# New material architectures through graphene nanosheet assembly

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## Abstract

Over the last decade, graphene research has developed into a large and multi-faceted field concerned with the synthesis, structure, properties, and applications of various ultrathin sheet-like carbon forms. This article presents a historical perspective on ultrathin carbons, and on the traditional role of the "graphene layer" as a conceptual model for describing crystalline polymorphs in $sp^2$-based carbon materials. Bulk carbons can often be usefully modelled as physical assemblies of distinct graphene layers whose length, curvature, packing, and orientation determine carbon properties and their observed anisotropy. The article then gives a brief perspective on the emerging subfield of graphene research that uses nanosheets as physical building blocks to assemble new material architectures. In analogy with macroscopic sheets of paper or fabric, graphene nanosheets can be manipulated by stacking, wrapping, folding, wrinkling, or crumpling, to make novel carbons not accessible through traditional routes based on molecular or solid-state precursors. These include aerogels, crumpled particles, encapsulation sacks, and a variety of engineered films structures that can be planar or microtextured. While much work has been done in this graphene subfield, important research opportunities remain. Among these are the creation of hybrid structures involving graphene nanosheets systematically combined with other substances to form graphene-molecular hybrids, graphene-nanoparticle hybrids (2D-0D), graphene-nanofiber hybrids (2D-1D), and nanosheet heterostructures (2D-2D). Copyright © 2018 VBRI Press.

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## Introduction and historical perspective

Modern graphene research began in 2004 with the isolation and characterization of the monolayer form [**1**]. Much of graphene research has focused on understanding fundamental electronic properties, developing improved synthesis methods, or exploring the technological applications of this unique single-atom-thick sheet. An emerging subfield within graphene research, however, does not view the monolayer nanosheet as an end product, but rather as a precursor for new materials synthesis [**2-4**]. This subfield is the topic of the current perspectives article.

The isolated graphene monolayer is a new development, but the materials derived from graphene assembly are ultimately carbon materials - one of the oldest material classes. **Fig. 1a** shows charcoal sketches from the Chauvet Cave in southern France, where analysis of the black deposits suggests an age of approx. 30,000 years [**5,6**]. As 21st century carbon scientists looking at the drawings, one is struck by three impressions. The first is the beautiful artistry of these ancient Europeans, and the effects created by charcoal traces continue to make this medium attractive to artists today. Secondly, if the charcoal was taken from campfires or sites of human-initiated forest fires [**5**],

this can reasonably be regarded as an early use of synthetic carbon as a functional material - a dry-application pigment. Finally, this artistic achievement has something in common with the work that led to the 2010 Nobel Prize in Physics [**1,7**]. The ancient Europeans used a type of simple mechanical exfoliation to achieve thin films of optically absorbing $sp^2$-based carbon. Today we might call such deposits "multilayer graphene", especially in the case of pencil traces, which derive from graphite with its very well-developed graphene layer structure. A theme of this article is that all $sp^2$-based (non-diamond-like) carbons consist of graphene layers, even such common materials as charcoal produced by primitive methods such as heating wood through accidentally incomplete combustion.

