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Molecule-Based Transistors: From Macroscale to Single Molecule

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Abstract: Molecule-based field-effect transistors (FETs) are of great significance as they have a wide range of application prospects, such as logic operations, information storage and sensor monitoring. This account mainly introduces and reviews our recent work in molecular FETs. Specifically, through molecular and device design, we have systematically investigated the construction and performance of FETs from macroscale to nanoscale and even single molecule. In particular, we have proposed the broad concept of molecular FETs, whose functions can be achieved through various external controls, such as light stimulation, and other physical, chemical or biological interactions. In the end, we tend to focus the discussion on the development challenges of single-molecule FETs, and propose prospects for further break-throughs in this field.

Keywords: field-effect transistor, organic electronics, single-molecule junction, carbon nanotube, graphene

1. Introduction

A field-effect transistor (FET) is the cornerstone of the digital revolution.^[1-3] It is the core component of various electronic circuits. In a standard FET, current flows along a semiconductor channel connected to source and drain electrodes. and can be switched on and off by the gate electrode. The original FETs were mainly made of inorganic materials such as silicon and germanium, and silicon FETs have become the current mainstream. However, according to Moore's law, traditional top-down manufacturing techniques for siliconbased FETs have almost reached the limit of miniaturization.^[4] In addition, future electronic devices will also need to have functions required by specific applications, such as flexibility, light response, force monitoring and chemical/biological sensing. Therefore, in order to adapt to the trend of miniaturization and functionalization of electronic devices, it is necessary to design new field-effect devices and develop new materials for the devices.

Molecular electronics are one of the best choices for future electronic device applications, especially field-effect devices.^[5–12] Because they exhibit many inherent advantages, such as mechanical flexibility, light weight and adjustable electronic characteristics. In addition, through molecular synthesis and design, functional molecular electronic devices, such

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photodetectors and chemical/biosensors, can be as realized.^[13-16] Meanwhile, molecular materials also have advantages in assembly, from macro/nano single crystals and selfassembled monolavers to single molecules, which provides the basis for constructing FETs from macroscale to single molecule.^[17-20] In particular, the design and construction of FETs with single molecules can satisfy the need of miniaturization and functionalization of electronic applications. Due to the inherent molecular size of single-molecule FETs, it can overcome the development bottleneck of Moore's Law. Furthermore, single-molecule FETs provide a platform to study the laws of physics and chemistry at the single-molecule level. It can also meet the functional requirements of electronic applications, laying the foundation for ultra-high sensitivity sensing^[21-24] chemical/biological and environmental monitoring.^[25]

The emergence of carbon nanomaterials, especially singlewalled carbon nanotube (SWCNT) and graphene, also provide the material basis for the construction of molecular FETs, particularly as electrode materials.^[26,27] SWCNT can be considered to be formed by folding graphene flakes into cylinders along specific lattice vectors. They have good electrical conductivities, molecule-level diameters, and can be controlled from metal to semiconductor by changing the chirality.^[28,29] These properties make SWCNT ideal electrodes for constructing molecular devices, especially capable of forming molecularly matched contacts between electrodes and molecules. Graphene has the advantages of high conductivity and high carrier mobility, single atom thickness and conjugated planar structure, which allows organic molecules and electrodes to form good interfacial contacts through van der Waals integration.^[30-32] The excellent interfacial contacts can improve the performances of molecular devices, such as higher carrier mobility, higher device response speed, lower power consumption and enhanced on/off ratios.^[33] In addition, these carbon electrodes can be prepared with chemical groups at the ends, especially carboxylic acid groups, which provide the basis for single-molecule assembly through chemical bonding.^[26,27]

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In the past two decades, we have been devoted to the research of fabricating stable and reliable molecular devices, and exploration of molecular FETs from macroscale to nanoscale and single molecule. Through molecular design, interface design, electrode design and the regulation of generalized FETs, we can improve the original performances and add new functions such as sensing, storage, and photoswitching to molecular FETs.

2. Macroscale FETs

Organic field-effect transistors (OFETs) have become promising devices for electronic applications because of their advantages such as the diversity of molecular design, broad selection of materials, ease of manufacturing, low cost and large area processing of electronic components.^[8,34–36] In general, an OFET consists of source, drain and gate electrodes, a dielectric layer and a semiconductor channel (Figure 1).^[17] It usually takes metal (eg. gold or aluminum) as source/drain electrodes and heavily doped silicon or conductive metal as gate electrode. Organic semiconductor materials are used to construct conductive channel and insulator materials are used as dielectric layer.

