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Conjugated Carbon Monolayer Membranes: Methods for Synthesis and Integration

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Monolayer membranes of conjugated carbon represent a class of nanomaterial with demonstrated uses in various areas of electronics, ranging from transparent, flexible, and stretchable thin film conductors, to semiconducting materials in moderate and high-performance field-effect transistors. Although graphene represents the most prominent example, many other more structurally and chemically diverse systems are also of interest. This article provides a review of demonstrated synthetic and integration strategies, and speculates on future directions for the field.

1. Introduction

Assemblies of organic molecules in monolayer films are of longstanding interest due to their ability to control transport and release across interfaces, and to define surface chemistry, wetting behavior, as well as friction, lubrication, wear and other aspects of tribology. Such materials, often in the form of bilayers, are also critically important to the function and structure of nearly all biological systems. Historically, work on synthetic films has focused on chemically bound monolayers created by processes of self-assembly[1–3] and van der Waals collections of molecules in films formed with Langmuir-Blodgett techniques.[4–6] Renewed and expanded excitement in this broader field arises from recent reports of organic monolayers formed using these and related approaches as semiconductors[7] and gate dielectrics[8–13] in field-effect transistors, thereby demonstrating useful electronic properties in devices and even simple circuits. Most significantly, research on graphene, viewed as a class of conjugated carbon monolayer material, indicates that superlative electronic transport and mechanical properties can be achieved. Examples include elastic moduli in the range of 1 TPa,[14] electron field-effect mobilities up to 200 000 cm^2 V^{-1} s^{-1},[15–17] with ballistic transport characteristics over distances approaching a micron at room temperature,[15–18] and realization of exotic phenomena such as the half-integer Hall effect,[19–20] previously observed only in the highest purity and most sophisticated inorganic semiconductor structures.[21]

Some of the earliest graphene devices used small pieces of films exfoliated from bulk samples of highly ordered pyrolytic graphite (HOPG) using Scotch tape,[22] in a largely uncontrolled process that is nevertheless extremely useful for research purposes. Although certain classes of transfer printing techniques[23,24] might allow exfoliation to be used in realistic applications, direct synthetic methods can provide not only more scalable integration strategies but also improved control over chemical, morphological and dimensional properties of the materials. This article provides a brief review of progress in this rapidly evolving field of conjugated carbon monolayer membranes, with an emphasis on synthesis and techniques for

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manipulating these materials. The topics include not only routes to graphene but also to more chemically diverse systems, in layouts ranging from flat films and membranes to ribbons, suspended ''drumheads'', pleated sheets, balloons and tubes.

2. Synthetic Approaches

Most envisioned applications of these classes of membranes demand synthetic methods that are capable of creating large area, uniform monolayer sheets or ultrathin films of small flakes or ribbons. Means for transferring these materials from the substrates on which they are synthesized or assembled to other surfaces for device integration are also typically required. This section focuses on the first challenge; the next describes progress on the second. The synthesis approaches include those that are designed specifically for graphene or graphene-like materials and others that are more broadly useful, as discussed in that order in the following.

2.1. Reduced Graphene Oxide from Graphite

Exposing graphite, in powder form, to mixtures of sodium nitrate ($NaNO_3$) and sulfuric acid (H_2SO_4), and oxidizing agents such as potassium permanganate ($KMnO_4$) can produce a form of graphite that is highly functionalized with hydroxyl, epoxide, and carboxyl groups.[25] Sonication of this material, referred to as graphite oxide (GO),[26] in water leads to suspensions of exfoliated monolayer flakes of GO that can be formed into ultrathin films by spray coating,[27,28] vacuum filtration,[28–31] drop casting[28,31] and related techniques. Figure 1a provides a schematic illustration and Figure 2a provides an image. The vacuum filtration method is notable because self-limiting flow fields tend to produce films with thicknesses in the monolayer range. Thick deposits of flakes stacked in lamellar geometries are also possible, by increasing the suspension volumes and deposition times.[30] Chemical reduction achieved, for example, by exposure to hydrazine vapor (N_2H_4) followed by thermal annealing (200 °C) in inert environments can remove the functional groups to yield films of reduced GO.[29] Such films are electrically conducting, with semi-metallic character in field effect transistor devices that is qualitatively similar to those built with pristine graphene, but with far inferior characteristics owing to incomplete reduction and defects.[27,29] The electron mobility of individual reduced GO flakes is between ~2 and ~200 cm^2 V^{-1} s^{-1}.[29] Near monolayer films composed of large collections of flakes exhibit values of ~0.2 cm^2 V^{-1} s^{-1},[29] likely limited by

