Fabrication and functions of graphene-molecule-graphene single-molecule junctions



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ABSTRACT

The past two decades have witnessed increasingly rapid advances in the field of single-molecule electronics, which are expected to overcome the limitation of the miniaturization of silicon-based microdevices, thus promoting the development of device manufacturing technologies and characterization means. In addition to this, they can enable us to investigate the intrinsic properties of materials at the atomic-or molecular-length scale and probe new phenomena that are inaccessible in ensemble experiments. In this perspective, we start from a brief introduction on the manufacturing method of graphene-molecule-graphene single-molecule junctions (GMG-SMJs). Then, we make a description on the remarkable functions of GMG-SMJs, especially on the investigation of single-molecule charge transport and dynamics. Finally, we conclude by discussing the main challenges and future research directions of molecular electronics.

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I. INTRODUCTION

The intriguing idea¹ of integrating individual molecules into integrated circuits has encouraged researchers to devote their energies to molecular electronics over the past few decades, resulting in new techniques and methods to characterize and modulate the conductivity of single molecules, for example, mechanically controllable break junction (MCBJ),^{2,3} scanning probe microscopy (SPM),^{4,5} electromigration break junction,^{6,7} electrochemical deposition junction,^{8,9} surface-diffusion-mediated deposition junction,¹⁰ and so on. On the basis of these methods, scientists have realized various functions within single-molecule devices, including switching,^{11–13} rectification,^{14,15} transistor,^{10–18} thermoelectric energy conversion,^{19–21} electroluminescence,^{22–24} and other functions,^{25,26} which are favorable to direct observation and fundamental understanding of numerous physical phenomena, from the traditional study of charge transport to the development of quantum interference, optoelectronics, spintronics, and other research.²⁷

However, the sophistication of these single-molecule technologies has become an obstacle to their large-scale manufacturing and commercialization. In addition, the high atomic mobility and strong coupling effect of the electrode–molecule interface are common in molecular devices with metal electrodes, which give rise to the destruction of molecular junctions upon oxidation or electromigration and limit the device functionalization.²⁸ To this end, graphene is naturally one of the most suitable candidates for nanoscale electrodes because of its good compatibility with organic molecules and easy preparation of the array electrodes. In combination with molecular engineering, researchers have connected the reasonably designed molecules with the end of graphene electrodes via an amide covalent bond or π - π stacking interactions. Single-molecule devices constructed by amide covalent bonds have smaller contact resistance, which makes it easier to distinguish different conductance signals in electrical measurements. Strong covalent bonds can ensure the robust stability of the device and undergo multiple solvent changes, which have obvious advantages in single-molecule dynamics research. Moreover, the molecule-electrode coupling effect can also be regulated by molecular engineering. However, the synthesis of molecules containing two terminal amine groups is relatively difficult in comparison with the π - π stacking method in which conjugated groups such as anthracene and pyrene are mostly used as anchor groups. Based on the graphene-molecule-graphene single-molecule junctions (GMG-SMJs), significant advances^{29–32} have been made in the study of photoelectric switches, charge transport properties, and intrinsic understanding of physical, chemical, and biological processes at the molecular level, and the development opportunities are endless.

II. FABRICATION OF GMG-SMJs

The size resolution and reproducibility of the fabricated graphene nanogaps have remained challenging, which restricts the development of molecular electronics. Several research groups have carried out the preparation and functionalization of graphene-based nanoelectrodes, which might lead to further breakthrough works on this platform. Cao et al.³³ developed a dash-line lithographic (DLL) method to solve this problem. First, they grew single-layer graphene (SLG) on copper foils via a chemical vapor deposition (CVD) method and transferred it to silicon wafers with the oxide layer (300 nm). The Au electrodes were then deposited on the graphene sheet by means of photolithography and thermal evaporation to form ordered electrode arrays, followed by electron beam evaporation of a 40-nm-thick SiO₂ layer to passivate metal electrodes. By using ultrahigh-resolution electron-beam lithography and gradual oxygen plasma etching, carboxylic acid-terminated graphene point contacts were constructed, forming open circuits. At last, the target molecules with two terminal amine handles were connected to the nanogapped graphene electrodes by forming amide covalent bonds in pyridine. The successful establishment of single-molecule junctions was indicated by the resurgence of electrical currents. Figure 1 shows the structure of the single-molecule junction. This methodology not only curves the problem of the low success rate in the preparation of molecular devices but also fabricates well-defined contacts between molecules and electrodes with excellent reproducibility and stability. Its advent will certainly provide new impetus for the development of molecular electronics and unlimited opportunities for the exploration of basic scientific problems.



FIG. 1. A structural depiction of GMG-SMJs. Reprinted with permission from Cao et al., Angew. Chem., Int. Ed. 51, 12228 (2012). Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

Prins et al.³⁴ developed a method to form nanometer-separated few-layer graphene electrodes by feedback-controlled electroburning and further reported room-temperature gating of molecular junctions. First, they deposited few-layer graphene on doped silicon substrates coated with 280 nm of thermal silicon oxide, and then Cr/Au electrodes were patterned by electron-beam lithography and subsequent metal evaporation. Finally, the feedback-controlled electroburning was performed in air at room temperature. Figures 2(a) and 2(b) show the changes in graphene electrodes before and after electroburning and corresponding conductance variations. The conductance of graphene continuously reduced throughout the feedback-controlled electroburning process until nanometer intervals formed, and the low-bias resistance of most devices was in the range of 500 M Ω to 10 G Ω after electroburning. The atomic force microscopy (AFM) characterization suggested that electroburning started from the edges in the central region of the flake, predominantly on one side. The long-term stability and gateindependent transport across the gap were confirmed by electrical measurements, which made it possible to measure three-terminal charge transport. To demonstrate this, they deposited anthracenefunctionalized curcuminoid molecules [1,7-(di-9-anthracene)-1, 6-heptadiene-3,5-dione, abbreviated as 9Accm, see Fig. 2(c)] on



FIG. 2. (a) Schematic of the feedback-controlled electroburning process. (b) *I–V* traces of the evolution (green arrow) of the feedback-controlled electroburning. (c) Schematic of the single-molecule transistor. (d) Chemical structure of the deposited molecule. (e) *I–V* characteristics of the nanogapped electrodes before and after being bridged at 300 K. (f) Dependence of the *I–V* characteristics of the device on the applied back-gate voltage measured at 300 K. Reprinted with permission from Prins *et al.*, Nano Lett. **11**, 4607 (2011). Copyright 2011 American Chemical Society.



