

## CATALYSIS

# Catalyst: The Renaissance of Molecular Electronics

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Prof. Xuefeng Guo received his PhD from the Chinese Academy of Sciences and then was a postdoctoral scientist at the Columbia University Nanocenter until 2007. He joined Peking University as a professor under the “Peking 100-Talent” Program in 2008. In 2012, he received support from the National Science Fund for Distinguished Young Scholars of China. His current research is focused on functional nanometer and molecular devices.

At the beginning of 2016, a paper published in *Nature* acknowledged that the worldwide semiconductor industry would abandon its pursuit of Moore's law.<sup>1</sup> Moore's law states that the number of transistors in a dense integrated circuit doubles approximately every 2 years—which has generally meant that the chip's performance will too. This has promoted the rapid development of microelectronics, thus leading the world into the information era. However, the doubling trend has already begun to falter as a result of the heat that is inevitably produced when more and more silicon circuitry is jammed into the same small area. Rather than focusing on Moore's law, the semiconductor industry has agreed to let the performance of chips and the applications follow. Then, what's the ultimate limit in the miniaturization of electronics? Molecular electronics

again came into the view of scientists to provide an alternative direction for this tremendous challenge.

## History and Progress

Utilizing one or a few molecules as an electronic component, though logically understandable at present, was revolutionary when Aviram and Ratner first put forward this thought in 1974.<sup>2</sup> With theoretical calculations, they designed an organic molecule with the structure of D- $\sigma$ -A, which could function as a rectifier. At that time, this proposal was something between science fiction and the state of the art, but it aroused great interest among scientists from different backgrounds. The use of organic molecules as the functional center has several advantages, such as low cost and smaller size. In addition to these, the most exclusive advantage is the endless possibility of structures and functionalities offered by chemical synthesis.

However, the question of how to anchor a single molecule or a few molecules to two electrodes had confused experimental researchers for many years. Obviously, the popular top-down method, though mature in the fabrication of complementary metal-oxide semiconductors (CMOSs), cannot meet the fabrication of molecular junctions. Thanks to the development of scanning tunneling microscopy (STM) and later atomic force microscopy in the 1980s, researchers began to realize that these could be useful tools for investigating the conductance of single molecules. The first significant work occurred in the late 1990s, when Reed, Tour, and colleagues developed a mechanical controller to fracture a notched gold wire into a nanogap, thus realizing a real single-molecule device.<sup>3</sup> Since then, different approaches to fabricating single-molecule devices have sprung up, making it more accessible to probe the conductance characteristics of individual molecules.

Charge transport through molecular junctions is quantum mechanical in nature, thus enabling scientists to reveal and understand the function of materials at both the atomic and molecular levels. In addition to realizing various functionalities, molecular electronics could lead to the direct observation of novel effects or the fundamental discovery of physical phenomena that cannot be accessible in bulky materials. Up until now, many experiments have been carried out to explore charge-transport mechanisms through molecular junctions, resulting in considerable research advances in both functionalities and quantum phenomena.

In the past decade, groundbreaking research in building specific functionalities of molecular devices has emerged. Rectification, thermoelectricity, switching, negative differential conductance, spintronics, and the gating effect have all been realized in molecular junctions. However, in these previous reports, few molecular electronic devices can rival silicon-based electronics in performance—there are indeed some big steps. In 2014, Schull's group at the University of Strasbourg in France made the first single-molecule light-emitting diode, which has the same electroluminescent mechanism as that in conventional organic light-emitting diodes, by using a conducting polymer polythiophene spanning between two metallic electrodes.<sup>4</sup> In 2015, Venkataraman's group at Columbia University realized single-molecule diodes with a rectification ratio of more than 200—an important step for maintaining a high signal gain as the devices shrink (see review by Xiang et al.<sup>5</sup>). In 2016, our group demonstrated a fully reversible two-mode, single-molecule electrical switch consisting of a single diarylethene molecule sandwiched between nanogapped graphene electrodes; this switch showed unprecedented levels of accuracy, stability, and reproducibility.<sup>6</sup> In addition to these,

some breakthroughs in spin control at the atomic and molecular levels have been reported. In 2014, Wernsdorfer's group at the Centre National de la Recherche Scientifique in France realized coherent manipulation of single nuclear spin by using only an electric field because of the hyperfine Stark effect.<sup>7</sup> Earlier that year, IBM Research–Almaden produced the world's smallest magnet and demonstrated that it is possible to use that magnet—an individual holmium atom—to store a single bit of data.<sup>8</sup> In addition to utilizing organic molecules, Xu's group at the University of Georgia constructed a molecular rectifier by using designed DNA strands.<sup>9</sup>

