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Modification of CuPc/graphene interfacial electronic structure with F_{16}CuPc

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ABSTRACT

The electronic structure between organic and solid electrode is a crucial issue in obtaining high-performance organic-based electronic devices (e.g. organic photovoltaic and organic light-emitting diode). In this communication we report that the electronic properties of phthalocyanine CuPc/graphene interface can be modified by sequential deposition of hexadecafluorophthalocyaninatocopper (F_{16}CuPc) on the CuPc/graphene interface due to the interactions of F_{16}CuPc with graphene. This method can be used to alter the energy barrier heights between graphene Dirac point and organic's highest occupied molecular orbital and lowest unoccupied molecular orbital at the organic/graphene interface by simple deposition of another electron acceptor or donor layer on this interface.

The heterogeneous interface between organic and solid electrode is critically important in organic-based electronic devices (OEDs). Besides its technological importance, the interface is also the birthplace of a multitude of fascinating discoveries in fundamental science [1]. Organic photovoltaics (OPVs) have attracted growing attention due to their potential applications in low cost, environment friendly, and flexible solar energy conversion devices. The energy conversion efficiencies of OPVs depend sensitively on the interfacial structure and electronic coupling between organic molecules and the solid electrodes, and those between organic layers [2–5]. For organic light-emitting diodes (OLEDs), the electroluminescent efficiencies and operation voltages greatly rely on the electronic properties of the organic/electrode interfaces [6]. It is now generally accepted that carrier transport in most organic/solid interfaces is largely injection-limited [7]. Hence, interfacial phenomena represent a challenging and important area of organic-based science and technology. Modifications have been applied to both organic/cathode and organic/anode interfaces in the OEDs [8,9] to influence charge injection barriers and afford varying degrees of enhanced device properties. However, the exact interfacial electronic structure and its mechanistic roles remains incompletely defined; therefore better understanding of the electronic structure of the organic/solid electrode interfaces is important to further improve the OEDs performance [10].

Transparent and conducting electrodes are needed for both OPVs and OLEDs. Common electrode materials available in the market are indium tin oxide (ITO) and fluorine-doped tin oxide. The conventional choice of ITO anode for OPVs constitutes as much as 30% of the total fabrication cost of solar cells. The diminishing supply of indium and tin elements, and their rising cost motivate scientists to search for an alternative electrode material [11]. Moreover, ITO is fragile and cannot be used in flexible electronics or thermally processed at high temperature due to element diffusion at the organic/ITO interface, which will hinder further development of organic devices [6]. A soft membrane type material, that is mechanically tough and flexible, is needed to replace ITO. Graphene, a monolayer of sp^2-bonded carbon atoms, has been proposed as a new-generation multifunctional, transparent, and conducting electrode [12–18]. The attractiveness of graphene arises from its excellent transparency, high electrical conductivity, good chemical robustness, and mechanical flexibility [17,19–21]. In principle, charge carriers in an individual graphene sheet are delocalized over the entire sheet and

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can travel thousands of interatomic distances without scattering. In addition, graphene only adsorbs 2.3% of the light intensity from infrared-to-visible light per graphene monolayer [22]. The low light absorption combined with its high conductivity makes graphene ideally suited for many optoelectronic devices as a transparent electrode. Furthermore, cost should not be a major issue for the production of graphene since it can be produced by chemical vapor deposition (CVD) using methane (CH_4) as the gas feed, diluted in hydrogen (H_2) or argon (Ar) [22,23]. Large-area growth and roll-to-roll processing of graphene are now entering into trial commercial production. CVD-deposited graphene films can be transferred onto glass for use as transparent and conducting electrodes. P-type copper phthalocyanine (CuPc) is widely used as an electron donor in the OPVs and as a buffer layer in the emissive and electrode interface in OLEDs [24–26]. The study of the interfacial electronic structure of CuPc/graphene is thus of fundamental and applied significance to achieve high-performance OPV and OLED devices.

Abundant results have shown that large Fermi level (E_F) shift of graphene from its Dirac point (E_D) could be realized by surface organic doping depending on the electron affinity and coverage of organic molecules [27–29]. Change of graphene charge carrier concentration (electron or hole) due to surface organic doping has been detected [30]. In this communication, we study the electronic structure of the CuPc/graphene interface using ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The manipulation of the interfacial electronic structure of CuPc/graphene by sequential deposition of hexadecafluorophthalocyaninatocopper (F_{16}CuPc) on the CuPc/graphene interface has been realized. The interaction between F_{16}CuPc molecules and graphene causes graphene E_F to shift from its E_D resulting in p-type doping of graphene because of the high electron affinity of F_{16}CuPc molecules, and consequently changes the energy barrier heights (EBHs) between graphene E_D and CuPc HOMO and LUMO levels. The purpose of this study is to understand the effect of the deposited organic molecules (F_{16}CuPc) on the electronic structure of graphene and formerly deposited organic molecules (CuPc) interface. Current results would be helpful in understanding the performance of the layer-by-layer organic devices based on graphene electrodes.