FIG. 3. Schematic representation of the MCBJ measurement setup. Reprinted with permission from Caneva *et al.*, Nat. Nanotechnol. **13**, 1126 (2018). Copyright 2018 Nature Publishing Group.

the nanogapped devices. Figure 2(d) is a schematic representation of the device. After deposition, the conductance of the device increased and was dependent on the gate-voltage at room temperature [Figs. 2(e) and 2(f)]. The conductance increases toward more positive gate values at different gate voltages between -10 V and 10 V. Such gate-dependent transport manifested to be more obvious at low temperature (10 K). They further noted that this approach was also applicable to CVD-grown few-layer graphene and that the scheme to fabricate controllable nanoscale graphene electrodes based on feedback-controlled electroburning was increasingly improved.

In addition, the preparation of graphene-based nanoelectrodes by the MCBJ technology is also a relatively extensive method. Caneva *et al.*³⁵ transferred single-layer graphene onto a polymercoated metal substrate, which was then etched into a butterfly shape, while the surrounding excess polymer was removed. The sample was mounted in a three-point bending configuration (Fig. 3) with a central pushing rod beneath the sample and two countersupports on top of the substrate at both ends. The graphene gap was obtained by gradually bending the substrate. The process could be closed as indicated by a sharp decrease in conductance, realizing the adjustment of the gap size with high precision and stability. In this regard, such an MCBJ platform has a potential use for quantum tunneling-based sensing of (bio)molecules.

Tan *et al.*³⁶ took a different approach, creatively using graphene-coated copper wires as electrodes. They fixed two parallel wires on the flexible substrate by the "head-to-head" configuration, keeping the ends 10–20 μ m apart without touching. At the beginning of the measurement, a stepping motor together with the piezo stack pulled down the middle part of the substrate, causing the two electrodes to gradually approach and reach the limit. Then, the piezo stack started to separate the two contacted graphene electrodes while monitoring the real-time current. A schematic diagram of this platform is shown in Fig. 8(a), and the related work based on this platform will be introduced in detail in the following article.

III. SINGLE-MOLECULE SWITCHES

Over the past decades, scientists have focused on using single molecules as the key building blocks of logic gates, diodes, and transistors to perform the basic functions of digital electronic devices at the molecular scale.¹³ Among them, the use of light,³⁷ electric field,³⁸ temperature,³⁹ and even chemical modification⁴⁰ to activate molecular switches between bistable or even multiple states is the most attractive tool. However, the ability to control the conductance of molecules at the molecular level by external modes, especially implement reversible switching, is still a challenge in this field. In view of this, a series of switches on the platform of single-molecule devices based on graphene electrodes were constructed and finally achieved a reliable and reversible switch, which will be described below.⁴¹

To construct photoswitches at a single-molecule level, Jia et al.⁴² connected the diarylethene (DAE) derivatives [1-3 in Fig. 4(a)] to graphene nanometer electrodes by covalent bonding, as mentioned above. As a typical photochromic molecule, diarylethene can undergo reversible transitions between two distinct isomers with open/closed conformations when exposed to light irradiation, affecting the planarity and conjugation of the whole molecule while the length of the molecule changes negligibly between two (open- and closed-configuration) isomers. These remarkable electronic and structural properties, coupled with thermal stability and fatigue resistance, make diarylethene molecules as ideal candidates for fabricating light-induced molecular switches. Combined with their previous work,⁴³ they intentionally designed these three molecular structures through molecular engineering, so as to reduce the coupling effect at the electrode-molecule interface. Compared with 1, 2 has a perfluorinated unit instead of the hydrogenated cyclopentene, while 3 has a methylene group (CH₂) between the terminal amine group and the functional center on each side. These modifications decrease the electron density on the central alkene unit and cut off π -electron delocalization, respectively. As a result, the energy levels of 2 are lower than those of 1, and those of 3 are even lower. The calculated results confirmed it and supported the design of regulating the molecule-electrode coupling strength through molecular engineering.

All of the single-molecule devices achieved the transition from the low-conductance (off) state to the high-conductance (on) state under ultraviolet (UV) irradiation [Fig. 4(b)]. This observation should be attributed to the isomerization of DAE molecules, which went through the open, unconjugated conformation to the closed, conjugated conformation. In order to explain why the closed state has higher conductance than the open state, they calculated the zero-bias voltage transmission spectra of the GMG-SMJs [Figs. 4(c) and 4(d)]. The transmission spectra of open and closed conformations are distinctively different near the Fermi level. The HOMO and LUMO of DAE molecules with closed conformation are delocalized π -conjugated orbitals that provide good conductive channels, thus leading to two significant transmission peaks located on each side of the Fermi level (about -0.05 eV and 1.2 eV). In addition, the average on/off ratio of 1, 2, and 3 was ~60, ~200, and ~300, respectively. These results indicate that the interface coupling plays a key role in the on/off ratio. However, the fabrication of reversible molecular photoswitches still remains a challenge.

