photoexcited carriers of graphene being very short [39]. Similar to the case of graphene nanoplatelets the reaction between graphene/SiC(001) and phenazine dye in the dark does not show any modification of the graphene surface, confirming that it is not energetically favourable.

In order to identify the model for the molecular overlayer on the graphene/SiC(001) surface, DFT calculations have been performed. Four phenazine molecules were placed on top of the graphene layer and the system was allowed to relax. The positions of the molecules on the surface were chosen on the basis of STM images. The resulting relaxed model of the graphene surface modified by the phenazine molecules is shown in figure 2.

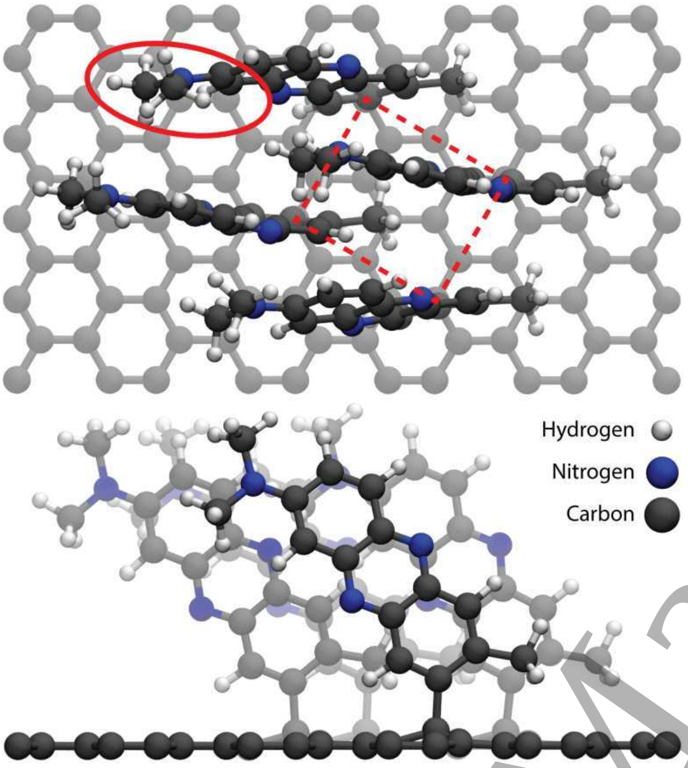

Figure 2. Top and side views of the relaxed model of the phenazine modified graphene surface. The unit cell of the molecular overlayer is highlighted by the dashed line. The oval indicates the top part of the phenazine molecule that is visible on the STM image (figure 1(f)).

The covalent bonding between the molecules and graphene atoms results in an out-of-plane displacement of the latter by 0.6 Å (see figure 2, bottom part). This number agrees well with previous DFT results obtained for small aromatic molecules attached to a graphene surface [40]. In order to accommodate the methyl groups attached to the bottom part of the phenazine molecules the latter adapt a tilted position on the graphene surface. This leads to a slight bending of the lower methyl groups away from the graphene surface and a marginal out-of-plane displacement of the graphene atoms that are directly under these methyl groups. In turn, the main body of the phenazine molecules undergoes no significant stretching or twisting. The molecules interact with each other through molecular π orbitals. This allows them to align almost parallel to each other. It is noted that the outer two molecules of the relaxed model show more twisting than the inner two molecules (see figure 2, top part). The outer two molecules only have a single neighbour each due to limitations with the simulation size and symmetry; therefore the inner two molecules have a more realistic configuration.

Raman spectroscopy has been used to characterise the phenazine/graphene/SiC(001) samples due to its sensitivity to the degree of defect sites introduced into the periodic graphene lattice [41]. Raman spectra (figure 3) recorded using a 514 nm laser source show characteristic D, G and 2D frequencies at 1365 cm^{-1}, 1600 cm^{-1} and 2732 cm^{-1}, respectively, for both pristine graphene (curve 1) and molecular modified graphene samples (curves 2-4). In turn, the Raman spectrum recorded from pure phenazine dye (curve 5) exhibits a featureless fluorescence background. The high intensity of the peak D and the presence of peak D’ in the spectrum of pristine graphene on SiC(001) indicate a high degree of defects due to numerous nanodomain boundaries on the surface, which is typical for graphene grown on cubic SiC [29, 36, 37].