junction resistances between flakes. The elastic moduli of individual pieces of reduced GO are ~0.25 TPa,[32] also somewhat lower than pristine graphene. Other methods can accomplish exfoliation and solution suspension without chemical functionalization. For example, organic solvents such as N-methylpyrrolidone with surface energies similar to graphite have been used effectively.[28] Even in such cases, however, the electrical properties are not significantly improved over those made from reduced GO. In spite of these non-ideal aspects, films of the type described in this section have characteristics that might make them attractive as flexible and/or transparent conducting coatings in displays, touch screens or related devices.

2.2. Graphene Nanoribbons from Carbon Nanotubes

A different approach to graphene uses carbon nanotubes as an alternative to HOPG and graphite powder for the carbon source material. Figure 1b and Figure 2b provide an illustration and an
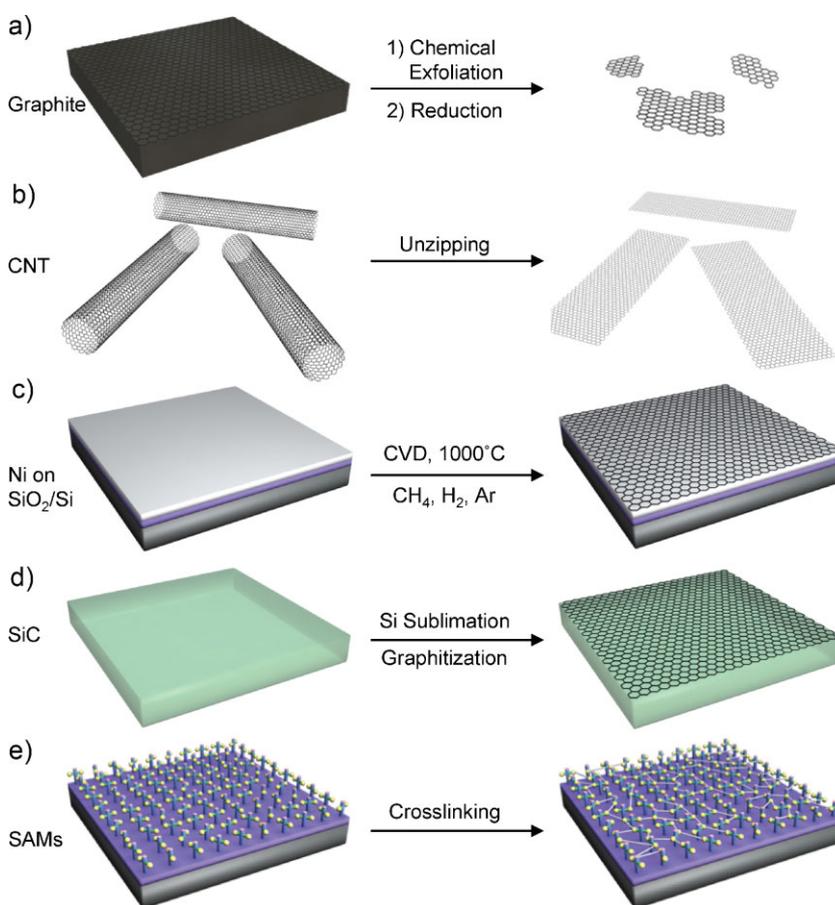

