Two-Dimensional Materials Inks

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ABSTRACT:

The development of new and more accurate fabrication technologies has, in the past few years, boosted interest in advanced device manufacturing. 2D materials, thanks to their diverse properties and dispersibility in liquid carriers, constitute a rich toolbox for ink-based applications. However, the lack of standardized production methods offering a good compromise between performance and affordability has so far been a limiting factor for the application of 2D inks. In this Review, we provide a comprehensive description of the steps involved in device fabrication for different applications, from material selection and ink formulation to printing strategies and device assembly. We conclude with a critical overview of the main scientific and technical limitations currently faced by 2D inks and the related printing technologies and discuss their market penetration and implementation stage.

TOC: Two-dimensional materials are some of the best candidates for printed technologies. This review provides an insightful overview on inks formulation processes, from materials selection and deposition techniques to applications. Future commercialization of printed devices is also thoroughly discussed.

[H1] Introduction

Layered materials are a diverse group of materials exhibiting a broad spectrum of electronic, electrochemical and photonic properties[1–3]. Despite the interest of these bulk properties, the true potential of layered materials is unlocked when they are exfoliated to 2D layers[4]. Graphene, the most popular 2D material, exhibits superior electric conductivity and mechanical

strength compared to graphite, its bulk counterpart[3]. Several other layered materials such as transition metal dichalcogenides (TMDs), transition metal oxides (TMOs), hexagonal boron nitride (hBN) and MXenes[3,5–7] show similar enhancements when prepared in their 2D form. However, the full exploitation of layered crystals requires adequate approaches for the mass production of 2D layers and their use in device fabrication[3,4]. Recently, the rapid development of solution-processed electronics has expanded the interest in 2D materials and their applications, offering the promise of simple, cost-effective, reliable, high-throughput and scalable production methods[3,5,6,8,9]. Moreover, materials processing in the liquid phase is a versatile technique, offering tunable dispersion viscosity, concentration and particle size[3,10]. The liquid-phase processing of 2D materials is an attractive production method, adaptable to a wide range of deposition techniques[3,5,6]. Its development has led to the general concept of 2D 'inks', solution-based media for several non-patternable and patternable deposition methods, such as printing, spin-coating and drop casting[6,10–13]. In fact, 2D inks are no longer limited to the realm of academic research: graphene inks are already available as commercial products for screen printing, and MoS_2 inks for spin and spray coating[14,15].

2D inks are being developed at a fast pace owing to their potential for industrial applications, which include energy harvesting and conversion, sensing, flexible displays and smart packaging[3,7–9]. The focus is not only on the selection of materials and solvents, but also on scalability, cost, production methods and environmental issues[11]. This Review surveys the current developments in 2D inks, intended broadly as solution-based media composed of nanomaterials dispersed in a fluid carrier (a solvent or a mixture) allowing processing from the liquid state[11]. After providing an overview of the diverse types of layered crystals and of their most important properties and applications, we discuss the isolation of the materials and their stabilization in a liquid carrier, as well as the adaptability of the resulting ink to a variety of deposition methods. We emphasise in particular liquid-phase exfoliation (LPE) techniques owing to their accessibility, simplicity and scalability. We also cover the available methods for 2D inks deposition and patterning and their requirements, and conclude by discussing the emerging applications, technological limitations and commercial opportunities for 2D inks.

[H1] 2D Materials and properties

2D materials share a series of advantages that arise solely from their near-atomic thickness, which endows them with an extremely high surface area, excellent mechanical strength and

easy regulation of their properties by surface modification and functionalization; these properties are advantageous for applications driven by surface reactions such as catalysis, energy storage and sensing[16]. Furthermore, it is relatively simple to build heterostructures out of several types of 2D materials, obtaining new properties and overcoming some of the individual limitations of each material[1].