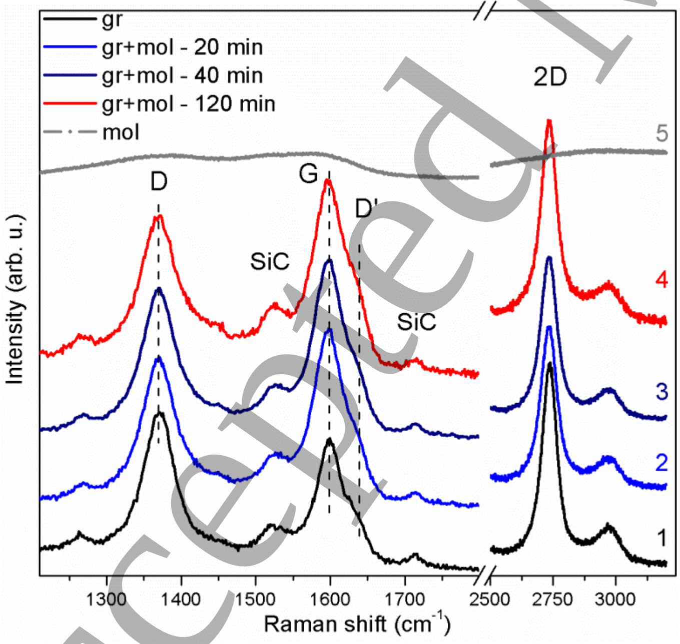

Figure 3. Normalised Raman spectra recorded using a 514 nm laser source from pristine graphene/SiC(001) (curve 1), pure phenazine dye (curve 5) and modified graphene/SiC(001) samples after exposure to phenazine molecules under white light for 20 min, 40 min and 120 min (curves 2, 3 and 4, respectively).

After graphene exposure to phenazine molecules for 20 min, the intensity of the peaks D decreases relative to the intensity of the peak G. The I_D/I_G ratio changes from 1.05 observed for the pristine graphene to 0.8 observed for the sample modified for 20 min. This can be explained in terms of changes applied to a graphene layer during its functionalisation. In this study the nanocrystalline graphene (with numerous nanodomain boundaries [29, 36]) on cubic SiC transforms into the nanocrystalline graphene with low value of sp^3 hybridisation (every eighth carbon atom of an individual nanodomain is affected according to STM and DFT data). Furthermore, the distance between newly introduced defects after attaching the molecules to graphene is around 0.5 nm (figure 1(f)), and there is no significant increase in graphene surface rippling due to bonded molecules as shown by the DFT model in figure 2. Previously reported Raman studies of graphene with different defect densities show that the I_D/I_G ratio increases with the number of defects until reaches maximum for an interdefect distance of 3 nm [42, 43]. In turn, the I_D/I_G ratio decreases for an increasing number of defects if an interdefect distance is below 3 nm [42]. This is due to the fact that defect contributions will not sum independently anymore if two defects are closer than the average distance an electron-hole pair travels before scattering with a phonon [44, 45]. Therefore, phenazine molecules covalently bonded to the graphene/SiC(001) form sp^3-type defects separated by 0.5 nm leading to the I_D/I_G ratio decrease in the corresponding Raman spectra.

The Raman spectra for modified samples exposed to phenazine molecules for 20 min, 40 min and 120 min (figure 3, curves 2-4) exhibit almost identical intensities and positions of all peaks. The I_D/I_G ratio is equal to 0.8, 0.8 and 0.78 for 20 min, 40 min and 120 min exposure, respectively. This indicates a fast reaction between the molecules and the graphene/SiC(001) surface, which is completed in first 20 min, similar to the case of graphene nanoplatelets [28]. Previously reported reactions based on diazonium chemistry aimed at functionalisation of graphene by small aryls often require long reaction times (up to 25 hours) and subsequent annealing at high temperatures (up to 500 °C) to reach a monolayer coverage [15, 46-49]. It was also shown that small aryls react with each other on graphene surface forming covalently bonded irregular structures [15]. In contrast, phenazine molecules do not react with each other to form covalently bonded networks [28] and therefore cannot be covalently bonded to the phenazine molecules already attached to the graphene. The results presented here show that after 20 min of white light induced reaction a maximum molecular coverage of the graphene surface is achieved. This indicates a fast and self-limited growth of the phenazine overlayer on the graphene surface.