To overcome this issue, they further took the strategy of incorporating three methylene (CH_2) groups into each side of the molecular backbone [Fig. 5(a)], in the perspective of molecular engineering, to decrease the energy level of molecule–electrode coupling that may





quench the molecular excited state.⁴⁴ Fortunately, they successfully implemented reversible and reproducible switching of diarylethenereconnected molecular junctions with graphene electrodes under ultraviolet and visible radiation [Fig. 5(b)], which was confirmed

by real-time conductance detection. The theoretical predictions for both closed and open molecular forms are in agreement with the experimental current–voltage characteristics. Furthermore, stochastic switching of the closed junction between two conductive modes



FIG. 5. (a) Schematic of the DAEreconnected GMG-SMJ that highlights the expansion of the molecular bridge by methylene groups. (b) *I-t* curves of the device exposed to ultraviolet (UV) and visible (Vis) radiation. (c) Stochastic switching between two conductive states of individual closed DAE molecules at 180 K (d) *I-t* curves of stochastic conductance switching at 180 K. Reprinted with permission from Jia *et al.*, Science **352**, 1443 (2016). Copy right 2016 AAAS.

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FIG. 6. (a) Schematic of the device that highlights a reversible isomerization of the azobenzene unit between trans and cis forms triggered by either optical or electrical stimuli. (b) I-V characteristics of TTDA molecular junctions at different temperatures. (c) I-t curves of the device exposed to ultraviolet and visible light at low bias voltages. Reprinted with permission from Meng et al., Nat. Commun. 10, 1450 (2019). Copyright 2019 Nature Publishing Group. (d) Schematic and atomic force microscopy image of a graphene/Fe-SCO/graphene singlemolecule junction. The scale bar is 500 nm. (e) Spin-crossover bistable I-V characteristics of Sample 3. (f) Representative current, I, color plot as a function of the bias voltage, V, and decreasing temperature measured for Sample 3. Reprinted with permission from Burzuri et al., Nanoscale 10, 7905 (2018). Copyright 2018 Royal Society of Chemistry. [(g) and (h)] Schematic of hexaphenyl aromatic chain SMJs and the corresponding stochastic switching at 120 K. Reprinted with permission from Xin et al., Nano Lett. 17, 856 (2017). Copyright 2017 American Chemical Society.

[Figs. 5(c) and 5(d)] could be observed in the temperature range of 160–240 K, which might be related to a diarylethene conformational change, possibly driven by transient molecular charging, that is, changing occupation of the molecular HOMO. In a word, this work constructs a fully reversible, two-mode, single-molecule electrical switch with unprecedented levels of accuracy, stability, and reproducibility.

Recently, Meng et al. developed a kind of single-molecule junction with azobenzene as the core function and realized the dual-mode switching device induced by light and electric field.⁴⁵ Azobenzene derivatives, as typical photochromic materials, are able to isomerize back-and-forth between two states (cis/trans) under irradiation of different wavelengths of light (UV/visible), which would inevitably change the structure and polarity of the azobenzene unit. In view of this, they immobilized an azobenzene unit at the side position of a terphenyl aromatic chain, between graphene point contacts, to construct a robust GMG-SMJ [Fig. 6(a)]; it was designed in such a way as to avoid the possible instability of molecular junctions resulting from the length change during isomerization. At sourcedrain bias in the range of -0.05 V to -0.20 V, the I-V curves of the working devices represented asymmetric stochastic switching between two distinct conductance states [Fig. 6(b)], and the switching rate was accelerated by increasing the temperature. The real-time current measurements, conducted at different bias voltages ranging from -0.05 V to -0.30 V in the dark and under vacuum, confirmed this switching behavior. The calculated on/off ratios of the conductance switching were in the range from ~2.00 to ~2.46, showing little dependence on bias voltages. At a small positive voltage of 0.01 V, for ruling out the effect of the electric field, the single-molecule device performed reversible switching between high- and low-conductance states with an on/off ratio of ~2.1 under altering UV/vis light irradiations [Fig. 6(c)]. The similar on/off ratio with stochastic switching above suggested the same isomerization process. They theoretically attributed low- and high-conductance states to trans and cis forms, respectively. Further theoretical calculations suggested that applying negative voltages could isomerize azobenzene from trans to cis gradually, which was in good agreement with their experimental results.

Burzuri et al.46 reported electron transport through individual spin-crossover (SCO) molecules coupled to few-laver graphene (FLG) electrodes via π - π stacking and observed a distinct bistability in the conductance of the molecule. In this work, they used graphene, rather than metal, as electrodes because the structural distortions induced in single molecules by their contacts to metallic surfaces are well known to modify their magnetism and even quench the SCO mechanism. They anchored SCO molecules [Fe(L)₂](BF₄)₂·CH₃CN·H₂O, abbreviated as Fe-SCO, to two FLG electrodes using the aforementioned method. A schematic representation of the FLG/Fe-SCO/FLG junction and an atomic force microscopy (AFM) image of the graphene electrodes are shown in Fig. 6(d). Two pyrene ending-groups lay further from the edges, facilitating a coupling to graphene electrodes by π - π stacking. Figure 6(e) demonstrates I-V curves of a single-molecule junction at cryogenic temperatures, and two distinct states appeared, a largegap (LG) state (blue curve) and a small gap (SG) state (red curve). The low-bias current was suppressed in both cases, which was consistent with a characteristic of off-resonant transport in a Coulomb blockade regime. The blockade for the SG and LG states was lifted at $V_{\text{SG}} \approx 0.1-0.2$ V and $V_{\text{LG}} \approx 0.5$ V, respectively. They attributed such a sharp change in the resonant voltage from V_{SG} to V_{LG} in this molecular junction to an abrupt change in the molecular orbitals around the Fermi level of graphene, tentatively induced by the SCO transition. Figure 6(f) shows a representative color plot of I measured as a function of V in a device while decreasing the temperature. A telegraph-like switch was observed between well-separated states at any temperature, which was quite different from the fact that the bulk SCO transition must be at a specific temperature. It could be explained that the steric hindrance at the single-molecule level varied from bulk and the SCO transition might sensitively depend on the local geometry adopted by the molecule in the junction. These examples of molecular switches induced by light, electric field, and SCO not only provide a novel method to study the molecular reaction process but also provide a unique perspective for constructing future multifunctional nanodevices.