2D materials can be produced by bottom-up or top-down approaches[17,18]. Materials produced via bottom-up routes, such as chemical vapour deposition (CVD), atomic layer deposition (ALD) and molecular beam epitaxy (MBE), usually exhibit low defect density and high chemical purity[17,18]. However, high production costs, low yield and limited scalability affect the mass production of 2D materials by bottom-up approaches[17–19]. By contrast, top-down methodologies, such as layered materials cleavage and exfoliation in the liquid phase, are more suitable for industrial applications, as they are cost-effective and easily scalable[1,2,17–21] . Because of its high throughput, LPE is the most relevant approach in the framework of functional inks for solution-based applications.

In this section, we provide an overview of the most common 2D materials used in inks. Additionally,

Table *1* offers, in very simplified terms, a snapshot of the immense range of structures, properties and ink-based applications reported in the literature. **Figure 1** completes the picture by illustrating the structures of the discussed materials.

[H2] Single-Elemental 2D materials

To date, nine single-elemental 2D materials have been synthesized[22], including graphene, borophene, group IV Xenes (silicene, germanene, stanene) and group V Xenes (phosphorene, arsenene, antimonene and bismuthene).

Graphene (**Fig. 1a**) was the first material synthesised in its monolayer form, in 2004; it is in graphene that charge carriers were observed to behave as massless Dirac fermions for the first time[23]. The pivotal development of LPE[24], with its combination of quality and affordability, made graphene widespread, enabling its study for numerous applications that range from thin-film transistors to photovoltaics[24]. Graphene derivatives such as graphene oxide (GO) have been intensively used as a platform to obtain functionalized graphene-like materials for various purposes, including the linking with polymers, biofunctionalization or the production of reduced graphene oxide (rGO) [25,26]. rGO offers similar conductive and mechanical properties as pure graphene, at a reduced price point, making it appealing for composites and inks[3].

Unlike graphene, group IV Xenes (**Fig. 1b**) have a buckled honeycomb structure, such that Dirac fermions are present, but are accompanied by a stronger spin–orbit coupling than in graphene, opening a band-gap[27]. Owing to their intrinsic bandgap and its tunability by functionalization and external fields, Group IV Xenes have potential for different applications than graphene[22,28] and have led to a huge interest in electronics and quantum electronics, that enable Moore's law below 10 nm [27,28]. However, electronic applications are rarely developed with solution-processed materials owing to their strict requirements it terms of quality, size and positioning of the 2D sheets. Inks based on group IV Xenes are most commonly employed in energy storage applications, in which their size and elemental composition are advantageous compared to common materials (

Table *1*).

Group V Xenes (**Fig. 1c**) also have a non-planar honeycomb structure, and the atoms are arranged in two atomic planes. Their structure is strongly anisotropic, making some of their physical properties, such as carrier mobility, dependent on orientation[27]. Additionally, their bandgap decreases as the number of layers increases, making the mono and few-layered materials very interesting for optoelectronic applications[27].

[H2] Bi-Elemental 2D materials

The most prominent bi-elemental 2D materials[25] can be categorized in the following groups: hBN[27], 2D carbon nitrides (C_3N, C_2N, CN and C_3N_4) and TMDs, which have the composition MX_2 (M = Mo, W, … and X = S, Se, or Te)[28].

hBN (**Fig. 1d**) is an extremely stable 2D material that, like graphene, has outstanding mechanical properties, but unlike graphene is insulating. This combination of properties makes it very attractive as a thin insulator for electronics and as casing for optoelectronics[29].

Owing to their oxidation and reduction potentials, chemical stability and low price[30], carbon nitrides (**Fig. 1e**) have been proposed as technologically viable photocatalysts. 2D carbon nitrides provide further advantages, as they have a larger surface area with more active sites, their functionalization and decoration are easier and more effective and their electron transport in the in-plane direction is better[31]. These properties contribute to achieving better performance and unlock new applications[30].