Modern attempts to exfoliate graphite into thin, flexible forms began well before 2004. Starting in the mid-20th-century, graphite was exfoliated by formation of intercalation compounds (typically graphite bisulfate formed by graphite treatment with concentrated sulfuric acid and an oxidizing agent (e.g. $H_2O_2$, $Br_2$, $AsF_5$ or $FeCl_3$) followed by thermal shock to expel the intercalant and physically separate the layers [**8,9**]. This rapid process leads to massive Z-directional expansion
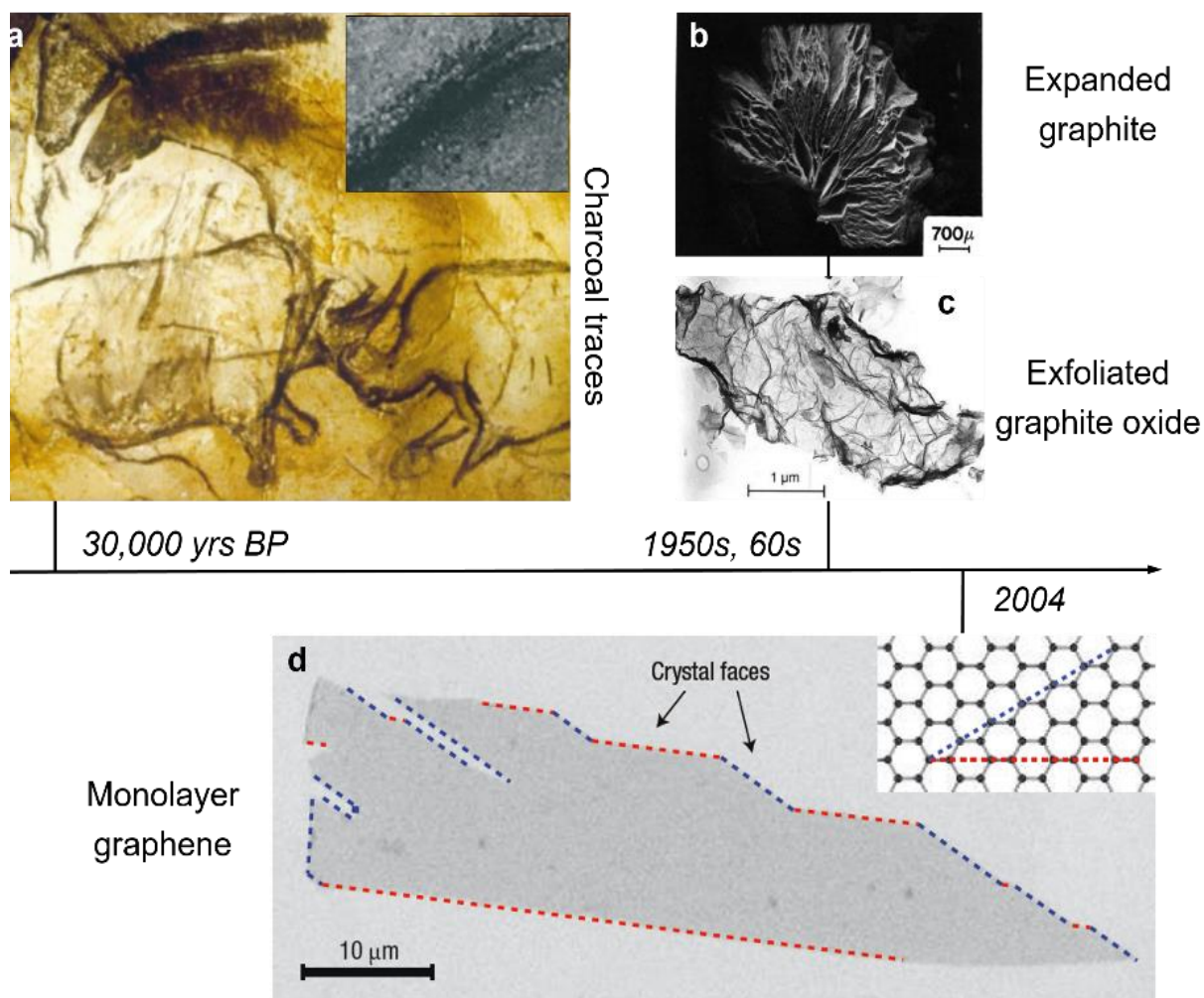
**Fig. 1. A brief history of ultrathin carbon materials.** (a) The charcoal-based painting in Chauvet Cave, southern France, ~30,000 BP [**5, 6**]. Inset: close-up view of the carbon deposit [**11**]. Reproduced with permission. Copyright 2001, Nature Publishing Group. (b) Morphology of expanded graphite made by intercalation and explosive thermal expansion, and often used after subsequent compression to make flexible graphite products [**12**]. Reproduced with permission. Copyright 1986, Elsevier. (c) Early electron microscope image of "sehr dünnen Kohlenstoff-Folien" (very thin carbon sheets) produced by thermal exfoliation of graphite oxide [**13**]. Reproduced with permission. Copyright 2010, Wiley-VCH. (d) Scanning electron micrograph from Geim and Novoselov showing a relatively large graphene crystal, whose faces are clearly zigzag and armchair edges (see inset [**7**]). Reproduced with permission. Copyright 2007, Nature Publishing Group.