Over decades, chemists have developed a nuanced understanding of stereoelectronics to establish how the electronic properties of molecules relate to their conformation. The recent advent of single-molecule techniques provides the means to probe this conformation.⁴⁷ In order to investigate how the intramolecular conformation of biphenyl dynamically affects its transport properties at the single-molecule level, Xin et al. rationally designed a hexaphenyl aromatic chain molecule, where the medial biphenyl was placed by a fluorene form to fix the dihedral angle, covalently sandwiched between nanogapped graphene point contacts to create stable single-molecule junctions [Fig. 6(g)].⁴⁸ Based on the systematic temperature-independent measurements, they found stochastic switching between two distinct conductance states in the I-V curves, which mainly occurred from 120 K and nearly stayed at a low-conductance state until 140 K [Fig. 6(h)]. When increasing the temperature, the switching frequency gradually increased and the current ratio of high/low-conductance states gradually decreased. Combined with theoretical calculations, they assumed that when the temperature was lower than 120 K, the activation was too low to promote the conformation switching, behaving as a high-conductance state in the electronic measurements. Once the temperature was higher than this threshold, the phenyl twisting mode was excited and the conjugation of the molecule was altered, resulting in stochastic switching between high- and low-conductance states and accelerating the switching rate. Such stereoelectronic effect-induced conductance switching investigations greatly facilitate the understanding of the relationship between conformation and electronics in aromatic systems and offer new design insights into developing novel types of molecule-based devices.

IV. SINGLE-MOLECULE CHARGE TRANSPORT INVESTIGATIONS

The ultimate goal of developing single-molecule devices is to apply them to integrated circuits. Thus, the ability to measure, understand, and control charge transport at the singlemolecule level is particularly important, and it is worthwhile devoting much effort to this. Xin *et al.* reported a class of aromaticring single-molecule junctions, realizing efficient control of singlemolecule charge transport via ionic-liquid gating.⁴⁹ They covalently wired individual molecules, electrochemically inactive phenylbased structures with different molecular lengths, into nanogapped graphene point contacts to form single-molecule devices [Figs. 7(a) and 7(b)]. For further measurements, they dripped a small droplet of the ionic liquid onto the devices for covering the array of graphenebased molecular junctions and the gate. The ionic liquid gate has an electrical double layer (EDL) of about 0.75 nm thickness, which can generate a strong electrostatic field within a small range of gate voltage, thus effectively regulating the molecular energy levels. Because the freezing point of the ionic liquid is low (~180 K), continuous gate control can be realized over a large temperature range. Furthermore, with the change in gate voltage from -1.5 V to 1.5 V, the conductance of biphenyl molecular junctions decreased monotonically, while the conductance of triphenyl and hexaphenyl first decreased and then increased. Therefore, with a small gate voltage, ambipolar charge transport in electrochemically inactive molecular systems was realized. Based on the theory, the transmission spectra of molecular devices under different gate voltages were calculated. The results showed that the change in gate voltages from negative to positive caused a downshift in the molecular orbitals of the triphenyl and hexobenzene molecular systems and an increase in the graphene Fermi level [Fig. 7(c)]. When the LUMO was closer to the Fermi level of the graphene electrode than the HOMO, the LUMO replaced the HOMO as the main contributor to the conductivity of the molecular junctions, indicating that the transition of carriers from the hole to the electron was realized via gate control. In conclusion, this work unlocks the critical bottleneck of building high-performance singlemolecule transistors and provides a reliable platform for studying the quantum transport effect related to the molecular orbital energy level.

Xu et al.⁵⁰ fabricated single-molecule transistors by obtaining nanometer-scale gaps from feedback-controlled electroburning of graphene constrictions and bridging these gaps with molecules using reaction chemistry on the oxidized graphene edges. In order to avoid misshapened or partially burnt graphene channels during the electroburning process, which usually occurred in graphene channels of arbitrary widths and shapes, they implemented an additional lithographic step before electroburning to shape the graphene with a 500 nm wide constriction in the center of the channel. Then, they performed condensation between the carboxylic acid groups on the graphene edges with a molecule terminated by two amine groups. When the N-hydroxysuccinimide (NHS) group was introduced to stabilize the activation of the carboxylic acid group with EDC, the reconnection yield was significantly increased. The estimated contact resistance for these covalent bonds of 4,4'-diaminobiphenylreconnected devices was quite large (>100 MΩ). They hypothesized that the break of electronic conjugation at the contacts confined the discrete molecular orbitals between the contacts [as represented in Fig. 7(d)], which may result in single-electron tunneling across the junction in charge transport measurements. To prove this, they measured the dependence of the conductance of reconnected devices with the gate bias in vacuum at 100 K. Figure 7(e) shows a 2D plot of the electrical current as a function of the drain-source bias (V_{bias}) and gate bias (Vgate), and several diamond-shaped regions with suppressed electrical conductance could be clearly observed, which were a typical signature of the Coulomb blockade effect in single-electron



FIG. 7. [(a) and (b)] Schematic of GMG-SMJs with the ionic liquid gate dielectric. (c) Energetic diagram of the alignment of molecular orbitals relative to the graphene electrode Fermi level in triphenyl and hexaphenyl singlemolecule transistors under different gate voltages. Reprinted with permission from Xin et al., Angew. Chem., Int. Ed. 57, 14026 (2018). Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA. (d) Diagram of single-electron tunneling across discrete electronic states isolated between two tunneling barriers. (e) Transporting current across a device as a function of the bias voltage and gate voltage at 100 K. Reprinted with permission from Xu et al., Nano Lett. 17, 5335 (2017). Copyright 2017 American Chemical Society.

transistors. In addition, the shape and size of Coulomb diamonds were related to the energy of the molecular electronic levels and electrostatic coupling to the electrodes.

