Tuning the molecular packing structure of metal-phthalocyanines on graphene by inserting interfacial copper nano grains

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A B S T R A C T

Graphene has been widely used in various organic devices as either electrodes or templates to obtain better device performance. Usually, organic molecules with planar backbone prefer to lie down on graphene leading to molecular $\pi-\pi$ stacking perpendicular to graphene substrate. However, for organic field-effect transistors, parallel $\pi-\pi$ stacking is superior to the perpendicular ones since it enhances the charge carrier's mobility between source and drain. This triggers studies on tuning the crystalline structures of organic thin film on graphene. For metal-phthalocyanines (MPc) which are widely used in organic field-effect device as active layer, so far MPc thin film with parallel molecular $\pi-\pi$ stacking on graphene hasn't been reported. In this study, we report a method to fabricate MPc films with single crystalline structure and molecular $\pi-\pi$ stacking parallel to graphene surface. Copper nano grains (CNG) were deposited onto graphene surface prior to the deposition of MPc films. MPc films with parallel $\pi-\pi$ stacking mode was obtained on graphene substrate which was covered by CNG with nominal thickness of 1 nm. This work provides a conceptually new approach to induce parallel $\pi-\pi$ stacking of MPcs on graphene in that no functionalization of graphene is needed.

1. Introduction

Organic thin-film (OTF) electronics have attracted vast attentions due to its low cost, easy fabrication and wide range of materials [1–8]. Nowadays, OTF devices have been used in broad applications such as display [9–12], photovoltaics [13–16], sensors and radio frequency identification [17–19]. Among various factors that influence the performance of OTF devices, the morphology and crystalline ordering of the OTF layers are particular important because of its determinative role in governing the charge carriers' mobility [20]. This has triggered extensive studies about the growth properties of OTF on various substrates, including metals, metallic oxide, silicon dioxide [21–24]. The ultimate goal of these studies is to find ways to fabricate OTF layers with desire properties such as controllable molecular orientation, single crystalline nature and smooth surface.

Graphene, a single-layer of carbon atoms tightly packed into a two-dimensional honeycomb lattice, is frequently used in various organic optoelectronic devices usually as an ideal electrode candidate owning to its fascinating chemical and physical properties, such as excellent thermodynamic stability, extremely high electric conductivity, outstanding optical transmittance and very strong mechanical stiffness [25–33]. Details about molecular orientation and packing on graphene substrate determine properties such as charge carrier's mobility and

charge injection across the interface between the organic materials and electrode [34,35]. For organic field-effect transistors (OFETs), charge injection and transportation are enhanced if the $\pi-\pi$ stacking direction of the molecules is aligned parallel to the substrate and the conducting channel. For organic photovoltaics (OPVs), however, efficient light absorption, exciton diffusion, and dissociation in thin films rely upon aligning planar molecules face-down to the substrate. Therefore, controlling the crystalline ordering and packing mode of organic molecule on graphene substrate is vital for graphene-related OTF devices.

While there has been substantial success in controlling the ordering of OTF with $\pi-\pi$ stacking direction perpendicular to graphene surface [36–41], there has been relatively less progress in controlling the ordering growth of OTF with $\pi-\pi$ stacking direction parallel to graphene surface. Aromatic molecules such as metal-phthalocyanines (MPcs), pentacene, and para-hexaphenyl (6P, also called para-sexiphenyl) usually adopt face-down orientation when deposited onto graphene substrate due to maximized $\pi-\pi$ interaction between organic molecule and graphene, leading to the $\pi-\pi$ stacking perpendicular to graphene. Lee et al. reported that the polymethylmethacrylate (PMMA) residues which is left on graphene substrate during the graphene transfer processes induced edge-on orientation of pentacene [42], resulting in $\pi-\pi$ stacking of pentacene in direction parallel to graphene substrate. However, recent studies demonstrated that this method is not

extendable to many other organic semiconductors such as copper-phthalocyanine (CuPc) and 6P [43,44]. In this study, we report a new approach to control molecular orientation and packing ordering of MPc thin film which can be tune by decorated graphene with a thin layer of copper nano grains (CNG) prior to the deposition of MPc thin film. Single crystalline MPc films is easily achieved using the method reported in this study.

2. Experimental details

Single layer graphene was fabricated on copper foil (Alfa Aesar, 25 μm for thickness and 99.8% for purity) using chemical vapor deposition (CVD) method. Briefly, copper foil was cleaned with ethanol and DI water and dried with purified Ar gas. Then, the copper foil was loaded into the quartz tube of CVD equipment and then pumped to $1 \lozenge 10^{-2}$ Pa. After that, copper foil was heated up to 1050 °C in 40 min with the presence of H_2 and Ar mixed gas. For graphene growth, high purified methane (99.999%, flow rate of 1sccm) was dosed into the CVD chamber while the copper foil was kept at 1050 °C for an hour. Finally, the copper foil was cooled to room temperature with the presence of H_2 and Ar. Flow rate of H_2 and Ar is set to be 20sccm and 800sccm respectively throughout the whole graphene fabrication process. The transferring of graphene to target substrate (SiO_2/Si wafer) was conducted with the well documented PMMA-assistant wetting transfer method. It was reported that PMMA cannot be completely removed by acetone [45], indicating that the as-transferred graphene is heavily contaminated by PMMA residues. It has been demonstrated that high temperature annealing at 500 °C can remove most of the PMMA residue, leading to a clean graphene/SiO2/Si sample. Hereafter, this sample is called graphene sample for simplicity.

