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PERSPECTIVE

On-Surface Synthesis and Molecular Engineering of Carbon-Based Nanoarchitectures

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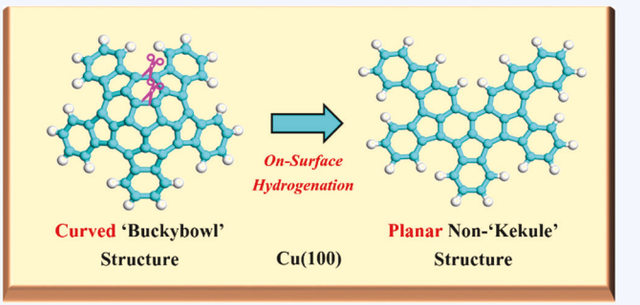
ABSTRACT: **On-surface synthesis *via* covalent coupling of adsorbed precursor molecules on metal surfaces has emerged as a promising strategy for the design and fabrication of novel organic nanoarchitectures with unique properties and potential applications in nanoelectronics, optoelectronics, spintronics, catalysis, *etc*. Surface-chemistry-driven molecular engineering (*i.e.*, bond cleavage, linkage, and rearrangement) by means of thermal activation, light irradiation, and tip manipulation plays critical roles in various on-surface synthetic processes, as exemplified by the work from the Ernst group in a prior issue of *ACS Nano*. In this Perspective, we highlight recent advances in and discuss the outlook for on-surface syntheses and molecular engineering of carbon-based nanoarchitectures.**



Carbon-based nanoarchitectures have attracted tremendous attention due to their rich chemical versatility (including the ability to form linear, sp; planar, sp^2; and tetragonal, sp^3, linkages), lightness, low cost, and extraordinary electronic and optical properties.[1,2] Over the past 30 years, groundbreaking discoveries have led to the achievement of linear, planar, and closed nanostructured (cage-structure) carbon allotropes, including fullerene (C_{60}),[3] single- and multiwalled carbon nanotubes (CNTs),[4] graphene,[5] graphene nanoribbons (GNRs),[6] graphyne (GY),[7] graphidyne (GDY),[8] and bowl-shaped polynuclear aromatic hydrocarbons (PAHs).[9,10] The exceptional properties of carbon-based nanoarchitectures not only enable countless scientific and industrial applications but also provide opportunities for the discovery of new areas in nanoscience and nanotechnology.[11−13]

Conventionally, these carbon nanomaterial-based scaffolds are realized by means of classical solution-based chemistry or top-down methods. However, these approaches experience formidable challenges when well-controlled, even atomically precise arrangements and electrical contacts are needed to integrate nanoarchitectures into (opto-)electronic and spintronic devices. By contrast, on-surface synthesis (*via* chemical reactions on solid surfaces) of covalent nanostructures utilizing the "bottom-up" approach enjoys outstanding success due to several beneficial features. First, on-surface synthesis provides a feasible route to the construction of complex nanoarchitectures from simple precursor molecules, which might traditionally be considered unachievable through wet-chemical strategies. In addition, the electronic and optical properties can be tuned by rational choice and functionalization of the precursor molecules. Second, with on-surface synthesis, the reaction is conducted under ultrahigh-vacuum (UHV) conditions without any solvent assistance, greatly decreasing possible sources of contamination. Third, *in situ* atomically resolved imaging and analysis of the reactants, intermediates, and products are enabled based on scanning probe microscopy (SPM) techniques, including scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM) particularly with CO-terminated tips as well as spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy, and near-edge X-ray absorption fine structure.[14,15] Note, this Perspective is by no means an extensive review of the applications of on-surface synthesis; interested readers are referred to other dedicated

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reviews that have more strategic and applications-oriented focuses.[13,16−22] In this Perspective, we highlight recent work as examples of the fabrication of surface-assisted carbon-based nanoframeworks and describe future opportunities and challenges in this field.