that converts the thin graphite flakes into "worms" (**Fig. 1b**) of "exfoliated graphite" or "expanded graphite" (EG), which has an internal structure consisting of thin graphite packets that remain connected at certain points. These EG "worms" can be rolled or pressed to reconstitute graphite sheets that now contain internal porosity separating ultrathin flakes and are thus flexible. This flexible graphite has thermal, electrical, and chemical properties inherited from the graphite precursor, but is soft and can be bent, rolled, or hand cut, and is used in a variety of industrial products ranging from high-temperature, corrosion-resistant seals to heat spreaders used as backing substrates in electronic devices [**10**].

This thermal expansion of intercalated graphite is similar to some processes used today to make multilayer graphene, or "graphene nanoplatelets", in which the thin packets in exfoliated graphite are more completely separated to make the distinct flakes or nanoplatelets desired for compounding into composite materials.

Another route to ultrathin carbon forms passes through graphite oxide as an intermediate. The term graphite oxide refers to the solid products of one of several protocols that use intercalative oxidation with oxidants sufficiently powerful to attack the graphite basal plane [**14-19**]. Early graphite oxide synthesis dates back to the 1800's, and for many years was the subject of research as a bulk material [**20, 21**]. Graphite oxide decomposes on heating to release gaseous products, which, in a manner similar to the intercalants described previously, exfoliate the bulk material into ultrathin layer packets, some approaching monolayer thickness. **Fig. 1c** shows an early example of these "sehr dünnen Kohlenstoff-Folien" (very thin carbon sheets) that today would be referred to as "reduced graphene oxide nanosheets". Graphite oxide also undergoes near-spontaneous exfoliation in aqueous

media, without heating, to make graphene oxide with the full complement of oxygen-containing groups originally formed through reaction in the expanded interlayer spaces of the bulk graphite. The graphite-oxide route to ultrathin carbons (graphene oxide or reduced graphene oxide) has become very popular due to the inherent scalability of this wet-chemical, natural-graphite-based process. Indeed, most research on graphene assembly into new carbon architectures (the focus of this article) use one of the bulk graphene-based materials (exfoliated graphite nanoplatelets or graphene oxide) rather than forms made by CVD or the tape-based mechanical exfoliation used in early fundamental studies (**Fig. 1d**).

### The graphene layer as a conceptual structural element in bulk carbons

The term graphene itself also predates the 2004 isolation and characterization. It is most often credited to Hans-Peter Boehm who in 1986 [**22**] proposed the term "graphene" as the hypothetical end member of the series of polyaromatic hydrocarbons of increasing molecular weight (**Fig. 2a**). These compounds all contain the "ene" suffix denoting the carbon-carbon double bond (benzene, naphthalene, phenanthrene...) and the last entry at the limit of very large molecular weight carries the prefix "graph" from the Greek *graphos*, for "writing".

In the decades following this proposed definition, and before 2004, the word "graphene" was used increasingly in the literature to refer to the hexagonal carbon sheets that were the constituent structural elements within all three-dimensional, $sp^2$-based carbon materials. In most cases (single-walled carbon nanotubes excepted), the materials consisted of sets of multiple "graphene layers", the "layer" designation implying one of many -- i.e. the imbedding of graphene monolayers in some larger structure [**23**] Many of the properties of bulk carbon materials can be understood through a conceptual model that depicts a complex carbon as set of ideal graphene layers, whose length, curvature, orientational patterns, and packing faults determine both the crystalline and porous structure. Of course real carbon materials are not just simple physical assemblies of perfect graphene layers, but this is nevertheless a useful model that is particular powerful for describing the anisotropic properties of carbons. The graphite lattice itself is highly anisotropic, being strong and stiff with all-covalent bonding in-plane, but soft and prone to shear failure and exfoliation due to weak Van der Waals forces between planes. Its chemistry likewise is highly anisotropic with the active sites for most chemical reactions lying at the edges (for ideal, defect-free layers) with low-reactivity basal surfaces that are inert to many processes including attack by most oxidants and grafting by many functionalization chemistries. For these reasons, documenting the graphene layer arrangements in a carbon material is immensely helpful in understanding the materials properties along different axes and on different external facets.