The deposition of CNG and organic material was performed on a home-made ultra-high vacuum (UHV) system which was described elsewhere [43]. Thermal deposition was used to prepare either copper layers or succeeding organic thin film. The deposition is set to be 1 Å/minute for copper and 6 Å/minute for organic materials. The deposition of metal and organic materials was monitored with a quartz micro-balance. The nominal thickness of CNG layer is varied from 0.1 nm to 1 nm while the thickness of organic thin film is fixed to be 30 nm otherwise mentioned. The surface properties of CNG-graphene were revealed by using atomic force microscopy (AFM, Bruker multimode 8), scanning electron microscopy (SEM, Zeiss) and Energy Dispersive Spectrometer (EDS). Morphologies of organic film were investigated using an AFM with a taping-mode. And the crystalline structures of organic films were revealed by X-ray diffraction (XRD) measurements which were conducted with a Philips X'Pert XRD facility using Cu Ka emission.

3. Results and discussions

Fig. 1 shows the morphology of CuPc films on clean and CNG-modified graphene substrates. On clean graphene substrate, CuPc molecules tend to nucleate into islands with distinct boundaries. The island-like CuPc grains is distinguishable from that of on as-transferred graphene which is characterized with tiny irregular grains [43]. It has been demonstrated that the grain size is highly sensitive to the properties of graphene surface such as density of PMMA contaminations and topographical defects [36,43]. CuPc molecules prefer to aggregate initially at these non-perfect sites and then grew into grains which is greatly influenced by the density of nuclei. Fig. 1b–d shows the morphology of CuPc film on CNG-graphene substrates. The morphology of CuPc film varied with increasing the nominal thickness of copper layer. Compared to CuPc grains on bare graphene, either the density or the size of island-like CuPc grains decreases substantially upon deposition of copper layer onto graphene. On the contrary, the density of the particle-like nucleation increases tremendously. We suppose that the copper on graphene may serve as new nucleating sites. Successive

deposition of copper results in more nucleating sites which leads to the decrement of the CuPc grain size. This hypothesis is supported by the observation that the grain size of organic film is further decreased when the thickness of copper layer increases (see Fig. 1c). Finally, the island-like grains are completely disappeared and worm-like organic grains become dominated when copper thickness is increased up to be 1.0 nm. This indicates that the crystalline structures of CuPc thin film have been modified by the thin copper layer between organic material and graphene.

In Fig. 2, we show the XRD results of CuPc film deposited onto clean and CNG-modified graphene substrates. For CuPc film on clean graphene substrate, XRD peaks at 2 θ= 26.72° and 27.66° dominate the spectrum. According to literature, these peaks correspond to (01$\bar{2}$) and (11$\bar{2}$) Bragg plane with interlayer distance of 3.42 Å and 3.32 Å respectively [46,47]. This indicates that CuPc is deposited on bare graphene with "lying-down" geometry, resulting in the molecular π−π arrangement perpendicular to substrate surface. This observation is well agreed with our previous reports [43]. Upon modifying the graphene substrate with Cu, we observed obvious depression of the lying-down mode. In addition, a weak peak begins to show up at 2 θ= 6.9° which corresponding to x-ray diffraction from (100) Bragg plane of CuPc with molecular interlayer distance of 13.02 Å. This peak represents standing-up molecular geometry which means that the molecular plane of CuPc is perpendicular to the CNG-modified graphene surface, leading to the intermolecular π−π stacking parallel to substrate surface. The proportion of lying-down component is further decreased with increasing of Cu thickness. Finally, lying-down component is completely disappeared when the nominal thickness of Cu layer is raised up to 1.0nm. On the contrary, the proportion of standing-up mode is quickly increased with the increment of copper layer and maximized when the thickness of copper layer is increased to be 1.0nm. The variation of XRD peaks demonstrates that the molecular π−π stacking of CuPc film is changed from perpendicular mode to parallel mode when graphene surface was covered very thin copper layer. Parallel π−π stacked CuPc is propitious to the transportation of charge carriers in the direction parallel to substrate surface such that the film structure is favorable for OFET devices.

For comparison, we investigated OTF properties of zinc-phthalocyanine (ZnPc) and iron-phthalocyanine (FePc) which are discriminated with CuPc only by the central metal atom. Fig. 3 shows the XRD spectra of ZnPc and FePc films on bare and CNG-modified graphene surface. Obviously, these results resemble the case of CuPc film very well. This indicates that both ZnPc and FePc are arranged with intermolecular π−π stacking perpendicular to substrate surface when deposited onto bare graphene. However, the intermolecular π−π stacking will be switched to be parallel to substrate surface by modifying graphene with copper layer prior to organic deposition. It is known that OTF structures usually are determined by the molecular orientation of organic molecules at the first few layers on substrate, which is governed by the balance between molecule-substrate (M-S) interaction and intermolecular interaction [21]. MPcs have similar geometrical and electronic structures, leading to the similar intermolecular and M-S interaction. Based on this knowledge and the aforementioned observations, we conclude that this method, to fabricate single crystalline OTF with parallel π−π stacking structure, is extendable to other MPcs which have the same molecular backbone and are distinguish with each other only by the central d-metal.

Usually, MPcs prefer to be adsorbed on metal substrates with lying-down geometry, i.e. their molecular plane parallel to substrate surface mainly due to the maximized π−d like M-S interaction or site-specific interaction of d-orbitals of MPcs with substrates [48,49]. And the lying-down geometry usually leads to perpendicular π−π stacking of MPcs [37–39,50]. Bearing this knowledge in mind, perpendicular π−π stacked MPc rather than parallel mode should be expected to be observed on CNG-modified graphene. However, the present observation seems to be disagreed with the general knowledge. To understand the