TMDs (**Fig. 1f**) are intensively studied,[32] mainly because many of these materials are semiconductors, unlike graphene, and can be used as building blocks for electronic and optoelectronic devices. The TMD materials family is relatively large and presents a broad range of properties, which make these materials suited for applications ranging from optoelectronics to photocatalysis and energy storage. The solution processing of TMDs has enabled the development of TMD-based printed devices, including supercapacitors[33], batteries[34] and sensors[35].

[H2] MXenes

Since their discovery in 2011, the family of MXenes (**Fig. 1g**)[36], which includes transition metal carbides, carbonitrides and nitrides, has rapidly expanded to more than 30 synthetized members. Initially, these materials attracted attention because of their performance in energy storage. However, in the past few years, their applications have expanded to a variety of fields such as optoelectronics, catalysis and biomedicine[37].

Typically, the structure of MXenes is hexagonal close-packed, with interleaved layers of M (transition metals) and X (C or N)[38]. Their surface terminations (-O, -OH and -F) can be controlled during synthesis and through post-synthetic treatments, and play an important role in determining the material properties[39]. These surface groups allow MXenes to combine high hydrophilicity with ease to bond to various species[37]. Because their synthesis always involves LPE, processing via liquid dispersions is the main way to incorporate MXenes in devices. Their applications range from electromagnetic shielding to wearable sensors (Table 1).

[H2] 2D Metal Organic Frameworks

Metal–Organic Frameworks (MOFs, **Fig. 1h**) are an extremely big family of hybrid organic–inorganic materials with over 70000 indexed members. They exhibit a very high tunability, as it is very easy to change their ligands and metallic centres and hence significantly alter their

functionalities[40]. MOFs have been used for many applications, including catalysis, drug delivery, sensing, electronics and water purification[40].

2D MOFs (also known as metal–organic frameworks nanosheets, MONs) are attractive because of their large accessible surface[41]. MONs can be directly synthesised in 2D or exfoliated from layered MOFs. Mechanical exfoliation and dry grinding can be used for the preparation of MONs, but LPE is by far the most common exfoliation technique[40]. The many available synthesis methods are an advantage of MONs, but their biggest strength is that they can be further modified by post-synthetic treatments, providing an even higher synthesis flexibility[40].

[H2] 2D Transition Metal Oxides

The TMO family of materials has an exceptionally rich structural diversity, resulting in a wide variety of potential applications, ranging from photonics to catalysis[42,43]. One thing all 2D TMOs have in common is the presence of oxygen ions on their surface: being strongly polarizable, these ions generate specific energy states that make 2D TMOs electronically very different from their bulk counterparts and can induce changes in their electronic properties, resulting in magnetism or superconductivity [43].

Some TMOs, like MoO_3 and V_2O_5[42], naturally form layered structures and can be exfoliated by LPE; others, such as SnO_2 and TiO_2, do not form layered crystals, thus, for ink-based applications they are mostly prepared by bottom-up wet syntheses.

[H2] 2D Perovskites

The perovskite family of materials encompasses dozens of members with the chemical structure ABX_3, where A and B are cations and X is an anion[44]. Perovskites have attracted attention in optoelectronics, mainly for photovoltaics and LED applications, due to their tunable bandgap, slow carrier recombination, high defect tolerance and solution processability[45]. For instance, they have experienced a rapid development as photoabsorbers in thin-film solar cells, enabling efficiencies above 25% in just a few years[46]. However, stability is a challenge for perovskites, as degradation under moisture, light and heat[47] hinders their practical application. Recently, it has been demonstrated that when synthesised as 2D layers, perovskites show a much higher stability[47] and larger bandgap and exciton binding energy[48].

Akin to TMOs, perovskites are not necessarily layered materials, and only the sub-family known as Ruddlesden–Popper perovskites form van der Waals layered crystals[48]. Hence, whereas 2D Ruddlesden–Popper perovskites are achieved by exfoliation, other 2D perovskites are generally obtained by colloidal synthesis[49].