**Fig. 2b** shows an outstanding example of the "graphene layer" conceptual model: its use in the classification of 1D carbon polymorphs. Baker and coworkers [**24**] fabricated a series of carbon nanofibers with contrasting crystal conformations all at 600 °C but using different organic precursors and catalysts. Based on TEM studies they concluded that "the alignment and crystalline perfection of the platelets (i.e. graphene layers) is a parameter that is governed by the nature and shape of the catalyst particle (under reaction conditions) and orientation of the precipitating faces." Orientation of graphene layers along the fiber axis gives what are commonly referred to as carbon nanotubes, with their strength, stiffness, and axial conductivities of interest in composite materials, while other orientations have poor axial strength and conductivity but high concentrations of active sites and the graphene layer edge planes [**24**] of interest in other applications such as catalysis or useful for high-density surface functionalization. This "catalytic engineering" [**24**] is one method for creating materials that systematically exploit the intrinsic anisotropy of the graphite lattice by manipulating the planes into desired directions. Similar control can be achieved using liquid crystalline precursors that one can align along preferred directions using the phenomenon of 'surface anchoring", in a route known as "liquid crystal engineering" [**25**] of carbon structures, named in tribute to the Baker *et al.* paper of 1995 [**24, 25**]. Another example from our laboratory are carbon films composed of vertically aligned graphene layers, whose top surfaces exist entirely of graphene edge sites and show rapid intercalation/deintercalation kinetics for lithium ions under electrochemical driving forces [**26**].

The graphene layer model has also been used to classify bulk carbon materials as hard or soft (**Fig. 2c**). Some organic substances can be thermally decomposed into carbons, that upon further heat treatment at very high temperature (> 2000°C), become synthetic graphite with anisotropic grains each consisting of long, straight, aligned (002) lattice fringes and ABA, or Bernal, stacking between layers. Such materials are referred to as "graphitizable carbons" or "soft carbons" and many of these are found by observation to have passed through an intermediate fluid phase in the initial carbonization step. The graphene layer model provides an explanation for this behavior in the high mobility of the polyaromatic intermediates, which align (sometimes involving discotic liquid crystal phases transitions [**27**]) and then solidify into small graphene layers with approximate, meandering alignment along a single axis (**Fig. 2c**, top left). High-temperature heat treatment can convert this structure to graphite, since the transformation requires only the perfection of the initial order rather than wholesale rearrangement or rotation of large graphene layer structures.
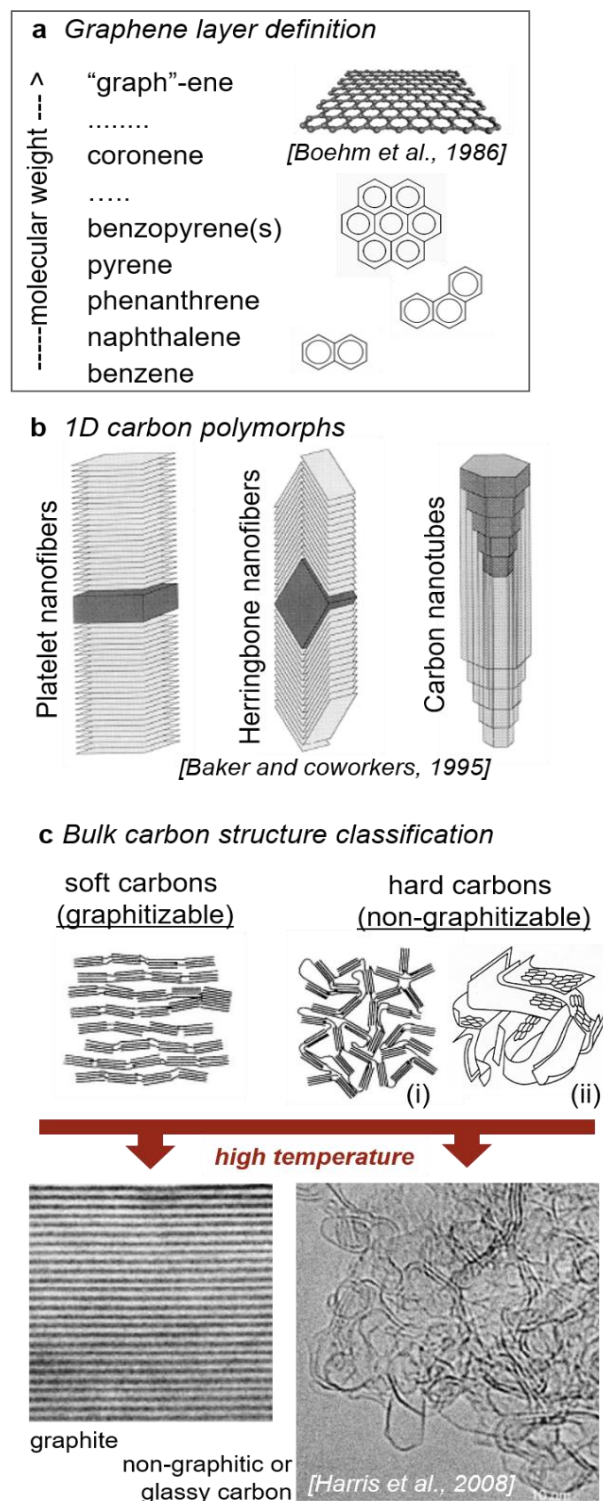
**Fig. 2.** The graphene layer as a conceptual structural unit in bulk carbon materials. (a) the definition of graphene as the hypothetical end member of the series of polyaromatic hydrocarbons at the limit of infinite molecular weight [**22**]. (b) Schematic of graphene layer arrangements in 1D carbon nanoforms created by "catalytic engineering", where catalyst particles are marked as dark grey, precipitated graphite platelets (graphene layers) as light grey [**24**]. Reproduced with permission. Copyright 1995, American Chemical Society. (c) Use of the graphene layer concept to describe bulk structures in hard carbons and soft carbons [**28-30**]. The Harris et al. image is for an activated carbon after high-temperature annealing [**28**]. Reproduced with permission. Copyright 2008, IOP Publishing.