In OFETs, the source electrode injects charges into the conductive channel; the drain electrode collects charges flowing out of the conductive channel; the gate electrode induces carriers in the organic semiconductor layer close to the dielectric layer to form a conductive channel. The intensity of the electric field passing through the dielectric layer can be



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Figure 1. Schematic diagram of a typical FET structure. Reprinted with permission from Ref. [17], Copyright 2020 American Chemical Society.

adjusted by the gate voltage, and the concentration of induced carriers in the semiconductor layer can be changed accordingly. Therefore, the current between source and drain electrodes can be controlled by the gate. By adjusting the thickness, dielectric constant, impedance and other parameters of the dielectric layer, the performance of the OFET will be affected. In addition, there are four heterogeneous interfaces including the interface within semiconductor layer, electrode/semiconductor interface, semiconductor/dielectric interface and semiconductor/environmental interface in OFETs. All the interfaces can be regulated by organic molecules with different usages in OFETs. Therefore, an effective and promising approach has been proposed to enhance the performance of the original OFETs and add new functions to the devices.

2.1. Molecules as the Conductive Channel



Xuefeng Guo received his Ph.D. in 2004 from the Institute of Chemistry, Chinese Academy of Sciences, Beijing. From 2004 to 2007, he was a postdoc at the Columbia University Nanocenter. He joined the faculty as a professor under "Peking 100-Talent" Program at Peking University in 2008. His current research is focused on functional nanometer/molecular devices. The organic semiconductor channel material determines the performance of OFETs and is the core of the device. By regulating the semiconductor channel, the key performance of the device can be improved, such as on/off ratio,^[37] threshold voltage^[38] and carrier mobility.^[39] In this section, we summarize recent works in designing small-molecule organic semiconductor materials and controlling their assembly morphology to be used as semiconductor layers of OFETs, which can improve on/off ratio and mobility or other performances of OFETs. At the same time, more functions have been introduced into the device through molecular design, such as bio-sensing,^[40] humidity or pH detection,^[41] and information storage.^[42]

As organic semiconducting materials, oligothiophenes and polythiophenes show great potential in OFETs due to their relatively straightforward synthesis and flexible structural design. However, they have disadvantages such as assembly defects and the sensitivity to photo-oxidative doping/bleaching, which limit their application in OFETs. To eliminate intrinsic defects and restore the stability of the OFETs, we designed and synthesized two liquid crystalline oligothiophene derivatives (Figure 2a), which have been modified by strategically placed long alkyl side chains. They are assembled and used as conductive channels for fabricating OFETs. Due to the deeper highest occupied molecular orbital (HOMO) energy level and high-quality assembly, the constructed OFETs have high field-effect mobility up to 6.2 cm²V⁻¹S⁻¹ and good air stability (Figures 2b and 2c).^[43] To further improve the molecular assembly quality and device performance, we proposed a biomimetic design using phosphonate. The alkylterminated molecule has a phosphorus (P) group at the end, forming amphiphilic molecule that can self-assemble well (Figures 2d and 2e). The growth trajectory of such organic semiconductor thin films has also been monitored in situ, which helps us to understand the mechanism of assembly. Specifically, the fundamental mechanism of single crystal film growth by evolutionary selection approach and the change of free energy under different growth models are proposed (Figure 2f).^[44]

Furthermore, we modified the pentathiophene core with strategically placed double-sided long alkyl chains and used solution-processed sol-gel HfO_2 thin films as ultra-thin gate dielectrics to form a controllable OFET with self-assembled monolayer films. In such OFET, each molecule is exposed to



Figure 2. Strategies for regulating the performance of OFETs by different molecular designs of the conductive channel. (a) Molecular structures of two liquid crystal oligothiophenes. (b) SEM image of the self-assembled microribbons with molecule 2. (c) Corresponding transfer characteristics of a single crystal device. Reprinted with permission from Ref. [43], Copyright 2012 Wiley-VCH. (d) Single-crystal structure of C_7P -benzo[b]benzo[4,5] thieno [2,3-d] thiophene. (e) Schematic illustration of the nanocluster-involved nonclassical nucleation mechanism. (f) Free energy curves in different models vary with reaction coordinates. Reprinted with permission from Ref. [44], Copyright 2019 Springer Nature. (g–i) Schematic and sensing mechanism of a FET with self-assembled monolayer. Reprinted with permission from Ref. [45], Copyright 2015 Wiley-VCH.

the air and can be in full contact with the surrounding environment, which makes the device with a high detection sensitivity.^[45]

Furthermore, due to its low operating voltage and longterm water resistance, it is an ideal device for chemical and biological sensing and in-situ detection (Figures 2g–i). Overall, these results provide a new path to achieve device application performance through molecular engineering and self-assembly.

2.2. Molecules for Modification of the Conductive Channel

The electrode/semiconductor interface greatly affect the performance of the devices.^[7,46] Charge injection at the electrode/semiconductor interface is complex, especially the presence of dipoles at the interface on the side of organic semiconductor affects the interface properties. Therefore, optimizing the contact interface between electrode/organic semiconductor layers and reducing the injection barrier between them through the usage of molecules for modifying the effect of different interfaces are the effective strategies to improve the device performance.