Tan *et al.*³⁶ investigated the charge transport properties through graphene–fullerene–graphene hybrid junctions using a cross-plate MCBJ technique. They bridged the fullerene between two copper wires coated with CVD-grown graphene via van der Waals interaction to build single-molecule junctions [Fig. 8(a)] and tuned charge transport by inserting fullerenes with a variety of energy gaps. Figure 8(b) displays typical individual conductance–displacement curves for graphene/blank or single- C_{60} , C_{70} , C_{76} , and C_{90} /graphene junctions. It was found that a higher molecular conductance plateau corresponded to a larger molecular size, notably the conductance of C_{90} , which was nearly half an order of magnitude higher than that of C_{60} . As shown in Fig. 8(c), the conductance of graphene– fullerene–graphene junctions increased with the size of fullerenes from C60 with ~7 Å to C_{90} with ~9 Å. The reason was that the increase in the HOMO of fullerenes was enough to compensate for

the decreased electrical conductance. To further explore the effect of the conjugation degree on charge transport through graphenefullerene-graphene junctions, they investigated the conductance of hydrofullerene $C_{50}H_{10}$, whose π system was partially interrupted by ten hydrogen-bonded carbon atoms [see the structure in Fig. 8(d)]. The measured conductance was located at 2.2×10^{-6} G₀, which was almost one order of magnitude lower than that of conjugated single- C_{60} , and the displacement distribution was shorter than that of C_{60} . These results indicated that the C₅₀H₁₀ molecule was aligned with the short axis in the junctions, and the interrupted conjugation of the π system significantly changed charge transport. In addition, they fabricated graphene-fullerene-graphene junctions consisting of a D_{2h} symmetric C₁₂₀ fullerene dimer and nitrogen-doped fullerene dimer (C₅₉N)₂ [Figs. 8(e) and 8(f)], respectively, to tune charge transport via heteroatom doping. The measured conductance values and plateaus of C₁₂₀ were similar to those of C₆₀, while the conductance of graphene/single-(C59N)2/graphene increased by 150%. It could be explained that the introduction of nitrogen heteroatoms



FIG. 8. [(a) and (b)] Schematic mechanically controlled break graphene-fullereneiunctions and junctions and chemical araphene structures of C₆₀, C₇₀, C₇₆, and C₉₀. (b) Conductance-displacement curves for graphene/blank or single-C₆₀, C₇₀, C₇₆, and C₉₀/graphene junctions. (c) Conductance of graphene-fullerene-graphene junctions and the HOMO-LUMO gap values of fullerenes vs the number of carbon atoms in fullerenes. [(d) and (f)] Schematics of graphene/singlefullerene/graphene junctions of C₅₀H₁₀, C_{120} , and $(C_{59}N)_2$, respectively. Reprinted with permission from Tan et al., Nat. Commun. 10, 1748 (2019). Copyright 2019 Nature Publishing Group.

into the fullerene led to significant perturbations of the geometric and electronic character. The density functional theory (DFT) simulations revealed that the introduced nitrogen created two transport resonances around -0.5 eV within the HOMO–LUMO gap of C₁₂₀, and the localized states on the two N atoms dominated the two peaks around -0.5 eV.

Gehring *et al.*⁵¹ harnessed graphene-based lateral singlemolecule devices with gold microheaters to study the gatedependent thermoelectric properties of C₆₀ molecules. The device structure is shown in Fig. 9(a), a bow-tie shape graphene on top of gold lead with four contacts for precise measurements of temperature difference across the graphene junction. A gold microheater was fabricated 1 μ m away from the junction to create a temperature gradient. They used feedback-controlled electroburning to first form graphene nanogaps and subsequently coupled C₆₀ molecules functionalized with pyrene anchor groups [Fig. 9(b)]. Three selected devices (Devices B, D, and G) where the Coulomb



FIG. 9. (a) Schematic representation of the device. (b) Chemical structure of the functionalized C_{60} with pyrene anchor groups. [(c) and (d)] Current map as a function of back-gate and bias voltage before and after molecule deposition for three devices. (e) ac zero-bias conductance and thermovoltage as a function of back-gate voltage for three devices. Reprinted with permission from Gehring *et al.*, Nano Lett. **17**, 7055 (2017). Copyright 2017 American Chemical Society.

diamonds were close in the accessible back-gate region with addition energies >400 meV were discussed. Figs. 9(c) and 9(d) show the corresponding current maps as a function of back-gate and bias voltage at 77 K before and after molecule deposition. The regions of Coulomb blockade could be observed after deposition originated from the formation of molecular junctions. To measure the gatedependent thermoelectric properties of the graphene-C₆₀-graphene junctions, they applied an ac voltage to the microheater and measured the thermovoltage V_{th} on the device for different back-gate voltages Vg. Because of the low signal-to-noise ratio inside the Coulomb blocked region, they focused on the high-conductance gate region around the Coulomb peaks [see gate traces in Fig. 9(e)]. The bottom section of Fig. 9(e) shows the measured gate-dependent thermovoltage signal whose trajectory is similar to a sinusoidal curve, for Devices D, G, and B, recorded at $\Delta T = 45 \pm 9$ mK, $\Delta T = 100 \pm 20$ mK, and $\Delta T = 180 \pm 36$ mK, respectively. They found that the deduced values of maximum Seebeck coefficients S_{max} were more than 1 order of magnitude larger than those found in STM break junction experiments of C₆₀ and used a simple model for an isolated Breit-Wigner resonance to explain these results.