In order to explore the electronic properties of the phenazine-graphene hybrid system, scanning tunnelling spectroscopy measurements have been performed. The spectra from pristine graphene/SiC(001) and phenazine/graphene/SiC(001) are shown in figure 4 where each spectrum is the result of averaging over a few hundred spectra taken within a single graphene domain using a grid of specified points. STS measurements repeated on different areas of the phenazine-graphene system show that the spectral features are reproducible.

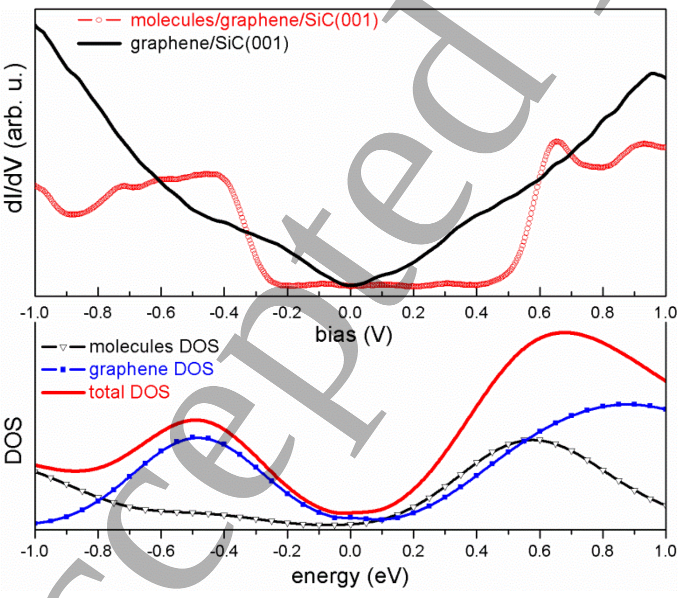

Figure 4. STS measured from pristine graphene/SiC(001) and the phenazine/graphene/SiC(001) samples (top) compared to the calculated total density of states (DOS) for the phenazine/graphene and the partial DOS for the molecules and the graphene (bottom).

STS of pristine graphene/SiC(001) displays no band gap showing the typical behaviour for a gapless material. In turn, the spectrum of phenazine-modified graphene exhibits two prominent features in the vicinity of the Fermi level at -0.4 eV and 0.65 eV. Extrapolation of these spectral features towards zero intensity gives a band gap of approximately 0.8 eV. The calculated total density of states (DOS) for the four-molecule model of the phenazine/graphene system exhibits two DOS features in the vicinity of the Fermi level at -0.45 eV and 0.65 eV, showing a good agreement between the theoretical and experimental results. Furthermore, the partial DOS calculated separately for the molecules and the graphene show that the occupied states in the vicinity of the Fermi level mainly have a contribution from the graphene. In turn, the unoccupied states in the vicinity of the Fermi level consist of both the molecule and the graphene states. This is a direct confirmation that a covalent modification of graphene by phenazine molecules leads to a phenazine/graphene hybrid with a sizable bandgap.

4. Conclusions.

In this study we have shown that photochemically generated phenazine radicals react with graphene grown on technologically important cubic silicon carbide leading to a covalent modification of the graphene surface. The results demonstrate a self-limited growth of one monolayer of the phenazine molecules that are standing up on the graphene surface and exhibit a short range order with a rectangular unit cell. DFT calculations based on STM results reveal the model for the phenazine overlayer and show that the molecules are covalently bonded to every eighth carbon atom of the individual graphene nanodomain. STS results supported by total DOS calculations exhibit that the phenazine-graphene hybrid structure has a band gap of 0.8 eV. Therefore, we can confirm the applicability of this simple photochemical method for band gap modification of surface supported graphene layers functionalised by large organic molecules such as dyes.

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