Single-layer graphene (SLG) was synthesized in a CVD furnace on copper (Cu) foil with a 1.5 inch-diameter quartz tube at 970 °C. After loading the Cu foil substrate into the quartz tube, the system was evacuated to 40 mTorr and then heated to the desired temperature in a gas flow of 6 sccm of H_2. Afterwards, the Cu foil was kept for 20 min in a gas flow of 6 sccm of H_2, followed by 6 sccm of H_2 and 35 sccm of CH_4 for 30 min at 970 °C before the sample was cooled down to room temperature with 10 sccm of H_2. Then the prepared SLG sample was transferred directly into the photoelectron spectroscopic (PES) measurement system, where the molecules were deposited on the SLG substrate without any further treatments. The SLG on the Cu substrate (SLG/Cu) was proved by Raman spectra by considering the intensity ratio of the G and 2D peaks (see in Fig. s1A). The surface morphology of the SLG/Cu sample, measured with atomic force microscopy (AFM), is shown in Fig. 1A. One can see that the sample surface is rather rough due to the rough nature of the industrial Cu foil. As a result subsequent deposition of organic molecules (CuPc and F_{16}CuPc) on the SLG/Cu surface may not uniformly or layer-by-layer fully covers the graphene surface as indicated schematically in Fig. 1B. The PES measurements were performed in a VG ESCALAB 220i-XL ultrahigh vacuum surface analysis system connected with a molecule deposition chamber. The basic pressure of the system was 1×10^{-9} mbar. HeI ($h\nu = 21.22$ eV) UV light was used for the UPS experiments and a monochromatic Al Kα source ($h\nu = 1486.6$ eV) for the XPS analysis. Energy resolution was determined to be 0.1 eV for UPS by analyzing the width of the Au Fermi edge.

Fig. 2 shows the HeI UPS spectra of (a) SLG/Cu and sequential deposition of (b) 0.1 nm CuPc, (c) 0.3 nm CuPc, (d) 0.5 nm CuPc, (e) 0.7 nm CuPc, (f) 1 nm CuPc, (g) 0.2 nm F_{16}CuPc, (h) 0.5 nm F_{16}CuPc, and (i) 1 nm F_{16}CuPc films. The spectra shown in Fig. 2A are collected in the secondary electron cutoff (SEC) region. The definition of the binding energy (BE) of SEC (BE_{SEC}) is indicated Fig. 2A by extending the spectrum baseline and sharp secondary electron onset. The SEC slightly shifts to lower BE when CuPc is initially deposited on the SLG/Cu surface, then slowly increases again. Finally, nearly no BE shift is observed in SEC after deposition of 1 nm CuPc relative to that of the SLG/Cu substrate. In contrast, the SEC position moves noticeably toward lower BE with increasing deposition of F_{16}CuPc. After deposition of 1 nm F_{16}CuPc, the total BE shift of SEC is −0.28 eV relative to the SLG/Cu or 1 nm CuPc/SLG/Cu substrate. Fig. 2B presents the UPS spectra collected in the BE range from 4 to 12 eV. Three distinctive peaks are observed in the spectrum a. Peak II around 5.8 eV is defined as the mixture of graphene C 2p π and 2p σ bands. Peak III at about 8.7 eV is graphene C 2p σ bonds, and peak IV at 10.4 eV is assigned to graphene C 2s and 2p hybridized states [31]. Fig. 2C shows the UPS spectra of the valence band region (from Fermi level (E_F) to 4 eV). The peak I at around 3 eV in spectrum a is graphene C 2p π

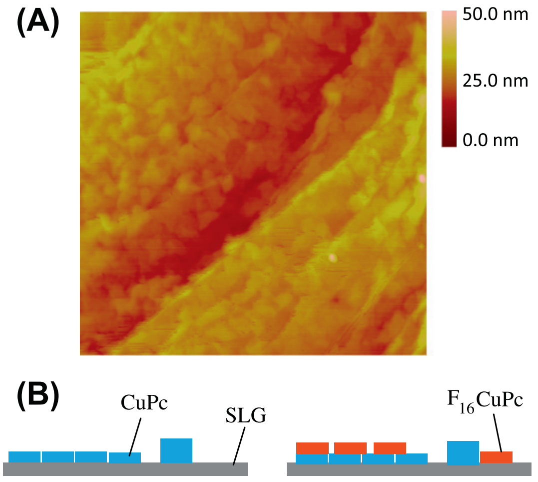

Fig. 1. (A) AFM image (2 μm × 2 μm) of SLG/Cu sample, and (B) schematic diagrams of the deposition processes of CuPc and F_{16}CuPc on the SLG/Cu surface.