Focusing on the integration of molecular functions into OFETs, a photochromic spirothiopyran (SP) self-assembled monolayer (SAM) is inserted into the electrode/semiconductor interface (Figure 3a) to modify the conductive channel. Due to the photoisomerization of SP molecules, the dipole moment of SP-SAMs is reversibly changed, which can tune the work function of Au electrodes. This leads to two different hole injection barriers at the electrode/semiconductor interface, which enables us to obtain a new type of OFET photodetector with high photosensitivity.^[47]

In addition, using a blend of solution-processed poly(3-hexylthiophene) (P3HT)–spiropyran directly as the semiconductor layer in the OFET, a reversible photo-switching function can be achieved (Figure 3b).^[48] Under ultraviolet (UV) irradiation, the conductance of the OFET gradually changes from a low state to a high state. Upon exposure to visible light, the reverse reaction occurs and the device returns to the original drain current value (Figure 3c).

2.3. Molecules for Modification of the Dielectric Layer

In addition to organic semiconductor channels, for the fabrication of high-quality functional OFETs, it is also important to design dielectric layers with appropriate gate characteristics to meet device requirements with desired functions.

2.3.1. Surface Modification of the Dielectric Layer

For the organic semiconductor/dielectric interface, carriers are generated and transport directly at the interface under the action of the gate electric field, so this interface is particularly important. Molecules can be used for surface modification of dielectric layers to regulate the electric characteristics of OFETs. For example, when the photochromic SP-SAM is sandwiched between the semiconductor transport layer and the gate dielectric layer to modify the surface of the dielectric layer, the carrier density in the conductive channel can be reversibly



Figure 3. Strategies for regulating OFETs by molecules used for modification of the conductive channel. (a) Schematic of the OFET architecture with Au electrodes modified by SP-SAMs. Reprinted with permission from Ref. [47], Copyright 2016 The Royal Society of Chemistry. (b) Schematic of a P3HT/SP OFET. (c) Switching effect of the P3HT/SP OFET. Reprinted with permission from Ref. [48], Copyright 2012 The Royal Society of Chemistry.

controlled by light irradiation (Figure 4a). The modulation of channel conductance and accompanying threshold voltage value can be used to implement the memory function.^[49] In order to realize the non-volatile memory function in OFETs, the dielectric layer is replaced with a photoactive hybrid bilayer dielectric, which consists of a photochromic diarylethene (DAE) SAM and an ultra-thin solution-processed hafnium oxide layer (Figure 4b). The non-volatile memory function of the device is programmed with optical signal and erased with electric signal. During this process, it can produce a large reversible threshold voltage shift. Moreover, the storage state can be maintained for a period of time, and the OFET has good capability of nondestructive signal processing.^[50]

2.3.2. Internal Modification of the Dielectric Layer

Using molecules for internal modification of the dielectric layer is another approach to regulate the electrical characteristics of OFETs. We have fabricated an OFET with mirrorimage photo-switching characteristics thanks to its hybrid gate dielectric layer formed with mixed photoactive materials. The hybrid gate dielectric layer is composed of a buffer polymer dielectric, polymethyl methacrylate (PMMA), and photoresponsivity titanium oxide (TiO₂) nanoparticles (Figure 5a). A detailed dynamic study indicates that the charge trapping/ detrapping processes can be performed reversibly on the interface.^[51] When using a mixture of PMMA and SP as the gate dielectric, the optical switching effect can also be realized (Figure 5b).^[52] As the photoisomerization of SP, the dielectric constant of the gate dielectric layer will change collectively due to the large change in the dipole moment of each molecule. This results in reversible photoelectric modulation of the capacitance of the gate dielectric layer. Replacing the hybrid gate dielectric material with SP-co-MMA copolymer (Figure 5c) can achieve better mixing, so the optical response rate of devices can be improved by nearly three orders of magnitude.^[53] Such devices with hybrid gate dielectric or copolymer gate dielectric generally have good reversible optical switching functions (Figure 5d).

2.4. Regulation of SWCNT/Graphene FETs

The approaches of controlling OFETs through interface modifications as described above, especially introducing photoactive molecules into the interface, are also applicable to SWCNT or graphene-FET systems, where SWCNT or graphene is used as a conductive channel for constructing FETs. We have described the importance of conducting channels in the previous section. Graphene and SWCNT themselves have special characteristics, such as high inherent sensitivity, high electrical conductivity, and high carrier mobility.^[54,55] Due to these excellent properties, the FETs using them as conductive channels show good performances. Furthermore, both graphene and SWCNT have the simplest



Figure 4. Strategies for regulating OFETs by molecules used for surface modification of the dielectric layer. (a) Schematic of an OFET sandwiched by SP SAMs in the semiconductor/dielectric interface. Reprinted with permission from Ref. [49], Copyright 2011 American Chemical Society. (b) Schematic of an OFET with a photoactive dielectric layer. Reprinted with permission from Ref. [50], Copyright 2015 American Chemical Society.