Hard carbons in contrast are typically produced by organic substances with significant oxygen content, and the growing aromatic structures remain cross-linked in the solid-state through the primary carbonization stage. The initial carbon (char) structure following primary carbonization (**Fig. 2c**, top right) has graphene layers with random orientations, and these are incapable of the large-scale rotation or reorganization needed to form graphite, even under very-high-temperature heat treatment. Many of these materials are porous, and that porosity can be associated with the inefficient layer packing. High-temperature heat treatment of these hard carbons does alter the initial structure, but only over short length scales as local rearrangements and atomic mobility seek to eliminate the active edge sites to produce shell-like or loop-like structures (**Fig. 2c**, bottom right) that are characteristic of glassy carbons. The relative lack of truncated edge-planes in these loop- or shell-like structures give glassy carbon a high degree of chemical inertness that is useful in electrodes or in applications involving corrosion resistance.

We hope it is clear that the graphene layer concept has played an important role in carbon science for a long time. The rise of graphene in the 21st century is nevertheless a revolution for our field, because for the first time we have access to isolated graphene layers to manipulate and use in materials synthesis. The graphene layers in bulk carbons are the product of *in situ* organic self-assembly, driven by chemical thermodynamics and the low-free energy of extended conjugated structures. Our ability to control this assembly was limited, however, to the selection of conditions (precursor, temperature, pressure) or the use of certain processing tricks designed to improve graphene layer alignment (such as fiber spinning with discotic flow alignment, hot stretching during polymer fiber carbonization, Z-directional compression). Today the ready availability of isolated graphene sheets opens up a completely new approach for creating designer carbon materials - an approach that involves the manipulation of these pre-formed graphene layers (next section).

### Building with graphene - nanosheet assemblies

This section describes the new "*ex situ*" approach to carbon material design and fabrication. Here one exploits high-quality graphene layers, typically prefabricated by nature and found within natural graphite deposits, and "extracts" them for use in directed reassembly processes. The reassembly may involve stacking, folding, wrapping, alignment, deposition, or gelation, which are processing steps associated with supramolecular, colloidal or soft matter behavior more than the reactive molecular-weight-growth processes that occur in traditional carbonization.