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Of the many on-surface "bottom-up" synthetic approaches for carbon-based nanostructures,[16] Ullmann coupling (between aryl halides) is a versatile and frequently used reaction for the irreversible C−C coupling on metal surfaces (*e.g.*, Cu, Pd, Ni). Upon thermal treatment, $C(sp^2)$−X (X = Br, I) bonds dissociate and then proceed to homocoupled products *via* C−C linkages [$C(sp^2)$−$C(sp^2)$ coupling] either *via* organometallic intermediates or direct covalent interaction.[19,23−25] The free halogen atoms generated during the dissociation process usually remain on the surface and can affect the formation of the products.[26] Grill and co-workers employed this strategy to cleave the carbon−halogen (C−Br) bond by annealing and subsequently forming C−C covalent linkages.[27] Since then, this strategy has been the most commonly used method for surface-assisted reactions, leading to the exploration of carbon nanoarchitectures.[28−33] To date, graphene-based nanostructures such as nanoporous (atomically precise nanoscale pores) graphene[34,35] and varieties of pure and doped GNRs,[28,36−43] as well as complex structures beyond graphene, such as nanoribbons of nonalternant graphene allotropes including phagraphene and tetra-penta-hepta (TPH)-graphene[44] and polycyclic nanoarchitectures composed of multiple fused pentagon-heptagon pairs[45] have been constructed using on-surface dehalogenative/dehydrogenative homocoupling reactions from simple planar brominated precursors. Following a similar strategy, Di Giovannantonio *et al.* fabricated the conjugated ladder polymer oligo(indenoindene) with unique optical and electronic properties.[46]

To circumvent the adverse effects of the byproduct halogen atoms, researchers have preferred other C−C coupling reactions, such as Glaser coupling,[20] cyclo-dehydrogenation,[47−49] and dehydrogenative coupling reactions.[50−52] For instance, the fabrication of chemically sensitive GY/GDY-related nanoarchitectures [C(sp)−C(sp) coupling] highly depends on Glaser coupling (using terminal alkynes), in which the byproduct is excess hydrogen gas.[18] Moreover, following the work of Zhang *et al.*,[53] the construction of carbon-based covalent nanostructures using terminal alkynes has progressed,[54−57] and the incorporation of different functionalities[58] with terminal alkynes such as trimethylsylyl ($-C{\equiv}C-SiMe_3$)[59,60] provides further versatility in the GY/GDY nanostructure.[61] In addition, fullerene and triazafullerene molecules were directly generated by thermal annealing (*via* cyclo-dehydrogenation) from planar PAHs precursors ($C_{60}H_{30}$ and its analogue $C_{57}H_{33}N_3$) on the Pt(111) surface.[62] Following a similar approach, defect-free single-walled CNTs (with lengths up to a few hundred nanometers) were formed using the well-designed precursor $C_{96}H_{54}$.[63]

Surface-mediated dehalogenation, dehydrogenation, and cyclodehydrogenation have been the most popular and important processes to realize C−C covalent linkages for novel organic nanostructures. Notably, rich on-surface chemistry has been developed in the past few years for curved buckminsterfullerene (C_{60})-fragment PAHs (so-called "buckybowls"),[9] which enables a transformation *via* cyclodehydrogenation and dehydrogenation from bowl-like structures to capped CNTs with varying degrees of excellent optoelectronic properties.[64] In particular, the smallest bowl-shaped fullerene fragment (*i.e.*, corannulene, $C_{20}H_{10}$) and its functionalized "buckybowl" building blocks (corannulene derivatives) have attracted tremendous attention.[65,66] These structures show interesting two-dimensional adsorption behaviors on metal surfaces,[67−69] such as diverse configurations (*e.g.*, "bowl-up" and "bowl-down"), tilted geometry, symmetry mismatch, and phase transitions, making them attractive precursors in the fabrication of well-designed PAHs.