[H2] Emerging 2D materials

Beyond the 2D materials families discussed above, which already have demonstrated ink-based applications, other emerging 2D materials are promising for 2D inks. These include group VI Xenes, such as tellurene and selinene, which have high stability and promising electronic and optoelectronic properties and have been used as modulators and phototransistors[50], 2D transition metal borides (MBenes), which are attractive due to their ferromagnetism and electrochemical properties[51], but have not been synthesized yet, and 2D polymers, that despite being at the initial stages of development hold much promise for membranes and sensing applications, albeit with some challenges, such as price and limited synthetic routes[52].

[H1] Liquid-Phase Exfoliation and Inks Formulation

LPE is a simple and versatile process for the production of 2D sheets in a variety of liquid media, and has the advantage of being scalable and compatible with printing techniques[53,54]. The good dispersibility of the resulting nanosheets facilitates materials mixing, allowing the formulation of composite or hybrid inks. Moreover, because the active components are already dispersed in a liquid carrier, the number of ink processing steps is minimized.

In LPE, layered crystals are delaminated by overcoming the weak van der Waals forces keeping them together. This process can be triggered by the collapse of cavitation bubbles (sonication-assisted exfoliation), shear forces (shear exfoliation), ion intercalation (electrochemical exfoliation) or particle collisions (**Fig. 2a**). However, LPE produces not only delaminated crystals, but also fragments and multi-layered micro and nano particles of all sizes and thicknesses. Thus, inks production always encompasses a sedimentation process in which larger particles sink to the bottom of the vial, followed by a centrifugation treatment to remove non-exfoliated material and to collect the 2D-material-rich supernatant (**Figure 2b**). Owing to its simplicity and versatility, LPE has been extensively used to produce dispersions of several 2D materials (**Figure 2c**).

In this section, we discuss the fundamental principles, advantages and disadvantages of the most used LPE approaches, along with the optimization process for the inks.

[H2] Sonication-Assisted Exfoliation

Sonication-assisted exfoliation (SAE) starts with the dispersion of a bulk layered crystal in a solvent, followed by material exfoliation by ultrasonic energy and removal of the non-exfoliated material by centrifugation.[55] Exfoliation is induced by alternating expansive and compressive ultrasonic waves travelling through the solvent, which can lead to cavitation events involving gases or microscopic voids present in the liquid. As the bubbles expand, their inner pressure considerably decreases, such that after their reach their maximum size they undergo a violent collapse[56]. If the system presents asymmetries, such as solid boundaries or other bubbles in the vicinity of the collapsing bubble, the process results in the ejection of a high-speed microject, which induces the delamination or fracture of the layered crystals (**Figure 2a** and Figure S1). The solution is then centrifuged and purified.

Nanosheet re-aggregation can be prevented by selecting adequate solvents. This selection is usually based on solubility parameters (δ), which are a numerical estimation of the degree of interaction between two materials. The obtained dispersions can be stable for months or even years if their enthalpy of mixing, ΔH_m, is minimized[2,24].

$$\Delta H_m \approx \phi(1-\phi)\left[\left(\delta_{S,D}-\delta_{F,D}\right)^2+\left(\delta_{S,P}-\delta_{F,P}\right)^2+\left(\delta_{S,H}-\delta_{F,H}\right)^2\right] \quad (1)$$