Figure 5. Strategies for regulating OFETs by molecules used for internal modification of the dielectric layer. (a) Mechanism of the device with a TiO₂ hybrid dielectric layer. Reprinted with permission from Ref. [51], Copyright 2010 American Chemical Society. (b) Schematic of the device with a hybrid dielectric (PMMA+SP) layer. Reprinted with permission from Ref. [52], Copyright 2010 Wiley-VCH. (c) Schematic of the OFET with SP-co-MMA gate dielectrics. Reprinted with permission from Ref. [53], Copyright 2015 Wiley-VCH. (d) The switching effect of this type of OFETs with hybrid or copolymer gate dielectrics. Reprinted with permission from Ref. [52], Copyright 2010 Wiley-VCH.

chemical composition and atomic bond configuration in a 2D manner, thereby maximizing the surface-to-volume ratio. Since each carbon atom on the surface is fully exposed to the environment, any slight changes in the environment may cause the electrical properties of the SWCNT/graphene FETs to change drastically, thus forming the basis for ultrasensitive biosensing.^[28,56] In addition, through the regulation of interface, external functions can be added to the devices.

The molecules labeled with photochromic head groups are assembled to the surface of an individual SWCNT based FET (Figures 6a and 56).^[57] Due to the exposed conductive channel of SWCNT, the FET using semiconducting SWCNT as conductive layer has electrostatic sensitive characteristics, so that the conformational changes accompanying the molecular dipole change of these molecules can be sensed. When photoactive rotaxane molecules are used to modify graphene, the mirror photo-switch and non-volatile memory functions can be realized in the graphene FET (Figure 6c).^[58] The switching response behavior of the graphene device can be assigned to binary logic, which realizes a basic computation in the form of half adder and half subtractor.

In addition to the regulation of SWCNT/graphene-FETs with photoactive molecules, the system can also be extended to the regulation of SWCNT/graphene-FET by quantum dots. The advantage of using quantum dots for regulation is that it not only has electric field effects, but also has charge injection effects. For example, the functional SWCNT FET coated with photoactive TiO₂ quantum dots has been prepared through microfabrication and molecular assisted assembly (Figure 7a), which possesses mirror-image photo-switch effect. This effect is due to the photo-induced charge separation at TiO₂ quantum dots/SWCNT interface due to the matched energy structure, where electrons are injected into SWCNT and holes are left on the surface of the quantum dots. In this process, the p-type/n-type semiconducting channels show a rapid and significant current decrease/increase under UV irradiation, and have excellent reversibility when the UV light is switched off.^[59] Similarly, when PbS quantum dots are assembled to graphene FET, the hybrid graphene FET become a reversible photosensor with fine tunability (Figure 7b). This is because when exposed to light, the light-induced free holes can be effectively injected into the conductive channel, thereby producing the light response characteristics opposite to the TiO₂ system.^[60]

In addition, the additional effects of gas molecules are also introduced into the system with modified quantum dots. In an oxygen atmosphere, the ZnO quantum dots based SWCNT FET shows a sensitive response to UV light irradiation. This is because that the oxygen adsorbed on the surface of ZnO quantum dots will be photo-desorbed by capturing the



Figure 6. Strategies for regulating SWCNT/graphene FETs with photoactive molecules. (a, b) SEM image and schematic representation of a SWCNT-FET modified with photoactive molecule tagged with photochromic headgroups. Reprinted with permission from Ref. [57], Copyright 2005 American Chemical Society. (c) Schematic representation of graphene transistors assembled with light-activated rotaxane. Reprinted with permission from Ref. [58], Copyright 2013 Wiley-VCH.



Figure 7. Strategies for regulating SWCNT/graphene FETs by quantum dots. (a) Mechanism of a photoswitching SWCNT FET with TiO_2 nanoparticles. Reprinted with permission from Ref. [59], Copyright 2009 Wiley-VCH. (b) Schematic of graphene transistors decorated by PbS thin films. Reprinted with permission from Ref. [60], Copyright 2012 Wiley-VCH. (c) Mechanism of functionalizing the surface of SWCNTs FET with ZnO nanoparticles. Reprinted with permission from Ref. [61], Copyright 2009 Wiley-VCH. (d) Schematic of a multifunctional TiO₂/graphene hybrid transistor exposed to specific gases. Reprinted with permission from Ref. [62], Copyright 2016 Wiley-VCH.

photogenerated holes from the inside of quantum dots under UV light (Figure 7c), and the accompanying carrier concentration in SWCNT is changed. Therefore, the conductance of SWCNT FET with ZnO quantum dots can be regulated by UV light.^[61] For TiO₂ quantum dots modified graphene FET (Figure 7d), we achieve reasonable control over the carrier type and concentration in conductive channel by further introducing the redox molecules and light stimulation at the same time (Figure 7d). Upon exposure to specific gases, such as O₂ as an electron acceptor or NH₃/H₂ as an electron donor, the gas can further regulate the photo-induced charges at TiO₂/graphene interface. Therefore, an all-mirror-image sensing ambipolar graphene FET can be realized with controllable fast response rate, high stability, and ultra-low detection limit for gases.^[62]