Figure 1. Schematic illustrations of routes to graphene and related conjugated carbon monolayer membrane materials. a) Reduced graphene oxide (GO) flakes by chemical exfoliation from graphite powder. b) Graphene nanoribbons (GNRs) from carbon nanotubes. c) Graphene from CVD growth on metal films (e.g. Ni). d) Graphene from epitaxial growth on SiC by Si sublimation. e) Conjugated carbon monolayer membranes from chemical crosslinking of self-assembled monolayers (SAMs).
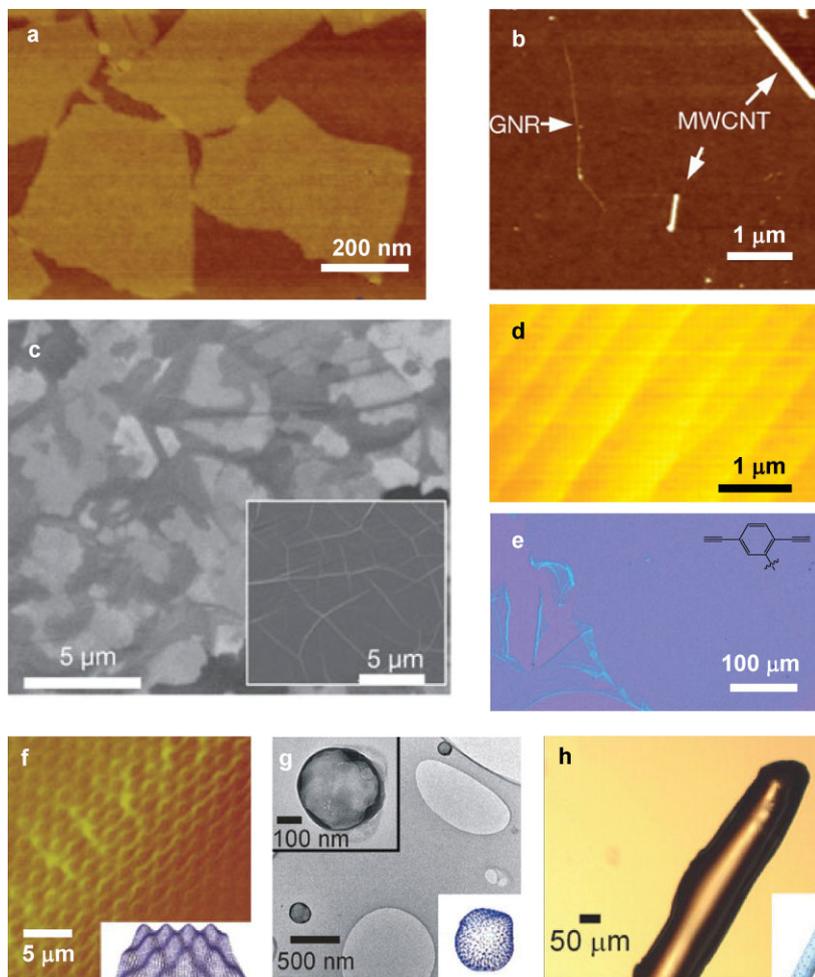
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Figure 2. Images of various types of conjugated carbon monolayer membranes. a) AFM image of reduced graphene oxide flakes drop-casted onto a Si wafer. Reproduced with permission from [31]. b) AFM image of a GNR and an unreacted MWNT after a chemical unzipping process. Reproduced with permission from [34]. c) Scanning electron microscopy (SEM) images of graphene films grown by CVD on a film of Ni (300 nm thick) and on a foil of Ni (1 mm thick) (inset). Reproduced with permission from [40]. d) AFM image of graphene layers grown over terraces of 4H-SiC. Reproduced with permission from [48] e) Optical image of a chemically crosslinked, conjugated carbon monolayer membrane transferred to an oxidized Si wafer. The chemical structure shows the active functional group of the monomer used to form this film. f) AFM image of this type of monolayer membrane, grown on a substrate with a periodic relief structure (depth ca. 35 nm) and then transferred to a flat oxidized Si wafer. The inset schematically illustrates the structure of this film. g) TEM image of monolayer balloons formed by growth on SiO_2 spheres followed by removal of the SiO_2 by etching in HF vapor. The insets show a magnified view (upper left) and a schematic illustration (lower right). h) Optical image of a tubular monolayer membrane formed by growth on a silica optical fiber followed by removal of the fiber by HF vapor. The monolayer tube is filled with liquid that remains from the etching process. The inset shows a schematic illustration. Images (e-h) reproduced with permission from [61].

of poly(methylmethacrylate) (PMMA).[34] Removing the PMMA releases GNRs. Multiwalled nanotubes (MWNTs) seem to be the preferred starting material for both processes; further advances may enable use of single walled nanotubes (SWNTs).[33] For many applications, the long, narrow geometries of GNRs offer advantages over small flakes that typically result from exfoliation from HOPG. In particular, such layouts, for widths narrower than ca. 10 nm, lead to bandgaps sufficiently large for use in transistors with good switching behavior,[34,35] but typically with much lower mobilities due to edge effects. Although carbon nanotube based routes are very recent, one could imagine, for example, implementing them with horizontally aligned arrays of SWNTs grown on quartz[36,37] to yield similarly configured arrays of narrow GNRs, for natural integration into planar electronic devices, such as field effect transistors.