In contrast to the planarization of buckybowls by thermally induced dehydrogenation, in a prior issue of *ACS Nano*, the Ernst group reported a distinctive approach to planarize a buckybowl molecule, pentaindenocorannulene (PIC), *via* hydrogenation and C−C bond cleavage (Figure 1).[70] Specifically, the temperature-induced C−C bond cleavage

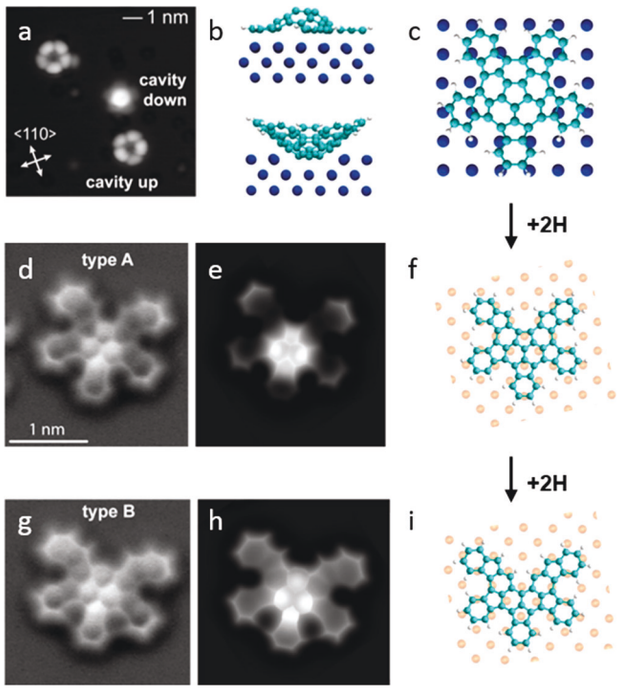

Figure 1. On-surface hydrogenation and resulting planarization of buckybowl pentaindenocorannulene (PIC) molecules. (a) Scanning tunneling microscopy topography (5 mV, 3 pA; CO-modified tip) of adsorbed PIC molecules on Cu(100). (b) Molecular models (side view) of PIC on Cu(100) in the cavity-down (top) and cavity-up (down) adsorption configuration. (c) Top view of cavity-up PIC model. (d−f) CO noncontact atomic force microscopy (nc-AFM) image (d), simulated atomic force microscopy (AFM) image (e), and density functional theory (DFT) model (f) of hydrogenated PIC (type A) after annealing to 490 K. (g−i) CO nc-AFM image (g), simulated AFM image (h), and DFT model (i) of further hydrogenated PIC (type B) from the type A structure. Adapted from ref 70. Copyright 2020 American Chemical Society.

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took place for the "bowl-cavity-up" PIC molecules in the specific sites (*i.e.*, in a hexagonal and, subsequently, a pentagonal carbon ring in the corannulene core), followed in each step by hydrogenating the respective C atoms in the otherwise C−C bonds. The latter was achieved *via* hydrogen transfer from the "bowl-cavity-down" PIC molecules due to surface-mediated dehydrogenation.

In a prior issue of *ACS Nano,* the Ernst group reported a distinctive approach to planarize a buckybowl molecule, pentaindenocorannulene, *via* hydrogenation and C−C bond cleavage.

The work by Ernst and co-workers highlights the variety and complexity of the chemistry of on-surface molecular engineering, which can be exploited to modify molecular configurations atomically and to tune their functionalities.[70] The complexity of this system results from the two molecular adsorption phases and the respective distinct roles in the reaction. Therein, the authors employed time-of-flight secondary ion mass spectrometry, which provided full elemental and molecular analysis with excellent detection limits. Furthermore, STM and nc-AFM with CO-functionalized tips revealed the molecular conformation and adsorption geometry, topographically identifying the individual precursor, intermediate, and product molecules. These results showed excellent agreement with density functional theory (DFT) simulations. This work enables the relationship between large polyatomic molecular adsorbates and metal surfaces to be examined quantitatively and unambiguously *via* submolecular resolution topography measurements.[70]