Several quantum phenomena—such as Coulomb blockade, the Kondo effect, quantum interference, and image-charge effect—have been observed in molecular junctions as well as in semiconductors. Importantly, these fundamental research efforts provide inspiration for the study of intrinsic and novel mechanisms that are unavailable in traditional ensemble methods. For example, the groups of Hou and Dong at the University of Science and Technology of China have done a series of excellent work in studying the optical process and photochemistry of a single molecule by the subtly controlled local nanocavity plasmons.<sup>10</sup> They found that the “forbidden light” from porphyrin molecules, which obeys Kasha's rule, provided new insight into the basic understanding of the emitting mechanism in molecules. Nuckolls's group at Columbia University observed two different conductance states in oligosilane molecular junctions, which they attributed to the stereoelectronic effect of the sulfur-methylene  $\sigma$  bond (see review by Xiang et al.<sup>5</sup>). In addition, Coote's group at Australian National University demonstrated the first experimental evidence of a nonredox, bond-forming process in Diels-Alder reactions accelerated by an oriented external electric field within STM-based molecular junctions.<sup>11</sup> Our group first

demonstrated the capability of molecular electronic devices in carrying out direct, real-time single-molecule detection in solution containing the certain substance and revealed the detailed dynamic information in host-guest interactions at the single-molecule level.<sup>12</sup> Tao's group at Arizona State University investigated different sequence-dependent charge-transport mechanisms existing in a DNA helix (see review by Xiang et al.<sup>5</sup>).

Correspondingly, theories explaining current-voltage characteristics in molecular junctions have been recently developed. Though many concepts were at first borrowed from semiconductor electronics, qualitative descriptions of electron transport through a single molecule have been established by the adaptation of non-equilibrium Green function techniques and are consistent with experimental data.