2.3. Graphene by Chemical Vapor Deposition

As illustrated schematically in Figure 1c, large area films of single and few layer graphene can be formed on metal surfaces by direct chemical vapor deposition from hydrocarbon gases, such as methane, at temperatures of ca. 1000 °C.[38–40] Certain aspects of these approaches have origins in work done on related systems in the 1970s.[41–43] Recent progress demonstrates that thin Ni films and optimized cooling conditions can yield films that are mostly one monolayer thick, with some disorder determined, at least in part, by the polycrystalline structure of the Ni.[38–40] Increasing the grain size in the Ni, or using single crystal metals such as Ru(0001),[44] can improve the uniformity and increase the size of the grains of graphene to areas of a few hundred square microns. The properties of the individual grains can approach those of mechanically exfoliated graphene from HOPG, as evidenced, for example, by electron mobilities as high as 4000 cm^2 V^{-1} s^{-1} and by observation of half-integer Quantum Hall

atomic force microscopy (AFM) image, respectively. Here, chemically reacting[33] or physically etching[34] a narrow strip along a nanotube yields a graphene nanoribbon (GNR). In the first case, GNRs form from oxidation of carbon bonds with potassium permanganate ($KMnO_4$) in concentrated sulfuric acid (H_2SO_4). This reaction produces oxidized GNRs that require further reduction using hydrazine to remove oxygen species at the edges.[33] The other approach uses Ar plasma etching of nanotubes, partially embedded in a film

behavior in films transferred from the growth substrate using methods described in a following section.[40] Figure 2c shows representative graphene materials formed in this way. Very recent work with Cu foils demonstrates uniform, single layer (ca. 95%, by area) graphene over square centimeters, also with mobilities up to 4000 cm^2 V^{-1} s^{-1}.[45] A notable feature of these chemical vapor deposition (CVD) approaches is the possibility for substitutional doping by introducing other gases, such as NH_3, during the growth.[46]

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2.4. Graphene from SiC

Epitaxial growth of graphene by thermal sublimation of Si from the surface of a single crystalline SiC wafer at 1200–1500 °C represents one of the first scalable methods to produce large area films of graphene.[47–49] Here, removal of Si leaves surface carbon atoms that reconstruct into graphene layers and grow continuously on the flat surfaces of suitably prepared (i.e. H_2 anneal at 1600 °C followed by controlled cooling) hexagonal SiC wafers (4H or 6H), including over atomic steps (see Figure 1d and Figure 2d). The thicknesses of the graphene deposits depend on annealing time and temperature.[49] Graphene can form on wafers that present either polar face (i.e. Si-face (0001) or C-face (000$\bar{1}$)). In both cases, the properties of the first layer of graphene are not understood clearly.[49] The overlayers, on the other hand, are known to have good properties despite submicron domain sizes,[50] where top-gated transistors show electron mobilities as high as 5000 cm^2 V^{-1} s^{-1}. SiC derived graphene is currently unique in its ability to enable large collections (i.e. hundreds) of devices (e.g. transistors) on a single substrate.[51] Further improvements in grain sizes and defect densities can be achieved by growth under an Ar atmosphere of ∼1 bar, rather than in ultrahigh vacuum (UHV) conditions. The Hall mobilities reported in these studies increased from 710 cm^2 V^{-1} s^{-1} (UHV) to 2000 cm^2 V^{-1} s^{-1} (Ar).[52]

