Two-dimensional conjugated polymers synthesized via on-surface chemistry

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Two-dimensional materials (2DMs) are an important subject in material science that have many interesting physical properties and significant potential applications in various technological areas [1,2]. Since the successful exfoliation of monoatomic graphene by Novoselov *et al.* [3] in 2004, a series of inorganic 2DMs, including transition-metal dichalcogenides (TMDs) [4], hexagonal boron nitride (h-BN) [5], metal nanomaterials [6], black phosphorus (BP) [7], and graphdiyne [8], have been obtained and investigated by fundamental studies in the fields of optoelectronics, catalysis, and energy storage [9–14]. Organic 2DMs, such as organic small molecules, polymers, and organic-inorganic hybrid materials, are emerging material systems currently attracting increasing attention owing to their unique advantages of a wide diversity of organic substrates, easily tunable properties/functionalities, and diversified syntheses at low cost and high efficiency [15–23]. Among the 2DMs, 2D conjugated polymers (2DCPs) with long-range periodic covalently bonded structures and fully-extended conjugations have received special attention from scientists working in different fields. The tunable bandgap and diversified topological structures by appropriate molecular design [24–28] endow 2DCPs, as a type of promising graphene analogue, with unique/tunable optoelectronic and spintronic properties, as well as promising applications in plastic optoelectronics and related functional devices/circuits [29–35].

For the above mentioned fundamental studies and device applications, the most crucial issue of 2DCPs is their quality, which includes molecular orders, 2D-conjugated structures that determine the energy bandgaps/alignments and functionality of materials, and material sizes.

Thus far, the preparation of 2DCPs with the desired compositions, thicknesses, sizes, defects, crystal polymorphs, and surface properties is the core topic. Various synthetic processes based on both “top-down” and “bottom-up” strategies have been developed [2,17]. On-surface chemistry synthesis, a very important “bottom-up” strategy, was developed to overcome the limitations of uncontrollable polymer thickness, low yield, and low structural integrity [17,36,37]. On-surface chemistry, sometimes referred to as 2D chemistry, is the coupling of active molecules on a flat interface to directly provide ordered and expanded nanostructures to polymers (Fig. 1a). The interface provides a restricted system for the growth of precursors, which are capable of forming planar structures that cannot be accessed in a 3D reaction environment. Compared with classical solution-phase processes, another advantage of the surface method is the contribution of the related reaction conditions and potential surface interactions to the stabilization of highly active substances and intermediates. Moreover, on-surface chemistry synthesis is advantageous for directing the orientations of molecules to form ordered structures, and hence, it has been explored for the possibility of effectively controlling the morphologies and structures of 2DCPs. Therefore, an interfacial reaction has great potential in synthesizing substances that cannot be prepared by the traditional chemical method. At present, on-surface chemistry methods based on Ullmann coupling, Schiff-base condensation, Suzuki coupling, etc., to synthesize 2DCPs have been explored. For the preparation of 2DCPs, there are currently three kinds of interfaces: gas–solid (mostly metal solid substrates with regular lattice structures), gas–liquid and liquid–liquid (Fig. 1b–d).

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Figure 1 (a) Schematic illustrations of on-surface chemistry for synthesizing 2DCPs under conditions of (b) gas–solid, (c) gas–liquid, and (d) liquid–liquid interface reactions.

The gas–solid interface without a solvent is the best means of studying the reaction process and creating more ordered structures. To analyze products directly at the molecular level, reactions are usually conducted directly in an ultra-high vacuum within the cavity of a scanning tunneling microscope (STM). Inspired by the pioneering investigations of the Ullmann coupling reaction *via* an on-surface chemistry setup by Hla *et al.* [38] in 2000, Grill *et al.* [39] formulated a strategy for the synthesis of covalently bound molecular nanostructures on a gold surface by the thermal annealing of active porphyrin molecules. This work paves the way for “bottom-up” synthetic stable 2D nano-architectures with possible future applications in molecular electronics. They also developed a sequential growth strategy to improve the quality of 2DCPs and made the construction of heterogeneous architecture highly selective (Fig. 2a) [40] by equipping a porphyrin building block with bromine and iodine side groups at orthogonal positions. Because of the different reactivities, the initial thermal activation of the iodine positions at low temperature resulted in a linear chain of porphyrin molecules and produced 2DCPs by the activation of the bromine positions through further heating. This strategy was able to maximize each molecule’s adaptation to the optimal structure and avoidance of defect formations. Many other reactions have also been reported on gas–solid interfaces [41]. Although the metal interface synthesis strategy has made considerable progress, the fabrication of wafer-scale 2DCPs is still challenging, which is essential for basic research and device

applications. The currently impressive and encouraging progress in the preparation of large-scale graphene, graphdiyne, and other 2D organic materials [42,43] should stimulate research into large-area 2DCPs *via* appropriate experiment designs aiming at achieving high quality and efficient output at low cost.