V. SINGLE-MOLECULE DYNAMICS INVESTIGATIONS

Apart from building reversible switches and studying the charge transport properties at a single-molecule level, we can also implement ultrasensitive detection of a single molecule in solution to investigate single-molecule dynamics. Thanks to GMG-SMJs anchoring organic molecules through covalent bonds, which ensured the stability and reliability of the device. In this section, we present several typical examples of the GMG-SMJ platform on probing dynamic processes at the single-molecule level, involving hostguest interactions, hydrogen bond interactions, and intermolecular chemical reactions.

As shown in Fig. 10(a), Wen et al. integrated a rigid and conjugated molecule incorporating bis-p-phenylene[34] crown-10 (BPP34C10) and two terminal amine handles, namely, BPP34C10DAM, into graphene point contacts. The successful fabrication of the device could be judged by the closure of the circuit.⁵² To gain more detailed information about the host-guest interactions at the single-molecule event, they initiated the complexation by introducing methyl viologen (MV²⁺), a widely studied guest for the BPP34C10 host, into the GMG-SMJ system. After immersion in a Me₂SO solution containing 1 mM MV 2PF₆ for 12 h and post-treatment, the resulted devices (MV²⁺ \subset BPP34C10) could be measured on the self-designed test system, including a temperature control module and polydimethylsiloxane (PDMS) solvent reservoir. The I-t curves of BPP34C10-SMJs, immersed in Me₂SO solution containing 1 mM MV 2PF₆, showed two distinct "high" and "low" states [Fig. 10(b)]. In combination with the observation of a change in conductance in the solid state after MV²⁺ addition [Fig. 10(c)], it could be concluded that the high- and lowconductance states corresponded to the complexation and dissociation behavior of the host BPP34C10 and guest MV²⁺ molecules. The theoretical calculation results also proved that electron (LUMO) transport was predominant for both BPP34C10 and the MV²⁺ ⊂ BPP34C10 complex in this particular graphene-based system, while the LUMO of the $MV^{2+} \subset BPP34C10$ pseudorotaxane SMJ was more delocalized, facilitating a better conductive channel.



FIG. 10. (a) Schematic representation of $MV^{2+} \subset BPP34C10\text{-}SMJ$. (b) *I-t* curves (black) of the above device and idealized two-level interconversion by using the QuB software. (c) I-V curves of graphene point contacts (black), BPP34C10-SMJ (red), and MV2 \subset BPP34C10-SMJ (blue) in the solid state. (d) Plots of the thermodynamic parameters deduced from singlemolecule measurements. (e) Plots of time intervals of the high two current states with the derived lifetimes of two states (τ_{high} and τ_{low}). (f) Arrhenius plots of association ($k_{\alpha} = 1/\tau_{low}$) and dissociation ($k_d = 1/\tau_{high}$) rate constants. Reprinted with permission from Wen et al., Sci. Adv. 2, e1601113 (2016). Copyright 2016 AAAS

the $MV^{2+} \subset BPP34C10$ -SMJ system, they could logically probe the thermodynamic and kinetic parameters of a host-guest complex [Figs. 10(d)–10(f)]. For example, the binding constants (K_{α}) could be derived from the Langmuir isotherm $K_{\alpha} = \alpha/(1 - \alpha)C$, where α is the fraction of the BPP34C10 host complexed with MV²⁺ and C is the concentration of MV²⁺. Other thermodynamic parameters, such as the Gibbs free energy (ΔG°), the enthalpy (ΔH°), and the entropy (ΔS°) for the complexation process, were deduced by using the van't Hoff equation, $-RT\ln(K_{\alpha}) = \Delta H^{\circ} - T\Delta S^{\circ}$ (R is the ideal gas constant and T is the temperature). In addition to the above mentioned, they derived a set of kinetic parameters from the idealized two-level flip-flops in I-t curves using the QuB software, such as the high and low current lifetimes τ_{high} and τ_{low} , and the corresponding (de)complexation rate constants $k_{\alpha} = 1/\tau_{low}$ and $k_{\rm d} = 1/\tau_{\rm high}$, at different temperatures in both Me₂SO and aqueous solutions. More importantly, the activation energies E_{α} and E_{d} of the (de)complexation processes could be derived by using the Arrhenius equation. These results are sufficient to show that the electrical testing system based on SMJs can effectively reveal thermodynamic and kinetic information at the level of individual molecules, paving a new way for the study of chemical/biological processes.

Building molecular machines that can be manipulated at the molecular level is what chemists have been trying to achieve. Although numerous artificial molecular systems with various topological architectures and responsive modes to external stimuli have been developed, controlling individual molecular machines and understanding the intrinsic principle at the single-molecule level are still facing enormous resistance because of the lack of efficient single-molecule analytical tools. Hence, Zhou et al. covalently integrated a conjugated molecular wire with a macrocyclic side group, a permethylated α -cyclodextrin (PM- α CD), into graphene point contacts, to explore single-molecule shuttling dynamics.⁵³ The device structure is shown in Fig. 11(a). All the measurements were conducted at different temperatures where GMG-SMJs were immersed in a water solution containing dodecanedioic acid, 1,12-dodecanediamine, and 12-aminododecanoic acid (negative, positive, and amphoteric charges on both chain ends, respectively). Correspondingly, in the current distribution histograms [Fig. 11(b)], they observed large-amplitude two-level or three-level conductance states. Indeed, pseudorotaxane movement processes between PM- α CD and alkylene chains with different charges lead to distinct reproducible large-amplitude signal oscillations within the time



FIG. 11. (a) Schematic of the device structure of GMG-SMJs formed by individual molecular shuttles. (b) I-t curves of molecular shuttle dynamics during 20 ms. (c) I-t curves of shuttling processes and four kinds of possible shuttling modes. Reprinted with permission from Zhou et al., Small Methods 3, 1900464 (2019). Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA. (d) Schematic representation of HBB-SMJs. [(e) and (f)] Enlarged I-t curves of an HBB-SMJ device in diphenyl ether at 323 K. Reprinted with permission from Zhou et al., Nat. Commun. 9, 807 (2018). Copyright 2018 Nature Publishing Group.

scale of a few milliseconds. In contrast, this time scale was quite different from that of typical pseudorotaxane association/dissociation processes. For analyzing the dynamic process of molecular shuttling, they took the case of amphoteric 12-aminododecanoic acid as a representative and divided four kinds of possible shuttling modes in Fig. 11(c), depending on the initial and terminal states. Among them, the two modes corresponding to the first two sketches represented the complete shuttling process, while the remaining two modes were the incomplete shuttle process. As the temperature went higher, the events of both incomplete and complete shuttling processes increased, but the proportion of the former decreased, indicating that the complete shuttling processes require more energy in the stochastic movements. Of course, what types of current states correspond to the association/dissociation processes still need further study.