2.5. Graphene and Related Materials by Chemical Synthesis

Theoretical calculations suggest that properties equally remarkable to but different from those of graphene might be possible in other two dimensional (2D) conjugated carbon networks, such as graphyne and graphdiyne.[53,54] In such cases, materials synthesis will likely require the techniques of organic chemistry[55] to provide a level of molecular control over the structure that would be impossible to accomplish with other routes. Past work demonstrates that two dimensional fragments of graphene and related materials can be achieved in large quantities, but with ultrasmall lateral dimensions (<5 nm), using Scholl coupling reactions on oligophenylene precursors.[56] Due to rapidly decreasing solubility with increasing size, larger formats might demand two-step approaches that begin with the assembly of two dimensional, monolayer films followed by chemical crosslinking, as shown in Figure 1e. Exposure to radiation provides one means to accomplish this crosslinking, to yield mechanically robust monolayer films using conjugated carbon molecular species formed either in self-assembled monolayers (SAMs)[57] covalently linked to solid supports or Langmuir-Blodgett films at liquid interfaces.[58] For example, self-assembled monolayers (SAMs) of biphenylthiols on gold form crosslinks upon irradiation with electrons.[57] SAMs processed in this manner are sufficiently robust to form freestanding membranes capable of transfer to other substrates, after removing the gold.[58] Pyrolysis of these materials, which are initially electrically insulating, under UHV conditions can convert them into a conductive form.[59] In another example, Langmuir monolayers of amphiphilic derivatives of polydiacetylenes can be crosslinked by exposure to UV light to yield monolayer films with some indication of semiconducting behavior,[60] although vastly inferior to graphene.

More advanced approaches rely on chemical crosslinking of SAMs to enable formation of planar membranes as well as structured films and those with fully 3D layouts ranging from spherical coatings, balloons, capsules, tubes and other complex topologies.[61] The original work on this system exploited aryl alkynes as monomers due to their highly conjugated, carbon functionality, and to their ability to be chemically crosslinked by alkyne metathesis,[62] oxidative copper coupling,[63] or palladium-catalyzed cross coupling.[63] To assemble SAMs of these molecules on oxide bearing substrates, pendant hydroxyl groups on an aryl ring can be reacted with 3-(triethoxysilyl)propyl isocyanate to yield a carbamate group linked to a siloxane tether.[61] Di-functional and hexa-functional monomers form SAMs readily on oxide and nitride substrates from heated solutions. Mo(IV)-catalyzed vacuum-driven alkyne metathesis[62] and Hay-type coupling conditions[63] can achieve the crosslinking, thereby forming mechanically robust conjugated carbon monolayers with thicknesses in the range of 1–2 nm. Spectroscopic studies and examination by atomic force microscopy, scanning tunneling microscopy and transmission electron microscopy indicate near-complete crosslinking into dense membranes that are largely free of holes or porosity.[61] Conducting the chemistry on flat substrates yields flat films. Structured supports lead to films with corresponding geometries. For example, silica fibers or colloidal spheres can be used to form tubes and balloons, after etching away the silica.[61] Figure 2e–h shows some examples of motifs this method accesses. The main disadvantage with these synthetic schemes is that the degree of order in the films is very low, thereby leading to poor electronic properties. Strategies that use crystalline substrates or other means to achieve large, ordered regions in the SAMs and crosslinking reactions that do not substantially degrade this order have the potential to lead to significant improvements. In their current form, these amorphous materials might be most useful in applications that rely on mechanical, wetting, chemical or related properties.