where ϕ is the dispersion's flake fraction, $\delta_{S,D}$, $\delta_{S,P}$ and $\delta_{S,H}$ are the dispersion (δ_D), polar (δ_P) and hydrogen (δ_H) solubility parameters of the solvent, and $\delta_{F,D}$, $\delta_{F,P}$ and $\delta_{F,H}$ those of the flake. According to Eq.1, ΔH_m can be minimized by matching as closely as possible the solubility parameters of solvent and flake. The solvents that stabilize some of the most commonly exfoliated materials and have solubility parameters in the optimal range are organic solvents, namely N-Methyl-2-Pyrrolidone (NMP), N,N-Dimethylformamide (DMF) and Isopropyl alcohol (IPA, Table S2). Unfortunately, the toxicity and/or high boiling point of these solvents is detrimental for industrial applications. Moreover, the yield of SAE is low. Longer sonication times can be used, but this usually results in nanosheet fragmentation. In addition, SAE is only practical at the laboratory scale, as it relies on small ultrasonic equipment, such as baths and sonic probes. Nevertheless, owing to its simplicity and versatility, several TMDs, TMOs and many other 2D materials have been exfoliated by SAE[1,54,57,58].

[H2] Shear Exfoliation

Shear exfoliation (SE) enables the production of high-quality 2D nanosheets while avoiding SAE's scalability issues[59]. Shear mixing has been widely used for the dispersion of loosely bound nanoparticles or pre-treated layered crystals, but owing to its low power, exfoliation under shear mixing was not expected to occur, or at most it was expected to proceed at a very low rate[20,60]. However, in 2014, a method for the large-scale production of graphene by shear mixing was developed[20]. Exfoliation is obtained by operating a set of rotating blades in a graphite/solvent mixture (**Fig. 2a**). At high shear rates ($> 10^4$ s^{-1}), exfoliation takes place, whereas below this threshold graphite flakes are poorly exfoliated. Interestingly, any mixer capable of achieving these rotating speeds can be used for graphene production, even a kitchen blender. To date, SE can produce graphene at an outstanding rate of 1.44 $g.h^{-1}$. More importantly, the method is scalable. Graphene prepared by SE in water/sodium cholate has been commercialized in 2014[20,61]. SE was successfully applied also to other layered crystals, namely hBN, WS_2, $MoSe_2$ and $MoTe_2$[20]. Similarly to SAE, the solubility parameters of both flake and solvent dictate the dispersion's stability.

[H2] Electrochemical Exfoliation

Electrochemical exfoliation (EE) is another widely used LPE approach. In this process, an applied bias voltage promotes the intercalation of foreign species into the interlayer spaces of the bulk layered crystals (**Fig. 2a**)[62]. The resulting expansion weakens the structure, such that delamination occurs spontaneously or by mechanical shaking or ultrasonication[62]. EE is usually conducted in aqueous solutions of inorganic salts or mineral acids (anodic exfoliation) or in organic solvents with lithium or alkylammonium salts (cathodic exfoliation)[17]. EE is a relatively simple technique, leading to the production of grams of exfoliated material in a matter of minutes or a few hours[19,60]. For instance, the electrochemical exfoliation of graphene in aqueous solutions of inorganic salts has a yield above 80%, and roughly 85% of the flakes are one to three layers thick[21]- This high throughput motivated the exfoliation of other materials[19], namely MoS_2[21] and black phosphorus[21]. However, anodic EE in water solutions interferes with the oxidation degree of the processed nanomaterials, which can be detrimental for certain applications. By contrast, cationic exfoliation in less environmentally friendly organic solvents usually results in high-quality 2D materials[17,19]. EE is one of the most commonly used techniques for 2D ink preparation[17,19].

[H2] Ink Processing and Optimization

2D inks can be directly prepared by LPE, but they do not always have the right properties for practical use in terms of material concentration and flake size. Moreover, most deposition approaches require precise rheological properties that may not be attainable just by exfoliation with pure solvents. Thus, it is common to tune the physico-chemical properties of the solvents by mixing them with polymeric additives, such as surfactants, polymers and pyrene derivatives[60]. For example, graphene cannot be simply exfoliated in water by LPE. However, a 0.3 $mg.mL^{-1}$ graphene dispersion (roughly 1% monolayer nanosheets) was produced through the sonication of graphite in a water/sodium cholate solution[63]; the process was then upscaled to industrial levels.[20] A mixture of triton x-100 and propylene glycol was used to lower the surface tension and increase the viscosity of water-based MoS_2 and WS_2 dispersions for ink-jet printing[4]. The obtained inks formed stable drops and caused no nozzle blockage[4]. This approach has been successfully implemented on several systems, such as graphene/WS_2[64], graphene[53] and MoS_2[53].