Because of its fundamental importance in many branches of science, the hydrogen bond is a subject of intense contemporary research interest. However, hydrogen bond dynamics at the molecular level have scarcely been investigated. Zhou et al. constructed hydrogen bond-bridged SMJs (HBB-SMJs) by attaching a ureido pyrimidine-dione (UPy) monomer molecule to graphene electrodes and further dimerization, as shown in Fig. 11(d).⁵⁴ Since the UPy molecule is easy to dimerize in a weak polar solvent and dissociates in a polar solvent, alternating the exposure of the devices to diphenyl ether and water can lead to conductance switching effects in SMJs, which could also verify the successful fabrication of the devices. In order to analyze the kinetic mechanism of the system, temperature-dependent electronic measurements in 1,1,2,2tetrachloroethane (TeCA) and diphenyl ether solvents were carried out, respectively, and the I-t curves are shown in Fig. 11(e). The current statistics obtained in TeCA solution presented bistable states, and the lifetime of low- and high-conductance states and the corresponding rate constants were deduced by using the hidden Markov model. Both rate constants and the ratio of low- and high-conductance states increased progressively with the increasing temperature. When exposed to diphenyl ether, a multimodal

distribution (at least four obvious peaks) was observed, indicating different mechanisms of intermolecular interactions through hydrogen bonding in different solvents. As the temperature increased, the proportions of the four current distributions changed, and the corresponding rate constants increased progressively. The current signals, labeled States 1-4, were presented at four different time-scale magnifications [Fig. 11(f)]. States 1-3 could last for milliseconds, suggesting that the molecules formed some new substabilization structures while maintaining the quadruple hydrogen bond array. Combined with theoretical calculations, they believed that States 1-3 were derived from intermolecular proton transfer among the terminal electronegative O/N atoms in quadruple hydrogen bonds and the lactam-lactim tautomerism. The difference in proton distribution between the two binding monomers by intermolecular proton transfer, and the change in conjugation degree caused by tautomerism, altered the charge transport properties of the molecular junction, thereby affecting the electrical conductivity. Through systematic theoretical studies for possible configurations by either an intermolecular proton transfer reaction or tautomerism, they proposed that there may exist 5 low-lying energy structures, corresponding to 3 conductance states. Moreover, the reaction barriers for intermolecular proton transfer and lactam-lactim tautomerism were ~0.35 eV and ~0.67 eV, respectively, and both of these transformations could be achieved at room temperature. The oxygen atoms of diphenyl ether formed hydrogen bonds with the hydroxyl groups of the lactimide to stabilize the configuration, while TeCA did not. Therefore, it was unlikely to carry out the enol-type configuration transformation, so only two conductance states could be observed. In addition, the local electric field could also be regarded as an external stimulus, such as the thermal stimulus, which may realize the alternation of five structures. This work proves the unique advantages of single-molecule electrical detection in the investigation of hydrogen bond dynamics and the unlimited potential of obtaining intrinsic information that is not available in traditional ensemble experiments.

Single-molecule detection provides real-time feedback on the state of single molecules, providing information beyond thermodynamic/dynamic complexity, and has unique advantages in studying the mechanism of chemical reactions. For example, Gu et al. carried out a typical, acid-catalyzed S_N1 reaction at the singlemolecule level by real-time monitoring SMJs with a 9-phenyl-9fluorenol center [Fig. 12(a)].⁵⁵ The I-t trajectories of the devices, measured in the mixed solution of acetic acid (HAc) and trifluoroacetic acid (TFA), presented two distinguishing current fluctuations that did not occur in the air. Theoretical calculations showed that the carbocation form corresponded to a higher conductance state at a low bias voltage for its sp^2 hybridization, which facilitated the valence electrons to be more conjugated and decreased the energy gap between the frontier molecular orbitals (FMOs). In addition, the conductance of the carbocation form varied along with the ratio of TFA, owing to the difference in the dielectric constant of TFA and HAc. Another possibility was that different solutions might affect the lifetime of carbocation. To analyze the thermodynamic and kinetic processes, current signals in *I*-*t* curves [Fig. 12(b)] were idealized into a two-level interconversion by using a QuB software, and they derived the lifetimes (τ_{high}/τ_{low}) of the acetate and carbocation forms from the probability distributions of the dwell times $(T_{\text{low}}/T_{\text{high}})$ of each conductance state. Subsequently, the rate



FIG. 12. (a) Schematic of a GMG-SMJ that shows the formation dynamics of a 9-phenyl-9-fluorenyl cation in an S_N1 reaction. (b) *I-t* curves (black dots) of the device in the solution of HAc-TFA (25%/75%, vol/vol). The red line shows the idealized two-level interconversion by using a QuB software. (c) Representative *I-t* trajectories of the competitive reaction mentioned above. (d) Schematic representation of competitive reactions of carbocation with Ac⁻ and Br⁻. Reprinted with permission from Gu *et al.*, Nano Lett. **18**, 4156 (2018). Copyright 2018 American Chemical Society.

constants, equilibrium constants, corresponding activation energies, etc. could be extracted. For further investigation on the competitive reactions between different nucleophiles, they introduced another nucleophile, cetyltrimethylammonium bromide, to an HAc/TFA solution (25%/75%, vol/vol) and observed a third state with medium conductance occurring in the *I*-*t* trajectory [Fig. 12(c)], which corresponded to the newly formed bromide [Fig. 12(d)]. More importantly, the carbocation form was an inevitable intermediate in the transition between the bromide and acetate forms, which confirmed the classical S_N1 mechanism.