3. Transfer Printing

The synthesis approaches described in the previous sections yield films on substrates that are often not desirable for their application in devices. As an example, the metal films needed for CVD growth provide low resistance transport pathways in parallel with the overlying graphene coating, thereby electrically shorting devices that are constructed on top. In other cases, such as graphene formed by sublimation on SiC, the areas are limited by the available sizes of the wafers. In these and many other situations, an ability to transfer the films from the growth substrate to a different surface, either selectively or in uniform sheets, is needed. Methods that use soft, elastomeric stamps have been exploited with considerable success for printing inorganic semiconductor nanoribbons/membranes[23,64] and aligned arrays of SWNTs.[65] More recently, adapted versions have been applied to graphene in various forms (i.e., derived from SiC,[66] CVD grown on Ni,[40] exfoliated from HOPG,[23,24] deposited from GO flakes,[29] and crosslinked carbon monolayers formed by chemical synthesis.[61]) Figure 3 schematically illustrates the process and shows some examples of transferred films. Thin polymer or metal films often serve as 'carriers' for the monolayer to facilitate
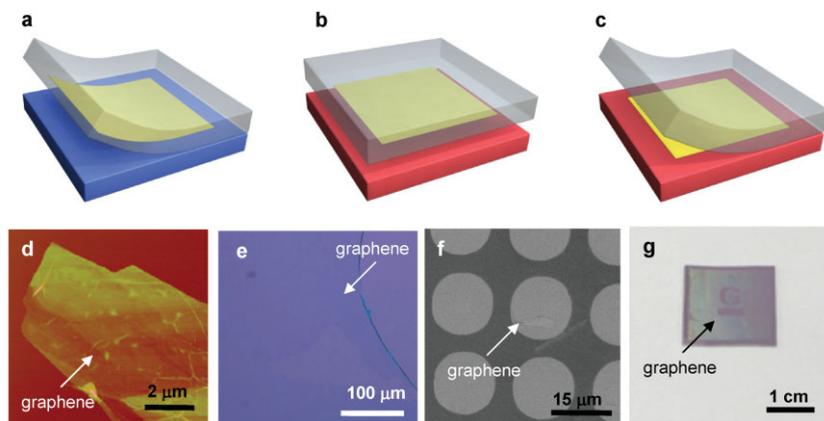
Figure 3. Schematic illustration of the transfer printing process and micrographs of representative examples. a) Applying an elastomeric stamp to a donor substrate (blue) and then quickly peeling it away lifts the film (gold). b) Van der Waals interactions adhere the film to the surface of the stamp, prior to transfer to a target substrate (red). c) Slowly peeling the stamp away transfers the film to the target, thereby completing the process. d) AFM image of graphene flakes (3-12 nm thick) transferred from a piece of HOPG to an oxidized Si substrate. Reproduced with permission from [23]. e) Optical image of a graphene sheet transferred from a SiC substrate to an oxidized Si wafer using a gold/polyimide carrier film. Reproduced with permission from [66]. f) Scanning electron microscopy (SEM) image of a collection of graphene flakes (0.9-5 nm thick) transferred from HOPG to an oxidized Si wafer using a rigid stamp. Reproduced with permission from [24]. g) Optical image of graphene grown by chemical vapor deposition on a Ni film transferred to an oxidized Si substrate with an elastomeric stamp. Reproduced with permission from [40].

transfer. Removing the carrier by selective etching completes the process. Lifting these films onto the stamps is most commonly achieved through non-specific van der Waals interactions with the surface of the stamp. These adhesive forces can be relatively strong at high peel rates, due to viscoelastic behavior of the elastomers that are typically used for the stamps.[67] By contrast, adhesion is comparatively weak at slow peel rates, thereby providing a kinetic control strategy for printing.[23] With these and other related methods,[24,29,34] transfer yields can approach 100%, even with the most challenging graphene[24,40] and monolayer systems.[61]

4. Prospects

The first reports of single layer graphene and its electronic properties in 2004[22,47] led immediately to broad, worldwide research activities on this material. Many of the basic properties are now understood, mainly from studies of individual flakes mechanically exfoliated from HOPG.[14–20,22] Parallel efforts on growth,[38–40,44–48,50–52] particularly in the last several years, have yielded methods that appear extremely promising for large scale sheets and films. Techniques of transfer printing[23,24,65] have been successfully adapted for use with these materials, thereby enabling their integration with diverse types of substrates. This collective body of work suggests that realistic, scalable routes to graphene and its implementation in important devices and systems are, or will soon be, available. Still, there remains much work to be done and opportunities to address. Immediate next steps might include, for example, a search for methods to form large area, aligned arrays of GNRs for applications in certain areas of electronics. A longer term future for work on synthesis and

integration might lie in the development of strategies capable of forming much broader and more chemically diverse classes of conjugated carbon monolayer membranes. Chemical synthetic approaches, like those described in Section 2.5, have promise, but present considerable complications that still require solutions to the significant challenges of control of morphology, degree of crystallinity and other characteristics that influence important physical properties. Substrate-templated growth, as demonstrated recently over small areas, provides an example of a potentially powerful scheme.[68,69] Development of these or completely different techniques represents an appealing direction for future research.

Acknowledgements

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