LPE is also a powerful approach for mixing materials, as different types of 2D nanosheets can be dispersed in the same solvent. For instance, isopropyl dispersions of MoS_2 and graphene were mixed to fabricate solar cell electrodes[65]. It is also possible to exfoliate more than one material at once, leading to the direct preparation of hybrid inks with tailored properties. MnO_2/graphene dispersions were prepared by one-pot ultrasound exfoliation of MnO_2 and graphite in isopropyl alcohol[66,67] and used for the deposition of ultra-thin supercapacitor electrodes. Materials exfoliated in less friendly solvents can also be collected and re-dispersed (and mixed) in more benign media, boosting their applicability[53,68]. So far, this approach has enabled the preparation of functional inks with concentrations as high as 15 $mg.mL^{-1}$ [18,69].

Finally, 2D inks prepared by LPE are composed of flakes with a wide distribution of sizes and thicknesses. For instance, graphene produced by shear exfoliation contains nanosheets with thicknesses varying from one to twenty layers[20], and MoS_2 nanolayers can exhibit lateral dimensions ranging from 30 nm to 150 nm (average ~85 nm)[70]. Centrifugation-based size selection can be used to separate flakes according to their size (Figure S3).

[H1] Deposition of 2D inks

Various techniques — drop casting, spin and spray coating, screen, gravure and flexographic, ink-jet and extrusion printing — have been developed for depositing 2D inks (**Figure 3**). These techniques differ significantly in technical characteristics and capabilities (**Figure 3i** and **Table 2**). For example, spin coating is the most accessible method for depositing ultrathin and transparent films, but is limited by the small coating area, and cannot be directly used for patterning[71]. [57] Flexographic, gravure and roll-to-roll screen printing processes are very fast, but require large ink quantities and have high prototyping costs. Digitally controlled ink-jet printing is highly attractive for lab-scale device fabrication as it can accurately deposit inks, ensuring high printing resolution, but it requires strict ink parameters for spatially uniform printing[4,5,72]. Some techniques, such as extrusion printing, enable the fabrication of complex 3D structures that can offer new functions to 2D materials. To adapt inks for specific techniques, it is necessary to tune the rheology, drying behavior, wettability and adhesion to the substrate, which are key to reproducible and precise ink deposition (Figure S4 and Table S2). Thus, selecting the appropriate deposition technique and designing detailed processing steps are prerequisites for successfully depositing 2D inks and achieving the desired patterns and functionalities for target applications. In this section, we discuss the processing details, ink requirements, properties and modification strategies of the main techniques used for depositing 2D inks, along with their advantages and limitations.

[H2] Drop casting

Drop casting, a method in which a thin solid film is formed by dropping a solution onto a substrate and letting the solvent evaporate (**Figure 3a**), is the simplest method for quickly depositing 2D materials. It does not require complex ink parameters, but generally results in inhomogeneities in film thickness and internal structure[73]. To improve the quality of as-formed films, methods including forming azeotropic mixtures[74], inert gas purging[75] and creating a saturated solvent environment[76] have been proposed to tune the evaporation behaviour of solvents and achieve uniform concentration distribution. Despite its disadvantages, drop-casting serves as an accessible and efficient method for film manufacturing. It even enables the fabrication of vertically oriented structures made of 2D materials by controlling the solvent evaporation process[77].

[H2] Spin coating

Spin coating, a method to produce uniform thin films by applying a solution on a spinning substrate (**Figure 3b**), produces high-quality and ultra-thin films. In principle, most as-prepared inks can be directly used for spin coating. However, the morphology of the final film strongly depends on the angular velocity, spin time, and ink concentration and viscosity[78]. Thus, all these parameters need to be carefully selected, and a gradient angular acceleration is often applied. It was shown that inks containing thinner nanosheets can exhibit higher relative viscosities at lower solid concentrations, which are beneficial for fabricating ultra-transparent films by spin coating[79].