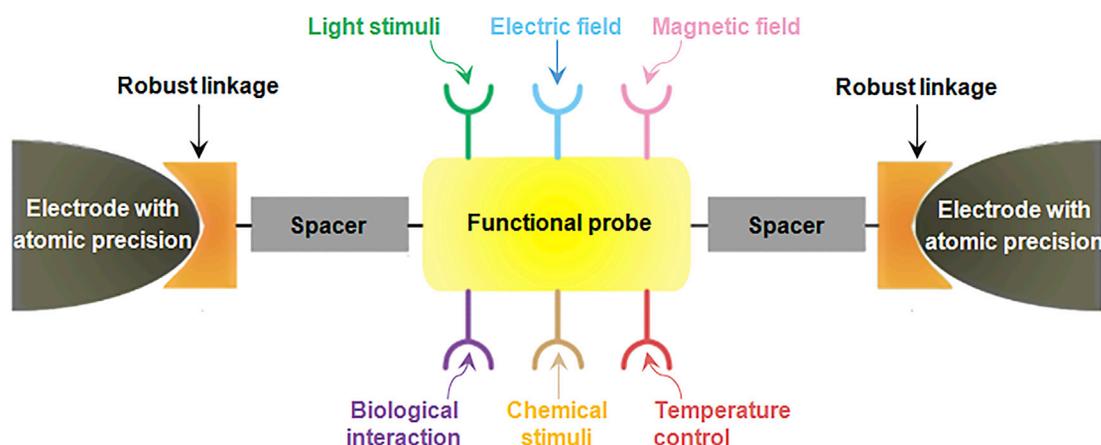
### Challenges

In spite of these exciting advances, we have to admit that some tremendous challenges still need to be overcome for the vision of practical molecular electronic devices. The most critical challenge in the field of single-molecule electronics is the variability among devices featuring the same structure of single molecules. When the device size decreases to the atomic and molecular levels, every atomic detail is able to affect device performance. At present, neither metal electrodes nor carbon-based point contacts can realize the control with atomic precision at the edges of the electrodes, thus leading to variable contact configurations at the molecule-electrode interface. For metal electrodes, because of the mobile metal atom, the bonding sites for the anchoring group in the molecule are different from device to device. What's more, the sizes of the molecule and metal electrodes are not compatible, leading to a situation in which one molecule bridges two electrodes and many other molecules are absorbed into the surface of metal electrodes.

This complexation significantly interferes with the conductance behavior of the bridging molecule. Accordingly, statistical conductance data obtained from STM-based junctions and mechanically controlled break junctions have revealed the fluctuations to some extent. This might be fatal, especially to the functionalization of single-molecule devices. For carbon-based electrodes, although the edge of a single-walled carbon nanotube (SWNT) or graphene nanogap is atomic and fixed, both different configurations at the edges and inhomogeneous electronic properties of SWNTs can lead to different molecular behaviors.

Stability is the basic requirement of the devices for real-life applications. In molecular electronic devices, we cannot ignore the fact that metal-electrode-based molecular junctions have poor stability. To realize resonant transport, it is usually necessary to apply several volts to only a few nanometer-length junctions to lead to non-equilibrium dynamics and strong interactions between molecular orbitals and the electric field gradient across the junction. Gold (Au), the popular material used for electrodes in molecular junctions, is highly mobile, and as a result, atoms at the Au electrode surface tend to diffuse because of the heating effect resulting from the electric field or elevated temperatures. In addition, lone-pair species (Au-S bonds) are typically used to bridge the molecule and the metal electrode. As well known in chemistry, these coordination bonds are easily ruptured or oxidized.

Another fundamental challenge of molecular devices is the integration capability, which is critically important for realizing a computing system. Up until now, almost reported measurements were carried out in ideal media at the laboratory level. However, the actual devices are far more complex and definitely introduce a range of interfering and running effects. For an efficient



**Figure 1. Schematic of Building Stable, Functional Single-Molecule Devices with Precise Control**

integration, two main critical factors should be taken into consideration. (1) Although the core part of molecular devices is intrinsically tiny, there are always long leads and large pads for outer connections, which prevent a full exploitation of its potential. (2) Instead of replacing the present CMOS technology, molecular devices could serve as complement parts in CMOS circuits in the near future. Therefore, molecular devices need to be CMOS compatible. In this aspect, carbon-based molecular junctions have the advantage and might be a good candidate for integration.

### Outlook

Still motivated by technological goals, molecular electronics continues to focus on the construction, characterization, understanding, and functionalization of molecular electronic devices. To this end, gate control of the conductance behaviors in molecular devices deserves hard work, and the inspiration of organic spintronics opens another window for the development of a new, less power-consuming field of molecular spintronics. This needs effective collaboration of researchers from interdisciplinary backgrounds: materials chemists, experimental physicists, computational theorists, and engineers.

Installing functionalities in molecular junctions mainly depends on molecular engineering.<sup>5</sup> Two main factors should

be taken into consideration. One is the intrinsic function of the molecular material itself. The other is the molecule-electrode interfacial coupling, which is related to the spectral density between the functional center of the molecule and the electrode. Within strong coupling, the molecular conductance is the best, but some functionalities could be quenched or screened by the electrodes.<sup>13</sup> The control of the molecule-electrode interfacial coupling is still one of the most challenging issues in molecular electronics. This can be realized via the design of different anchoring groups and/or incorporation of suitable spacers (usually methylene groups) between the functional center and the anchoring group in the molecular structure (Figure 1). Therefore, achieving the intrinsic properties of single molecules requires a compromise between the conductance and the functionality.