3. Nanoscale OFETs Based on Carbon Electrodes

In recent years, carbon nanomaterials such as SWCNT and graphene are particularly attractive because of their unique advantages when used as nanoscale electrodes. They have the simplest chemical composition, atomic bond configuration, large surface area and good electrical conductivity. Especially, both SWCNT and graphene are composed of carbon sixmembered rings with a work function of about 4.5–5.0 eV, which is compatible with organic semiconductors. In comparison with macroscale OFETs based on metal electrodes, nanoscale OFETs based on carbon electrodes have the similar working mechanism. However, because of the precise preparation of the carbon nanomaterial electrodes, the nanoscale OFETs have the characteristics that it can precisely control the

single-layer molecules of the semiconductor layer close to the dielectric layer. By applying a gate electric field to the device, the energy barrier between the molecular conductive channel and the carbon electrodes can be adjusted to improve the conductive characteristics of the device.

Among the carbon nanomaterials, SWCNTs are quasi-onedimensional ballistic conducting nanowires,^[67] which have the matched size with molecules, so high-quality contact between SWCNT electrodes and molecules can be formed. Furthermore, SWCNTs can be considered to be formed by folding graphene flakes into cylinders along certain lattice vectors, which leads to their diversity in structure and structureproperty relationships.^[63–66] With different chirality, SWCNTs can be divided into metal type (m) and semiconductor type (s), which have quite different energy band structures and corresponding electronic density of states (DOS). In general, s-SWCNTs are selected when they are used as semiconductor channels, and m-SWCNTs are used when they are required to act as metal electrodes in FETs.

Graphene has a two-dimensional single atomic layer structure, good conductivity, and high electron mobility up to $15000 \text{ cm}^2/\text{v}\cdot\text{s}$ at room temperature, which is much larger than the mobility of silicon crystals. Because of these advantages, graphene is a promising electrode material for high-performance new-generation electronic components, such as FETs. Compared with the metal electrodes for FETs, graphene has a molecular structure similar to organic semiconductors, resulting in extremely strong interaction between organic semiconductor, which can induce self-assembly between molecules and graphene electrodes through π - π interactions, forming a good interface contact. Furthermore, the hole injection barrier between graphene and organic semiconductor layer is lower. Such excellent interface contact and reduced injection barrier can improve the performance of molecular devices, such as greater carrier mobility, higher device response speed, lower power consumption, and enhanced on/off ratios.^[54,64]

3.1. Nanoscale OFETs Based on SWCNT Electrodes

To form SWCNT point contact electrodes, single m-SWCNTs connected with macro metal leads are cut through electron beam lithography and selective oxygen plasma oxidation etching to make gap less than 20 nm. Organic semiconductor molecules are physically self-assembled to the electrodes to form transistors with high efficiency current modulation by gate electrodes.

Specifically, by using m-SWCNTs as source/drain electrodes, the liquid crystalline material of tetra(dodecyloxy)hexabenzocoronenes (HBC) molecule can be stably connected between the SWCNT electrodes in a self-assembly form (Figure 8a). Since the size of these columnar nanostructures exactly matches the diameter of the SWCNT electrodes, the measurement of the photoconductivity of a single one-dimensional liquid crystal cylindrical core is realized. The device is very sensitive to environmental stimuli such as photons, so ultra-sensitive photoelectric devices with optical response are constructed.^[37] However, the molecular assembly achieved directly using droplets is usually a messy multilayer. To further



Figure 8. Examples of nano-FETs based on SWCNTs electrodes. (a) Schematic of modification of a FET with droplet HBC molecules. Reprinted with permission from Ref. [37], Copyright 2009 The National Academy of Sciences of the USA. (b) Schematic of a FET with self-assembled HBC monolayers. Reprinted with permission from Ref. [68], Copyright 2006 by The National Academy of Sciences of the USA. (c) Schematic of ultrasensitive monolayer photodetectors with CuPc LB monolayer. Reprinted with permission from Ref. [69], Copyright 2011 The Royal Society of Chemistry.

improve the quality of molecular assembly, we modified the molecular assembly form by covalently assembly the molecules onto the surface of the silicon wafer to form the molecular monolayer of polycyclic aromatic hydrocarbons (Figure 8b). When the polycyclic aromatic hydrocarbons monolayers are connected into the nano-gaps of SWCNT contact electrodes, their electrical properties can be measured. Because these devices consist of a single molecule layer exposed to the environment, their electrical properties change dramatically when they are exposed to electron-deficient molecules such as tetracyanoquinodimethane (TCNO), forming the basis for a new type of environmental sensors.^[68] In addition, the Langmuir-Blodgett (LB) assembly technique is also used to construct ordered molecular monolayers. Combining the excellent photoconductive properties of phthalocyanine (Pc) class compounds and the advantages of using SWCNT as point contact electrodes, the devices based on high-performance LB assembled copper phthalocyanine (CuPc) as an organic semiconductor monolayer show excellent ultra-sensitive optical detection performance (Figure 8c). Under the low bias voltage, the response coefficient of the CuPc photodetector is greater than 10⁸ A/W, and the detection capability is greater than 7×10^{15} cm Hz^{1/2}/W. Moreover, the devices have high repeatability.^[69]