Inspired by the new ability to assemble pre-fabricated graphene nanosheets, one of the first questions that arises is what to make? Interestingly, this *ex situ* sheet assembly approach has less in common
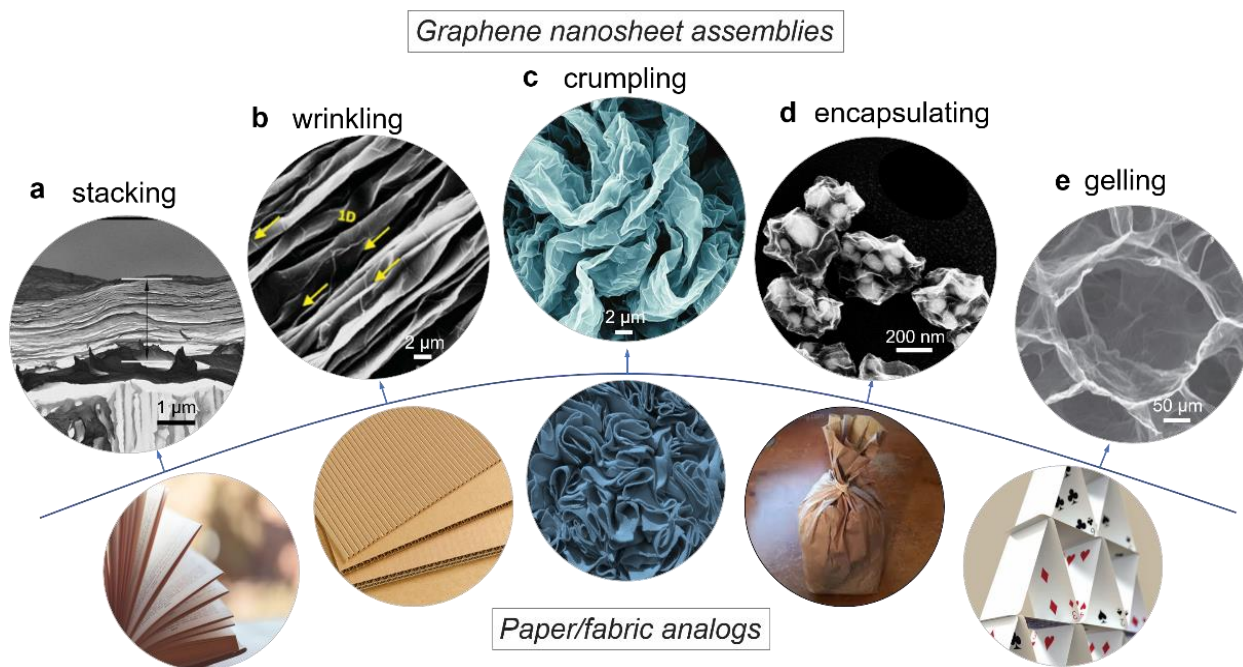
**Fig. 3.** Graphene nanosheet assemblies and their paper/fabric analogs. (a) Multilayer graphene film and its analogy with book pages [**33**]. Reprinted with permission. Copyright 2013, Nature Publishing Group. (b) Wrinkled graphene film and its analogy with corrugated cardboard [**34**]. (c) Crumpled graphene film and its analogy with crumpled fabric [**34**]. Reproduced with permission. Copyright 2016, Wiley-VCH. (d) Graphene nanosacks as encapsulating agents and their analogy with a paper sack [**35**]. Reprinted with permission. Copyright 2012, American Chemical Society. (e) Graphene aerogel structure and its analogy with a house of cards [**36**]. Reprinted with permission. Copyright 2012, Nature Publishing Group.