OUTLOOK AND FUTURE CHALLENGES

To date, the vast majority of on-surface syntheses have been based on thermally induced chemical transformations, as reaction temperature is the most readily controlled parameter in UHV among a variety of factors that determine reaction pathways and rates. To enable greater versatility of on-surface synthesis, additional stimuli should be developed to trigger reactions, such as light illumination, electric field, and tunneling current provided by SPM tips.[71−81] These unconventional approaches offer additional opportunities to observe novel molecular structures and properties that are unattainable *via* solution-based chemistry. For instance, Schuler *et al.* performed STM voltage pulses consecutively to induce the dissociation of the two C−Br bonds of a dibromoantharacene (DBA) molecule, ultimately generating a diradical that can reversibly turn into a strained 10-membered ring diyne by Bergman cyclization with switchable single-molecule magnetic properties.[82] Other complicated reactions including polyynes formation[83] as well as challenging carbon-based nanostructures such as cyclo[18]carbon[84,85] (sp-hybridized carbon allotrope) and kekulene[86] were also realized *via* SPM tip-controlled atomic manipulations. Another advantage of these new stimuli over traditional thermal treatments is the possibility for *in situ* real-time monitoring of reaction processes using SPM and spectroscopic techniques, providing deeper mechanistic insights into fundamental and complex chemical reactions. For example, C−Br bond photodissociation on insulators was realized by ultraviolet irradiation, which was demonstrated *via in situ* monitoring by laser desorption ionization, mass spectrometry, and XPS.[87]

In order to identify reactants, intermediates, and products of on-surface synthesis with single-molecule chemical sensitivity, SPM derivative techniques, such as STM inelastic electron tunneling spectroscopy (IETS) and tip-enhanced Raman spectroscopy (TERS), have been developed, providing vibrational fingerprints of individual molecules. Inelastic electron tunneling spectroscopy was originated in 1966 to study vibrational spectra of adsorbed molecules on a metal−oxide−metal tunneling junction by measuring the energy change of tunneling electrons with applied voltage.[88] Ho and co-workers spectroscopically visualized the C−H stretch mode of an isolated acetylene molecule using STM-based IETS,[89] pioneering single-molecule chemistry and vibrational spectroscopy.[90] In addition, IETS has also been performed to identify and to monitor intermediates and products *in situ* in tunneling-electron-induced surface reactions.[79,91] In particular, Meyer, Rieder, and co-workers achieved all steps of an Ullmann coupling reaction by a variety of molecular manipulations combined with inelastic-tunneling-induced molecular association. Weiss *et al.* demonstrated the powerful ability of IETS to identify reactive intermediates from products in the Ullmann coupling reaction.[92] In addition, Weiss, Rust, and co-workers investigated the correlation between the vibrations of a benzene molecule and its adsorption properties on Ag(110) surface.[93,94] The development of STM-IETS has enabled on-surface chemical reactions to be initiated and monitored at the single-molecule level.[90,95]

Following the work of the Ernst group, curved architectures will likely be more involved in on-surface synthesis, in light of increasing interest in and demand for unique, complex architectures with desirable properties. Consequently, further investigations of three-dimensional molecular conformations on surfaces are needed. However, SPM techniques cannot effectively investigate nonplanar molecular systems.[96] In contrast, TERS, which couples the spatial resolution of SPM with the chemical specificity of Raman spectroscopy,[97−99] can characterize nonplanar molecular systems or tilted molecular configurations at the single-molecule level in virtue of its unique surface selection rules.[100−102] With improved environmental control, TERS performed under UHV enables access to intramolecular features with down to Ångström-scale resolution,[103−109] thereby enabling the elucidation of molecular site-resolved chemical properties, such as doping, strain, and types and strengths of chemical bonds. In addition, because the substrates play fundamental roles in determining the stability and reactivity of reactants and intermediates and, thus, the reaction selectivity and pathway, direct characterization of the interaction strength between molecules and the substrates is of critical importance. Using the TERS approach described above, this issue will be readily addressed through the observation and investigation of phonon shifts of adsorbed molecules.