If molecular electronics are to move from the laboratory level toward real applications, it is critical to consider candidate materials for electrodes. Among different nanomaterials, carbon isotopes (such as SWNTs and graphene) seem more suitable as electrode materials for the construction of molecular devices.<sup>14</sup> This is because SWNTs and graphene are low-dimensional carbon nanomaterials entirely composed of immovable  $sp^2$ -hybridized carbon monolayers with rich car-

bon chemistry that allows the covalent formation of robust connections between molecules and electrodes. In addition, they have good size alignment and are naturally compatible with organic and biological molecules. However, none of the current techniques are able to create the nanoscale gap with atomic-level control. The precise formation of single-molecule electronics at the atomic level is key to promoting the rapid development of molecular devices toward practical applications (Figure 1).

Another unique feature of single-molecule devices is the fact that they contain only one or two molecules as conductive elements, thus distinguishing them as reliable platforms capable of translating the dynamic processes of either chemical reactions or biological functions into detectable electrical signals at the single-event level (Figure 1). This might open a mainstream approach to single-molecule electrical detection for the study of single-molecule and single-event dynamics in an interdisciplinary realm. In comparison with conventional optical techniques, this nanocircuit-based architecture is complementary but obviously has advantages, such as avoiding problems with bleaching and fluorescent labeling. These advantages offer endless opportunities for scientists to elucidate the fundamental mechanisms

underlying reactions and uncover important details of the most basic processes of life, which will immediately invite intense research activities.

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## CATALYSIS

# Reaction: Technological Aspects of Molecular Electronics

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Dr. Emanuel Lörtscher received his PhD with distinction (*summa cum laude*) in 2006 from the University of Basel in Switzerland and a master in physics in 2003 from the Swiss Federal Institute of Technology. He has been a research staff member at IBM Research since 2008. He has received various prizes, including the Swiss Physical Society Award for Applied Physics in 2007 and the Faculty Prize of the University of Basel in the same year. His current research focuses on fabrication, electronics, optics, and chemistry at the nanoscale for applications in novel computing applications, biology, medicine, and the Internet of Things.

Moore's Law—or the miniaturization of the complementary metal-oxide semiconductor (CMOS)—is about to end because performance no longer benefits from downsizing. Consequently, semiconductor research now focuses on employing novel materials and architectures to fulfill specifications requested by applications. This situation provides opportunities for fundamentally different electronic components, among which molecular electronics (ME) is considered again.<sup>1</sup>

## Challenges of CMOS Technology

Transistor scaling slows down because miniaturization has reached integration densities that cause unbearable thermal loads (averaged 200–300 W/cm<sup>2</sup>, locally >500 W/cm<sup>2</sup>), and future nodes are becoming unaffordable<sup>2</sup> in terms of fabrication investments. Hence, getting smaller is no longer the maxim.

Gate leakage, short-channel effects, and parasitics must be kept low so as not to consume energy when idle, for example. The semiconductor industry has faced similar issues during its life cycle—causing low yields, inhomogeneities in doping levels and driving voltages, reduced reliability, etc.—but it has always been able to overcome them, for example, by Si-on-insulator (SOI), strained Si, fin field-effect transistors (FinFETs), nanowires, high-k dielectrics, airgaps, 3D stacking, multicores, III/V integration, etc. Hence, CMOS will change, but it will remain the predominant technology for the coming years.

A successor must not only provide the same specs as International Technology Roadmap for Semiconductors (ITRS) and non-ITRS anticipated CMOS nodes but also outperform prevalent technology in at least one key aspect: power consumption, fabrication costs, and/or performance. The argumentation is therefore not solely technical but also economical to realign a multi-billion-USD industry. The successor can leverage CMOS platforms by being co-integrated wherever such novel components outmatch Si but only if they are process compatible. Top-down fabrication can be pushed to <5 nm where quantum effects and uncontrollable doping levels are detrimental for Si. At such dimensions, however, various bottom-up approaches might enter the game.

## State of the Art in ME

The promises of ME are intrinsic functionalities embodied in a molecular backbone, creating electrical responses, e.g., conductance, current rectification, resistance switching, etc. Such ultimately scaled building blocks can be synthesized identically with picometer control. Negative differential resistance, Coulomb and Kondo effects, quantum interference, and switching are only some of the interesting functionalities demonstrated.