3.2. Nanoscale OFETs Based on Graphene Electrodes

To form graphene nanogap electrodes, high-quality single-layer graphene sheet is first obtained on silicon substrate by chemical vapor deposition and subsequent transfer or by stripping techniques, and then covered with a polymethyl methacrylate (PMMA) layer. With patterned PMMA mask generated by electron beam lithography, graphene sheet is locally cut by an oxygen plasma etching process to achieve graphene contacts with nano-scale gap. Finally, organic semiconductor molecules are physically self-assembled between the graphene nanogap electrodes.

High-performance photosensitive nanoscale transistors are fabricated with the two-dimensional single-layer graphene nanogap electrodes. The transistor with P3HT prepared by dip coating as the functional semiconductor layer exhibits effective current modulation and high on/off ratio (Figure 9a). Due to the light response characteristics of P3HT, when the device is intermittently exposed to visible light, the current changes reversibly, and the calculated response rate of the device is as high as 8.3 A/W.^[70] However, the dip coating method is not precise enough to control the molecular assembly, so we propose to use copper phthalocyanine (CuPc) monolayer assembled by Langmuir-Blodgett (LB) process as the functional layer to form FET (Figure 9b). With the CuPc monolayer molecular structure, a high-performance photo-



Figure 9. Examples of nano-FETs based on graphene electrodes. (a) Device structure of a P3HT transistor made by dip-coating. Reprinted with permission from Ref. [70], Copyright 2009 Wiley-VCH. (b) Device structure of the transistor with a CuPc LB monolayer. Reprinted with permission from Ref. [71], Copyright 2010 Wiley-VCH.

responsive molecular FET with higher carrier mobility, higher on/off ratio and reliable reproducibility can be obtained.^[71]

4. Single-molecule FETs

With the rapid development of modern information technology, there is an urgent need to develop electronic components with smaller scale to promote the development of electronics field. The ultimate goal is to construct electronic devices with the molecular or even atomic size, hopefully by making singlemolecule/atom transistors.^[7,46] The field-effect function of single-molecule transistors can be obtained by adjusting the relative energy level positions between the molecular orbitals and electrodes. There are two approaches to achieve this: one is to shift the Fermi level of the electrodes, and the other is to shift the energy level position of the molecular orbitals through the gate electric field. In addition, the chemical or biological interactions may cause the conformational changes of molecules by which the energy level of molecules will be changed, thereby realizing a generalized field-effect function. Therefore, due to the molecular scale, rich diversity and designable functions, single-molecule transistors form the basis of a new class of chemical/biosensors with ultra-high sensitivity, which can directly detect single-molecule events in natural samples and monitor high-sensitivity biomolecular interactions in real time.^[23,24,72]

Unlike traditional macroscale OFET, single-molecule transistors usually use carbon materials (SWCNT and graphene, etc.) with molecular-scale nanogaps as electrodes. Single functional molecules are chemically assembled into the nanogap electrodes through stable amide bonds. Since the molecule-carbon electrode connection is robust enough, the prepared single-molecule devices are very stable.

4.1. Single-molecule FETs Based on SWCNT Electrodes

SWCNT electrodes with molecular scale nanogaps are constructed through a specific local oxidation process. Due to

strong oxidation, carboxyl groups are formed at both ends of the SWCNT electrodes. Single molecule with amine terminal groups on both sides is bridged to terminal carboxyl groups of electrodes with forming amide bond connections through dehydration reaction. These stable covalent bond connections make the single-molecule junctions very stable. And this chemical assembly allows the use of a variety of molecules to bridge and introduce functions (Figures 10a–c).^[41] In addition, the conductivity of the molecular junctions can be optimized and adjusted by matching the electronic energy level of the molecule to the SWCNT electrodes with specific diameter and chirality.