Although TERS investigations of on-surface synthesis are still in their infancy, some protocols have been developed for catalytic studies. For example, in addition to the laser used for exciting Raman scattering, one more incident light can be introduced to induce and to control on-surface reactions *in situ*, which can be real-time detected *via* TERS by providing site-resolved chemical information about the on-surface species. This scenario made its debut in the photocatalytic reduction process on a self-assembled monolayer of *p*-

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nitrothiophenol molecules adsorbed on gold nanoplates.[110] Recently, the Zenobi group performed ambient TERS to study selective hydrogenation of chloronitrobenzenethiol to chloroaminobenzenethiol on a bimetallic interface and provided direct spectroscopic evidence of hydrogen spillover.[111] In addition to TERS, high-speed STM[112] and *in situ* environmental scanning electron microscopy[113] also enable real-time imaging of *in situ* epitaxial growth of graphene on metal surfaces. Researchers have used ultrafast techniques, such as terahertz STM,[114] to trace a molecular reaction process with femtosecond time resolution. These state-of-the-art approaches, however, have not been applied to on-surface synthesis for the investigation of reaction dynamics. The time scale for on-surface synthesis remains largely unexplored, indicating a promising research arena in this field.

As a newly emerging research field, on-surface synthesis holds promise for a variety of practical applications, such as molecular nanoelectronics, catalysis, plasmonics, and spintronic and quantum devices.[115] In this respect, one major challenge is the development of well-controlled synthetic strategies that enable mass production for device fabrication, such as chemical vapor deposition used for large-scale graphene growth, instead of the current research-oriented UHV synthesis. However, most on-surface syntheses studied to date were conducted on metal substrates, taking advantage of the inherent reactivity of the substrate. To realize their full potential in real-world applications, synthetic functional materials will need to be electronically decoupled from their metal supports, which can be achieved by *in situ* synthesis on or post-transfer to a nonmetallic substrate. Toward this end, Kittelmann *et al.* presented an on-surface reaction (deprotonation) on a bulk insulator substrate ($CaCO_3$).[116−118] They demonstrated that the reactivity and templating of insulating substrates can be activated by modifying the molecule−surface interaction *via* annealing. Following a report on aryl−aryl covalent coupling realized on metal oxide semiconductors,[119] Kolmer and colleagues sequentially synthesized atomically precise nanographene and GNRs on rutile TiO_2 surfaces by the rational design of precursor molecules with judiciously chosen linking groups, paving the way for nanoelectronic device applications.[120,121] In the initial transfer strategies, poly(methyl methacrylate) served as a soluble protective layer,[122] a fairly similar approach to that employed for graphene transfer. One alternative method of electronic decoupling is intercalation, which has been widely used for epitaxial graphene.[123,124] Similar protocols have been applied to metal-supported molecular networks *via* postsynthetic intercalation using nonmetallic atomic layers.[125,126]

> On-surface synthesis holds promise for a variety of practical applications, such as molecular nanoelectronics, catalysis, plasmonics, and spintronic and quantum devices.

On-surface synthesis is an interdisciplinary research field involving collaborations between surface science and organic chemistry (Figure 2). Molecular structural properties and reaction mechanisms revealed by SPM facilitate the rational design of unique precursors, which, in turn, enables surface science researchers to synthesize novel nanoarchitectures with tailored properties and functionalities. In addition, on-surface synthesis could shed light on some long-standing, classic chemical questions that cannot be resolved *via* traditional chemical techniques, facilitating the understanding and elucidation of fundamental scientific issues. The iterative feedback loop between organic design and surface synthesis is a promising way to expedite the discovery and exploitation of new nanostructures and materials with exceptional properties.

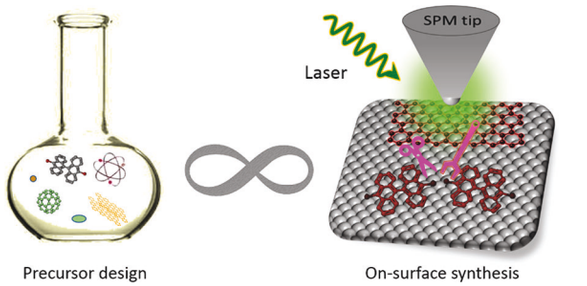

Figure 2. Feedback loop facilitates the mutual promotion between organic chemistry and on-surface synthesis.

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Notes

The authors declare no competing financial interest.

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