with traditional carbonization approaches (where graphene layers grow *in situ*) than it does with macroscopic paper- or fabric-based fabrication methods common in everyday life. As such, researchers have been able to easily envision microscopic versions of macroscopic objects such as multi-ply papers, sacks, crumpled paper balls, wrinkled or textured films or coating, or complex origami/kirigami artwork (**Fig. 3a-e**). The creation of such nanosheet assemblies has become a significant subfield in graphene research, and several recent reviews have covered the rapidly expanding literature [**3, 31, 32**]. While some of the early work on graphene folding used pristine graphene (from mechanical exfoliation or CVD), much of the recent work uses graphene oxide as the nanosheet precursor for several reasons. First, it is easily processed as an aqueous suspension, which under the right conditions (low-to-neutral pH, low ionic strength) maintains the identify of individual nanosheets in their atomically thin and flexible form and prevents uncontrolled aggregation or premature sheet-stacking that destroy the uniformity of the colloidal phase and the final product. Secondly, many applications of 3D nanosheet assemblies will ultimately require significant quantities of nanosheet precursor, and thus favor exfoliation-derived nanosheets that can more easily be produced at large scale.

The simplest of all nanosheet assemblies is the tiled film, which can be fabricated by GO suspension casting or filtration, and even forms spontaneously when GO suspensions are spilled and left to dry. If they are thick enough, GO deposits they can be removed from underlying substrate to become free-standing graphene oxide papers [**37, 38**] or can be left in place as ultrathin coatings or membranes on a backing support. Even this simplest architecture can show emergent properties and advanced functionality. Spontaneous hydration swells GO films and enlarges their interlayer spacing to create molecular sieve membranes that pass water but exclude solutes larger than about 0.9 nm in hydrated diameter [**39-41**]. Restricting hydration swelling and achieving precise control of the interlayer spacing is an active research area, and covalent cross linking [**42, 43**] or external pressure [**44, 45**] have been used to target particular separation challenges, including water desalination [**46**]. Rather than restricting swelling, an alternative goal can be interlayer space *enlargement* through pillaring agents, and precise channel size control can be used to create tailored ultrafiltration membranes. The simple tiled films can also serve as a starting point or platform for more advanced structures that incorporate engineered wrinkling or crumpling [**31, 47**]. Periodic wrinkle textures[**48**], isotropic compression-induced crumpling [**49**] or complex, multi-length-scale fractal-like patterns have been created in GO films to enhance surface area for catalysis, sensing applications or for stretchable barriers or devices [**50-54**].
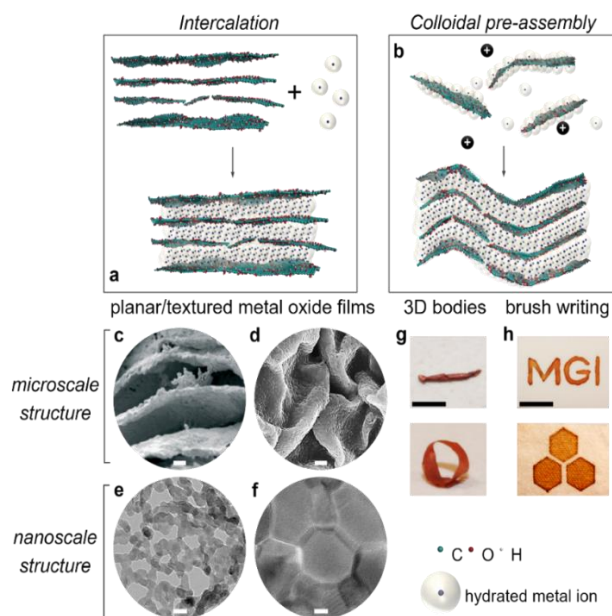
**Fig. 4.** Graphene templating for creation of metal oxide materials. (a, b) Two main approaches: intercalation methods ("pre-stacking methods") and colloidal pre-assembly (post-stacking methods"). (c) $YBa_2Cu_3O_{7-\delta}$ layered structures fabricated by the intercalation method [**61**]. Scale bar, 1μm. Reproduced with permission. Copyright 2015, Royal Society of Chemistry. (d) Crumpled $\alpha$-$Fe_2O_3$ film fabricated by the colloidal pre-assembly method. Scale bar, 1 μm. (e-f) Nanoscale morphologies of structures prepared from methods a and b, respectively [**62**]. Scale bar, 10 nm. (g) $\alpha$-$Fe_2O_3$ replicas of custom-designed 3D shapes [**62**]. Scale bar, 1 cm. (h) $\alpha$-$Fe_2O_3$ patterns fabricated from graphene metallized ink writing and airbrush painting on ceramic substrates [**62**]. Scale bar, 1 cm. Reproduced with permission. Copyright 2017, Wiley-VCH.

