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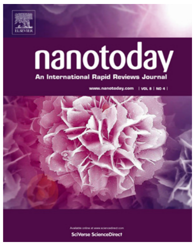

REVIEW

Recent progress in organic molecule/graphene interfaces

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Summary Graphene holds great promise in wide-ranging applications due to its novel electronic, thermal, mechanical, and chemical properties. In many applications, graphene needs to be integrated with other materials, it is thus important to understand the surface physics and chemistry of graphene. Understanding the adsorption behavior of organic molecules on graphene is an important issue to develop the full potential of graphene-based organic electronic devices. This article reviews the interfacial morphologies and electronic structures between organic molecules and graphene, prepared on different substrates. Generally, adsorption of organic molecules on graphene exhibits two important characteristics: (1) formation of well-ordered organic layers based on the graphene template and (2) occurrence of charge transfer between adsorbed molecules and graphene, offering the promise in tuning the electronic properties of graphene.

Introduction

Organic molecule/solid interfaces are attracting increasing interest for electronic and optoelectronic device applications due to their unique electronic properties [1—3]. A key requirement for the exploitation of these interfaces in electronic devices is the ability to control the interfacial charge transfer at device heterojunctions. The control of interfacial charge transfer requires engineering of the chemical environment at the interfaces at molecular level [4], because the orientation of adsorbed molecules and chemical bonds between molecules and solid will strongly affect interfacial electronic properties. Graphene, a two-dimensional (2D) sheet of carbon atoms, is a promising material for

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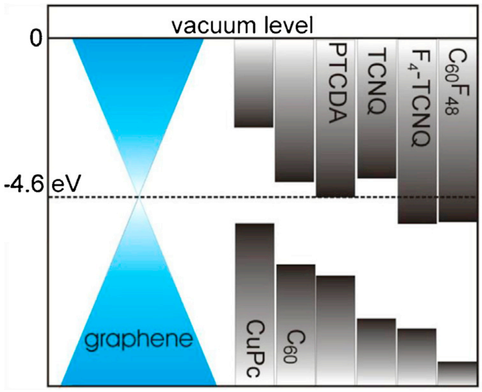

Figure 1 Energy alignment of different organic molecules with graphene.
From Ref. [17].

next-generation technology because of its outstanding electronic characteristics of 2D Dirac fermions [5—8], such as specific integer and fractional quantum Hall effects, a 'minimum' conductivity of $\sim 4e^2/h$ even at near-zero carrier concentration, Baryshnikov—de Haas oscillations with a π phase shift due to Berry's phase, high electron mobility (μ), up to $10^6\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, and near-ballistic transport at room temperature. These unique features make graphene potentially an ideal component for nanoelectronic devices [9—11]. Currently, a major challenge in graphene-based electronic devices is to create a valuable band gap in graphene and subsequently to make graphene p- or n-type by shifting the Fermi level down or up from its Dirac point [12], as required for many electronic applications. Substitutional dopants such as boron or nitrogen atoms has been applied to alter the electronic properties of graphene [13], but this approach strongly affects the charge carrier mobility in graphene layer, which hinders its applications in electronic devices. An alternative approach for shifting the Fermi level is to bring graphene in contact with other materials (i.e. organic molecules), which is named as surface chemical doping (SCD). SCD represents a valuable approach for controllable and non-destructive doping of semiconductors and nanostructures at low cost relying on charge transfer at interfaces, thereby facilitating the development of hybrid organic—graphene nanoelectronics. Depending on their functional groups, molecules adsorbed on graphene can withdraw/donate electrons from/into graphene, effectively doping graphene into p- or n-type, respectively. One main advantage of this process is that the integrity of graphene is generally preserved and charge donation may not strongly affect charge carrier mobility as substitutional dopants do. Using angle-resolved photoemission spectroscopy (ARPES), Coletti et al. [14] showed that holes can be doped into graphene by simply adsorbing electron-accepting organic molecules onto graphene surface. Fig. 1 shows the split between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of different common organic molecules referenced to the vacuum level in comparison to the Fermi-level (Dirac point) of graphene, which has been assumed a work function of 4.6 eV [15]. The HOMO—LUMO splitting and ionization potentials for the molecules have been taken from Ref. [16]. Since the LUMOs of tetrafluoro-tetracyanoquinodimethane (F_4-TCNQ) and fully fluorinated fullerene ($C_{60}F_{48}$) are below the Dirac point of graphene, therefore when they are brought into contact with graphene, electrons should transfer from graphene to these molecules. On the other hand, adsorption of weaker electron acceptor molecules like fullerene (C_{60}) should not result in a significant charge transfer and thus these molecules would not be efficient p-type dopants [17].

Since graphene is a semi-metallic material with a very high Fermi velocity ($V_F = 10^6\,\mathrm{m\,s^{-1}}$), individual graphene sheet has very high in-plane conductivities [18]. In principle, charge carriers in an individual graphene sheet delocalize over the entire sheet and can travel thousands of interatomic distances without scattering. Moreover, graphene only adsorbs 2.3% of the light intensity from infrared-to-visible light for each graphene monolayer [19]. The low light absorption combined with its high conductivity makes graphene ideally suited for many optoelectronic devices as a transparent electrode. Graphene has been proposed as a good candidate electrode in replacing indium tin oxide (ITO) for use in organic-based electronic devices (e.g. organic photovoltaic (OPV), dye-sensitized solar cell (DSSC), organic transistor, organic light-emitting diode (OLED)) [20—30]. De Arco et al. achieved OPV with better performances ($\eta \approx 1.2\%$) using graphene as the transparent conductor [31]. Graphene can cover an larger number of functions in DSSCs. Wang et al. reported a solid-state DSSC based on the organic compound spiro-OMeTAD1 (as the hole transport material) and porous TiO_2 (for electron transport) using a graphene-based transparent conductive film [32]. Graphene was incorporated into the nanostructured TiO_2 photoanode to enhance charge transport rate, prevent recombination and improve internal photocurrent efficiency [33], leading to a conversion efficiency $\eta \approx 7\%$, which is higher than that achieved with conventional nanocrystalline TiO_2 photoanodes in the same experimental condition [33]. Therefore, organic/graphene interfaces are of interest for optimizing charge injection from the graphene electrode into organic films. A fundamental understanding of organic/graphene interfaces is thus desirable. First, the interfacial energy offsets between graphene and the photoactive materials must be properly tuned in order to optimize charge transfer [34]. Second, the orientation of organic molecules on graphene surface should be controlled, because it will strongly influence the interfacial electronic properties. It is well established that the formation of 2D molecular networks on graphene is governed by a delicate balance between intermolecular interactions, such as covalent bonds, hydrogen bonds, van der Waals interactions, or metal-ligand and molecule-substrate interactions in the case of metal-organic networks. The quality of the first few layers of molecules is critically important as all important charge transport processes are confined to the first two or three monolayers [35]. It thus motivates the need to understand the interfacial structure between organic molecules and graphene.

In this article, we first review the morphologies and electronic properties at the interfaces between prototypical organic molecules and graphene. Then, we conclude with exemplary applications of organic molecule/graphene interfaces.