Next, they turned their attention to nucleophilic addition reactions at the single-molecule level.⁵⁶ Using the previous device manufacturing method, they constructed the single-molecule devices with 9-fluorenone as the functional center [Fig. 13(a)]. After adding NH2OH into mixed ethanol (EtOH)/H2O solution to react with 9-fluorenone, they observed distinct binary conductance states [Fig. 13(b)]. In order to figure out the reaction events associated with the two conductance states, they performed computational studies on reaction energy in the reaction process [Fig. 13(c)] and obtained the time scale of mutual transformation between the two adjacent states. Only the reversible reaction between the reactant state (RS) and the intermediate state (IS) happened at a time scale of a few microseconds, which was consistent with the dwell-time of the observed high- and low-conductance states. The calculated transmission spectra showed that the *p*-FMOs of the RS were closer to the graphene Fermi level than those of the IS, facilitating a better conductance. Hence, high- and low-conductance states originated from the RS and IS, respectively. The solvent-dependent experiments showed that the proportion of the low-conductance state, representing the reaction intermediate, gradually increased with the



FIG. 13. (a) Schematic of a GMG-SMJ that highlights a reversible nucleophilic addition reaction of hydroxylamine to a carbonyl group. (b) *I*–*t* curves (black) of GMG-SMJs immersed in the reactive solution (60% water in EtOH) at 298 K. The red line shows the idealized two-level interconversion by using a QuB software. (c) Reaction mechanism and energy profile of 9-fluorenone reacting with NH₂OH. (d) Lifetime changes of the low (black) and the high (red) states with different proportions of water. Reprinted with permission from Guan *et al.* Sci. Adv. **4**, eaar2177 (2018). Copyright 2018 AAAS.

increase in the water content, that is, the increase in solvent polarity. The extracted lifetime of the low-conductance state (τ_{low}) prolonged obviously with the increased proportion of water, while τ_{high} shortened [Fig. 13(d)]. It indicated that the increasing polarity was conducive to stabilizing the reaction intermediate. These results consistently proved that polar solutions could stabilize the intermediate and keep a stable configuration for a relatively prolonged period. The above results fully prove the reliability and accuracy of the GMG-SMJs for revealing elementary mechanisms of general chemical reactions.

VI. CONCLUSIONS AND PERSPECTIVE

As discussed above, scientists integrate rationally designed molecules into graphene nanogapped electrodes to construct stable graphene molecular junctions, giving a reliable logic circuit function and witnessing its ability of single-molecule detection. Nevertheless, molecular electronics still faces many challenges, in the field of both basic scientific research and industrial manufacturing.

One of the most critical challenges is the uneven quality of different devices. When the device reaches the level of single-atom or single-molecule size, even the slightest difference can affect its performance. For metal electrodes, it is difficult to reach the edges of the atomic level, and the uncertainty of the bonding positions of the anchor groups and the adsorption of many molecules at the interface will affect the charge transport property of the whole molecular bridge. However, although the edge of the electrodes at the atomic level can be obtained by using the carbon electrode, the accurate control and efficient preparation of the nanometer gaps between the electrodes cannot be guaranteed, and the configuration of the connected molecules is also unclear.

Another key issue is the device stability. Metal electrodes generally have high atomic mobility and strong interfacial coupling, which are liable to induce the oxidation or electromigration of the molecular junction and other destructive behaviors. Moreover, the thermal effects accumulated by the molecular junction at a high bias voltage are likely to result in the fracture of the molecular junction. One possible method is to construct single-molecule junctions with the good stability between graphene electrodes with the amide bond in one end and π - π stacking interaction in the other end, which requires molecules that have special structures. The possibility of successful connection may be higher than that of devices connected by covalent bonds at both ends.

In addition, appropriate theoretical calculation models should be established and developed. On the one hand, theoretical calculation can facilitate us to explain experimental phenomena and reveal the internal mechanism. On the other hand, it can instruct experimental design, including the design of molecular materials and device structure, realizing new functions of devices. It can be predicted that, under the relatively reasonable theoretical premise, the designed molecular devices will greatly improve the chances of achieving the desired function while avoiding the meandering exploration and unnecessary costs. Another point that cannot be ignored is that the data volume of the single-molecule measurements is huge, so the data collection and analysis should be impartial and systematic data processing models are worth further exploration.

In the future, in view of practical applications, microelectronic devices will definitely develop toward the direction of the atomic size, so as to accomplish more functions and faster processing capacity. Single-molecule electronics might be the useful choice for moving beyond Si-based microelectronics. From the perspective of basic research, single-molecule level detection can be realized through the platform of single-molecule devices to achieve the ultimate goal in the field of analytical chemistry. When the optical signal is combined with the electrical measurements, not only the synchronous detection of the molecular structure and conformation changes with high temporal resolution can be realized, for studying chemical reaction timing sequence, intermediates, etc., but also the types of photoelectric devices can be enriched. Another area is the research on the structural changes and potential charge transfer mechanisms of individual biomolecules, such as amino acids, peptides, and proteins, in living organisms, where the complexity of biomolecules provides new opportunities. It is foreseeable that this interdisciplinary field will play an active role in the research of physical phenomena, chemical reactions, and biological processes and finally develop practical applications for the benefit of the human society under the cooperation of materials scientists, physicists, chemists, biologists, and engineers.

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