In the single-molecule FETs, a part of functional properties mainly come from the s-SWCNT electrodes, whose conductance can be regulated by adjusting the diameter and chirality of the SWCNTs. For this type of device, different molecules including general organic molecules^[41] and DNA molecules^[73] have been used for single-molecule junctions. (Figures 10d and 10e), and similar properties can be observed, such as field effect switching. Specifically, when the molecule is successfully assembled into the nano-gap electrodes, the drain current can be regulated by the gate voltage. Meanwhile, the on/off ratio curve is similar to that of the SWCNT electrodes (Figure 10f), which indicates that the field effect mainly comes from the electrodes.^[41]

In addition to gate electric field regulation, the conductance of generalized FETs can also be regulated in other ways, such as the stimulate of light, other physical, chemical or biological interactions. This provides a platform for designing new type of single-molecule FETs with extended applications. Therefore, specific molecules are designed to achieve generalized gate regulation. For example, through the protonation and deprotonation of the polyaniline chain, the pH-adjusting single-molecule junction has been successfully constructed (Figure 11a).^[41] When the bridging molecules are photoactive molecules with photoisomerization function (such as diarylethene or spiropyran), their conductance can be turned on and off by light (Figure 11b).^[74] Extending the concept of generalized FET to biological systems, single-molecule devices that can be used to locate nanostructures (such as nanoparticles) are realized (Figure 11c).^[75] By bridging DNA sequences decorated by amine groups at the ends of different strands into SWCNT electrodes (Figure 10e), the electrical properties of complementary and mismatched strands can be measured, which indicates that the charge transport in DNA double strands depends on π -stacking integrity of base-pair duplex.^[73] With understanding the charge transport characteristics of DNA molecules, a single DNA aptamer is also bridged to nano-gapped SWCNT electrodes to construct singlemolecule junction, which can realize rapid, real-time singlemolecule sensitive monitoring. In this system, the interaction of target protein thrombin and aptamer can be selectively and reversibly detected (Figure 11d).^[76]

4.2. Single-molecule FETs Based on Graphene Electrodes

Graphene is a zero-gap semimetal, which does not have variable electronic properties as that of SWCNTs. Therefore, single-molecule FETs based on graphene electrodes have more uniform performance. Different from the graphene electrode



Figure 10. The regulation of single-molecule FETs based on nano-gapped SWCNT electrodes. (a–c) Preparation and AFM/SEM images of nano-gapped SWCNT electrodes. (d, e) Structure of molecules for single-molecule assembly including general organic molecules and DNA molecules. (f) Gating characteristics of a typical device. (a–d, f) Reprinted with permission from Ref. [41], Copyright 2006 American Association for the Advancement of Science. (e) Reprinted with permission from Ref. [73], Copyright 2008 Springer Nature.



Figure 11. Generalized single-molecule FETs based on SWCNT electrodes. (a) The design of a molecule with pH sensitivity. Reprinted with permission from Ref. [41], Copyright 2006 American Association for the Advancement of Science. (b) Schematic of single-molecule junctions with a photo-isomeric diarylethene molecule. Reprinted with permission from Ref. [74], Copyright 2007 American Chemical Society. (c) Schematic of single-molecule FETs with scaffolding for multiple assembly. Reprinted with permission from Ref. [75], Copyright 2007 American Chemical Society. (d) Device structure and sensing mechanism of a single DNA aptamer junction. Reprinted with permission from Ref. [76], Copyright 2011 Wiley-VCH.

fabricating method of nanoscale OFETs, the graphene point contact electrodes for single-molecule FETs are prepared by using the dash-line lithography (DLL) method.^[77] Specifically, the used graphene flakes are firstly prepared on silicon substrate by chemical vapor deposition and further transfer process or peeling-off techniques, and then spin-coated with a polymethyl methacrylate (PMMA) layer. Then, a design CAD file with 5 nm wide dashed line is used for electron beam lithography to form an array with holes smaller 10 nm in the PMMA mask layer (Figure 12). Through oxygen plasma etching, carboxyl-terminated graphene point contact arrays with a gap less than 10 nm was fabricated. The carboxyl groups at the end of the graphene point contacts react with assembled molecules with high yield.

Since the traditional dielectric layer is difficult to be extremely thin, it is difficult to apply the gate voltage to the single molecular channel. Therefore, it is necessary to develop new ways to adjust the current flowing through the assembled



Figure 12. Schematic representation of cutting graphene by DLL defined oxygen plasma etching to form indented graphene point contact arrays terminated by carboxyl groups. Reprinted with permission from Ref. [77], Copyright 2012 Wiley-VCH.

single molecules between the source/drain electrodes through the gate voltage. We propose using an ionic liquid gate to apply the gate electric field to the single molecular channel of the device through the effective double-layer electrostatic field induced by the gate voltage (Figures 13a and 13c). The electrical double layer thickness of the ionic liquid gate is about 0.75 nm, which can generate strong electrostatic field within small gate voltage range, thus effectively regulating the molecular energy levels (Figure 13b). Due to the low freezing point of ionic liquid (~ 180 K), continuous gate control can be achieved over a large temperature range. This device overcomes short-channel effect of traditional FETs and provides a reliable platform for studying quantum transport laws related to molecular orbital energy levels.^[78] Considering that the molecule-electrode interface is also a key factor affecting the performance of single molecular FETs, the molecules are designed to modulate the properties of single-molecule FETs by interfacial coupling adjustment. Through molecular engineering, different amounts of methylene were added between the diketopyrrolopyrrole (DPP) functional center and the anchor group (AMN-DPP, n=0-3) to control the interfacial coupling between the molecular functional center and the electrodes (Figures 13c and 13d). When there are 0 or 1 methylene groups, HOMO-pinning effect occurs in molecular junctions; and when there are 2 or 3 methylene groups, there is an ambipolar field effect across the devices.^[79]