In comparison with the gas–solid strategy, gas–liquid and liquid–liquid strategies are more robust because they do not require high-quality metal substrates with regular lattice structures, expensive equipment, or rigorous reaction conditions. Moreover, because of the fluidity of liquids, these strategies provide a flat and dynamic reaction environment favorable to efficient reactions and the preparation of large-scale 2D materials *via* facile modulation experimental conditions [44,45]. In 2016, Dai *et al.* [46] synthesized 2D covalent organic monolayers by the dynamic imine chemical method at the gas–liquid interface (Langmuir–Blodgett method) (Fig. 2b). Opening up new possibilities for the synthesis and structure–property relationships of 2DCPs, this attempt was the first time that the use of this interface obtained a monolayer sheet (0.7 nm thickness) with lateral dimensions of tens of micrometers. Recently, Liu *et al.* [47] successfully synthesized a wafer-scale ultrathin 2D imine polymer film with controllable thickness from a simple benzene-1,3,5-tricarbaldehyde (BTA) and *p*-phenylenediamine (PDA) building block by using a Schiff-base polycondensation reaction at the air–water interface. Creating the potential for new applications, such 2D polymer films exhibited excellent switching performance

Figure 2 (a) Hierarchical growth following sequential thermal activation of 5,15-bis(4'-bromophenyl)-10,20-bis(4'-iodophenyl) porphyrin (*trans*-Br₂I₂TPP) building blocks on Au(111) substrate. Molecular structure of *trans*-Br₂I₂TPP (left), STM image of linear chains of porphyrin molecules after heating to 120°C with iodine dissociation. STM image of 2D polymer networks after heating the same sample to 250°C following bromine dissociation. Reproduced from Ref. [40]. Copyright 2012, Nature Publishing Group. (b) Synthesis of 2D polyimine network from triamine and dialdehyde building blocks *via* LB method. Reproduced from Ref. [46]. Copyright 2016, John Wiley & Sons, Inc. (c) Synthesis of wafer-sized multilayer of 2D polymer at water-chloroform interface. Reproduced from Ref. [50]. Copyright 2016, Nature Publishing Group.

with high reliability and reproducibility in memory devices because their intrinsically porous structures were conducive to the formation of conductive filaments during device operation. However, they have no proven crystallinity or highly ordered structures, which are crucial to the formation of efficient π -conjugation and high charge carrier transport in conjugated polymers [19,48,49]. In 2016, Sahabudeen *et al.* [50] disclosed the synthesis of crystalline 2DCPs based on porphyrin building blocks *via* Schiff-base condensation reactions at gas-liquid/liquid-liquid interfaces by reversible polycondensation (Fig. 2c). Under optimized experimental conditions, the sizes of the obtained polymers could be scaled up to the wafer scale. Moreover, semiconducting property was confirmed for the monolayer 2D polymer, which had a charge carrier mobility of $1.3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in thin-film transistors without doping. More recently, Zhou *et al.* [51] further developed another simple and mild strategy to synthesize 2DCPs *via* Suzuki polymerization on a liquid-liquid interface. The products of the obtained porous graphene and porphyrin-containing polymers had large areas and were visible to the naked eye. For the porous graphene films, a carrier

mobility of $3.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was examined and the catalytic activity of the hydrogen evolution reaction was detected.

The aforementioned examples are pioneering studies in this emerging field of on-surface chemistry. Although the syntheses of some multilayer 2DCPs with controllable sizes and thicknesses at the atomic or molecular level have been realized by the interface synthesis strategy, many problems remain to be solved. The first problem is controlling the growth of 2DCPs to obtain high-quality products with definite crystalline phases, grain sizes, and grain boundaries. Also, the design of more convenient transfer methods is required because of the relatively low mechanical stability of 2DCPs. Finally, the applications of 2DCPs in optoelectronic devices are rare, while the resulting performances, such as charge and exciton transport, are still very low [29,30,50–52], and, in fact, are far from the expected values, which are highly dependent on controlling the structures of the 2DCPs at the atomic and molecular levels. Thus, increased efforts and the search for efficient reactions occurring at the surface for highly ordered structures at molecular level and desired energy band structure by molecular design are required in this

field. It is believed that more amazing results will be achieved in the future under the joint efforts of scientists from the fields of chemical sciences, material sciences, and device physics.

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Author contributions Dong H and Hu W designed the project. Li C and Dong H co-wrote the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

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界面合成二维共轭聚合物

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摘要 二维共轭聚合物具有平面共轭结构和分子中离域的 π 电子体系, 因而具有很强的平面内电荷传输能力, 表现出独特的物理和化学性质, 在光学、电学、传感等领域具有广阔的应用前景。但如何获得分子结构及形貌符合二维特征、且尺寸满足制作电子器件需求的分子非常困难, 是广大科研人员急需解决的问题。本文总结了界面合成二维共轭聚合物的方法, 讨论了这个领域目前面临的问题和挑战, 并指出了未来的研究方向。