### *Transcribing graphene architectures to other material systems*

Having created a variety of novel material architectures from graphene nanosheets, the field has begun to address the question of whether those architectures could be "transcribed" into other material systems. In analogy to the templating of RNA by DNA during gene expression, can we reproduce the textures created in the highly flexible, single-atom-thick graphene system into materials that are not available in nanosheet form and cannot be processed by direct wrinkling or crumpling?

Interest in using graphene as a growth template dates back at least from 2006 [**55**]. Graphene materials can serve as "one-sided" templates, where their atomically smooth surfaces guide the growth of a second material [**56, 57**], or "two-sided" templates, where growth occurs in a confined space between stacked layers. The two-sided confinement technique is especially powerful and requires either an intercalation step to expand the layers to create the 2D reaction vessel [**58**], or the use of some expanded graphene form, such as graphene oxide, whose functional groups part the layers enough to allow spontaneous entry of reactants [**47, 59**].

**Fig. 4** shows two examples of graphene-templated growth of metal oxides. In the intercalation approach, metal-ion precursors are introduced and diffuse into pre-stacked graphene oxide films where they form coordination complexes with oxygen-containing groups on GO surfaces (**Fig. 4a**). Heat treatment in air decomposes the functional groups to liberate metal atoms that react with oxygen and assemble in the confined gallery spaces into metal oxide films [**47, 60**]. An alternative method pre-mixes the metal precursors and graphene nanosheets and stacks the composite nanosheets into multilayer films (**Fig. 4b**). Similar annealing and oxidation steps yield layered metal oxides (see example in **Fig. 4c** [**61**]). The early work used planar GO templates, but recent studies have demonstrated that even complex wrinkled or crumpled graphene microstructures can be transcribed this way into metal oxides [**47**]. Most recently it has been pointed out [**62**] that the intercalation process itself limits the amount of metal precursor available for growth in GO gallery spaces, and this causes the formation of porous particle arrays (**Fig. 4e**) rather than fully-dense space-filling 2D metal oxide films (**Fig. 4f**). This recent study [**62**] demonstrated that high metal loadings could be achieved using the colloidal pre-assembly technique, if the surface charge on the hybrid metal-GO nanosheet precursors was properly controlled to ensure suspension stability [**62**]. The resulting suspensions are referred to as "metalized graphene inks" (MGIs), which can be printed or solution cast onto surfaces and converted by annealing and oxidation into dense, space-filling tiled ceramic films (**Fig. 4f-h**). Between the deposition and annealing steps, the films can be manipulated into 3D objects (**Fig. 4g**) or crumpled into textured films (**Fig. 4d**) whose microstructures survive the drastic transcription process from graphene to metal oxide [**62**].

Finally, there are many things yet to discover and understand in the field of graphene nanosheet assembly. One example is the systematic study of composites, where an almost infinite set of combinatorial possibilities exists for structures involving graphene nanosheets coupled with some other substance. These may be classified into graphene-molecular hybrids, graphene-nanoparticle hybrids (0D-2D structures) or graphene-nanofiber hybrids (1D-2D structures). There is also great interest in the self-assembly of 2D-2D nanosheet heterostructures - solids formed by co-deposition or association of graphene and one of the many types of inorganic nanosheet materials that are now being made by exfoliation or growth methods. Further, while many new material structures have already been fabricated and tested, the scientific principles that underlie nanosheet assembly have not been fully and systematically explored. The many-body colloidal interactions of flexible sheet-like solids with complex charge distributions on their surfaces are not well understood, nor are their interactions at interfaces or within the final solid bodies. This is particularly true of the 2D-2D nanosheet heterostructures - the science of conventional matrix-filler composites has been developed over many decades, while composites that self-assemble from 2D nanosheets, with neither a

defined filler or surrounding matrix phase, represent a new frontier for fundamental investigation.

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