Generalized single-molecule FETs can also be realized by directly designing functional molecules and further introduce other ways such as light stimulation to adjust the conductance of single-molecule junctions. For example, through molecular engineering, a stable single-molecule junction can be formed by covalently assembling single diarylethene molecule with photoisomerization function to nano-gapped graphene electrodes. This molecule is specially designed to introduce three methylene groups between the diarylethene functional center and the terminal groups for adjusting the interfacial coupling (Figure 14a). In this way, reversible photo-switching (Figure 14b) and a random switching at certain temperature range can be realized for the single-molecule junction. This device has unprecedented accuracy (on/off ratio ~ 100), stability (over a year), and reproducibility for photo-switching (46 devices, over 100 cycles) and random switching (10⁵ - 10⁶ cycles).^[80] Besides the diarylethene system, azobenzene is also a feasible chemical gate, which can effectively adjust the energy levels and spatial electronic structures between cis and trans conformations. And the isomerization of azobenzene can be used to implement conductance switching of single-molecule junctions. One way is to bridge azobenzene molecule between molecular-scale graphene point contacts (Figures 14c and 14d). Under light stimulation, reversible switching between different conductance states is achieved.^[81] Another way is to use azobenzene molecule as side group of bridge molecule (Figure 14e). Then, a fully reversible dual-mode singlemolecule transistor is obtained (Figure 14f).^[82]

5. Summary and Perspective

With the rapid development of molecular electronics, molecular FETs have attracted much attention. Due to their advantages such as low power consumption, high speed, miniaturized and high integration, they have become potential electronic components in the future. In this review, we have given a detailed introduction to the development of molecular FETs from macroscale to nanoscale and single molecule. We describe the development of different fabrication techniques of molecular devices through molecular design and assembly as



Figure 13. Ionic liquid gated single-molecule FETs based on graphene electrodes. (a, b) Schematic diagram and energy level structures of single-molecule FETs with an ionic liquid gate. Reprinted with permission from Ref. [78], Copyright 2018 Wiley-VCH. (c) Schematic illustration of GMG-SMJs with an electrical double layer of ionic liquids gating. (d) Molecular structures of AMn-DPP (n=0-3) with different numbers of methylene used as molecular spacers. Reprinted with permission from Ref. [79], Copyright 2020 Wiley-VCH.



Figure 14. Generalized single-molecule FETs based on graphene electrodes. (a) Schematic of a graphene-diarylethene-graphene junction. (b) Reversible photoswitching of the diarylethene junction. Reprinted with permission from Ref. [80], Copyright 2016 American Association for the Advancement of Science. (c) Structures of *trans* and *cis* isomers of azobenzene. (d) Schematic representation of a junction with a bridged azobenzene. Reprinted with permission from Ref. [81], Copyright 2013 Wiley-VCH. (e, f) Schematic representation of the junction with a side group of azobenzene and photo-switching characteristics. Reprinted with permission from Ref. [82], Copyright 2019 Springer Nature.

well as carbon electrodes design, and emphasize the important progress of molecule-based functional devices towards practical applications. These demonstrations significantly enhance the fundamental understanding of the correlation between molecular structure, assembly, and function, thereby providing new insights for the design of a new generation of practical multifunctional optoelectronics and sensors. Moreover, the regulation strategies of ionic liquid gate and other external controls such as light stimulation are demonstrated. These studies have promoted the basic research and application development of molecular FETs.

Despite these significant achievements, future research still faces great challenges, especially for single-molecule FETs. The following fields need to be overcome and explored. First, new processes need to be developed to fabricate stable and efficient single-molecule devices to meet the requirements of singlemolecule FET construction and further integration in the future. Then, more efficient ways of applying gate voltage to single molecule need to be developed, especially solid-state gate, to meet the research requirements of the device at low temperature and to be compatible with current semiconductor fabrication processes. In addition, molecular design is required to further improve gate regulation, such as increasing the on/ off ratio of single-molecule FETs. Based on the constructed devices, some basic scientific laws can be explored, such as quantum transport of single molecules and chemical reaction kinetic processes at the single-molecule level. At last, the applications of single-molecule FETs need to be further expanded, such as the construction of highly sensitive chemical/biological sensors. We trust that molecular FETs have the bright future for creating practical multifunctional integrated nanocircuits beyond Moore's law.

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PERSONAL ACCOUNT

This *personal account* introduces our recent works in the construction and performance of molecule-based FETs from macroscale to nanoscale and even single molecule.



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Molecule-Based Transistors: From Macroscale to Single Molecule