[H2] Spray coating

Spray coating, in which the solution is sprayed onto the substrate (**Figure 3c**), is a well-established industrial method that provides high-throughput and controllable ink deposition and uniform film coverage. Desired patterns can be obtained with shadow masks, and the agglomeration of 2D sheets can be alleviated by ultrasonication spraying[57,80]. Inks for spray coating should possess a relatively low concentration, relatively high viscous modulus, and an elastic modulus that ensures liquid-like behaviour and sufficient flowability while enabling the retention of the system integrity after deposition[81]. To improve the quality of deposited films, inks can also be modified by adding surfactants or employing two solvents to create Marangoni flow, which enables a more homogeneous redistribution of the nanosheets on the substrate (Fig. S4D)[82]. Spray coating is one of the most flexible and cost-effective deposition techniques for 2D inks, and it holds great promise for commercial applications.

[H2] Screen printing

Screen printing (**Figure 3d**) is another mass-printing method that allows pattern design[9]. During printing, the ink is squeezed to penetrate a pre-patterned stencil and deposits onto the substrate under a wide shear rate range (1–1000 s^{-1})[83]. Hence, screen printing inks should possess relatively high viscosity and shear-thinning features, ensuring that they flow to penetrate the stencil and spread under pressing, but also that the pattern integrity is retained once printing is finished. Considering that many as-prepared 2D inks exhibit low viscosities, binders are typically required[9]. Screen printing allows fast operation: the modified printing system in flatbed automated and roll-to-roll modes can have a speed of up to 70–100 m/min[84,85]. The development of inks that have the right viscosity without the need for binders is needed to eliminate post-treatment and preserve the functional properties of 2D materials.

[H2] Gravure and flexographic printing

Gravure and flexographic printing are roll-to-roll techniques that enable ultrafast and large-area ink deposition[86]. In gravure printing (**Fig. 3e**), the patterns are pre-engraved on a roller to form cells that transfer the ink and patterns to the substrate. Inks for gravure printing should contain low-boiling-point solvents and possess medium viscosities[3,12,87]. When printed, inks are subjected to three types of stretching forces: adhesive forces on the cell surface (F_{IC}) and substrate (F_{IS}) and the cohesive force inside the ink (F_I). Successful printing is achieved when $F_{IS} > F_{IC} > F_I$[88]. By contrast, flexographic printing (**Figure 3f**) is a relief process, in which the desired pattern is embossed in relief on a cylinder and is impressed onto the substrate after being inked [3]. The development of gravure and flexographic printing for 2D inks is still in its infancy, and only a few successful examples were reported because of the high prototyping cost and the required large ink quantities[86,87,89]. However, the great potential of these techniques for the commercial application of 2D inks, particularly owing to their ultrahigh speed, cannot be ignored[84].

[H2] Ink-jet printing

As a direct ink-writing technique, ink-jet printing (**Figure 3g**) can accurately deposit inks through digitally controlled ejection to form patterns in a material-conserving way[8,90]. It can also generate 3D structures[91]. However, achieving high-quality ink-jet printing is challenging because the deposition process is largely affected by ink parameters and printing conditions[3,4,58,90,92]. The printability of inks for ink-jet printing is usually predicted by a dimensionless inverse Ohnesorge (*Oh*) number (Z)[93]:

$$Z = \frac{1}{Oh} = \frac{\sqrt{\gamma \rho a}}{\eta} \quad (2)$$

where γ, ρ and η are the viscosity, density and surface tension of the ink, respectively, and a is the nozzle diameter. In principle, Z values in the range 1–14 result in stable ink jetting[3,94], but successful examples of inks with Z values beyond this range were also reported[4,95]. To adapt to the jetting process, inks should also possess low viscosity. However, in low-viscosity inks, during drying the inner solvent flows to the edges to replenish the evaporated solvent, resulting in the accumulation of deposited material on the periphery (the coffee-ring effect, Figure S4.B). Methods such as selecting high-boiling-point solvents, using two solvents, adding surfactants

or binders, and substrate surface treatment have been exploited to alleviate the coffee-ring effect and improve printability[4,8,58,90,96–98]. To achieve uniform patterns with smooth lines and even edges, the drop frequency, substrate temperature and printing speed should also be optimized[99]. Non-continuous patterns, such as quantum dots and microarray patterns, can also be realized using ink-jet printing[100]. Modified techniques that improve the printing quality are electrohydrodynamic-jet and aerosol-jet printing, which enable higher spatial resolution and homogeneity[91,101].

[H2] Extrusion printing

Extrusion printing, in which a filament of material extrudes through a nozzle layer by layer to form a 3D shape (**Figure 3h**), is specifically used for printing 3D structures and thick films [102,103]. Central to this technique is the preparation of paste-like inks that exhibit distinct shear-thinning behaviour and possess sufficiently high elastic modulus and shear yield stress[79]. 2D inks can be modified by introducing additives and increasing the solid content and the aspect-ratio of 2D sheets[79,104,105], which increases the viscosity. Moreover, due to the rich and tunable surface chemistry of 2D materials, ink properties can also be tuned by modifying the colloidal stability of the nanosheets[106–108]. For example, phase inversion of graphene oxide (GO) and MXene inks at low concentrations can be induced by the gelation of nanosheets, making the inks suitable for extrusion printing[107,108]. Important future directions for the extrusion printing of 2D inks include the development of straightforward methods to print additive-free 2D inks to better preserve the functionality of the 2D materials; improving the control on the assembly behaviour of the 2D materials and on the printed structure at the microscale and nanoscale during printing; and the ability to continuously print multi-material architectures with controlled composition and structure[109].

[H1] Applications

The outstanding solution-processability of 2D materials enables the easy and scalable manufacture of electrodes and devices with desired geometric configurations on various substrates. The advantageous properties of 2D inks are exploited in a wide variety of applications, including energy storage, sensors, electronics, optoelectronics and bioengineering (**Figure 4**,

Table *1*).

[H2] Energy storage

Electrochemical energy storage devices, in particular supercapacitors[110] and batteries[111,112], are essential in our daily life. However, commercial devices suffer from limited power or energy densities, thus struggle to meet the ever-increasing performance demands of arising technologies. 2D materials bring new prospects to this field. Their 2D layered structure results in more exposed active surface and richer ion transport channels for electrochemical reactions compared to their bulk counterparts, and their solution-processable nature enables large-scale and customizable device manufacturing.

2D materials, in particular graphene[108], TMDs[113], TMOs[95], transition metal nitrides[114], black phosphorus[115] and MXenes[89], hold great promise as electrodes for supercapacitors. They can all be easily deposited on various substrates or current collectors using different methods (such as spray coating, screen printing, ink-jet printing and 3D printing), and show good performance[3]. As an example, 3D-printed graphene electrodes with a porous and interconnected structure exhibited the desired electric double-layer capacitor behaviour and

showed an outstanding rate capability (86% capacitance retention from 0.5 to 100 A g^{-1})[108]. Excellent pseudocapacitive performance was also observed in spray-coated MoS_2[113], inkjet-printed δ-MnO_2[95] and 3D-printed $Ti_3C_2T_x$ MXene electrodes[116]. MXenes in particular have sparked substantial interest in the past few years owing to their ultrahigh electrical conductivity (up to 15000 S cm^{-1})[117], extraordinary redox activity and high electrochemical stability[118]. Moreover, advanced printing technologies (such as 3D printing) can efficiently improve the mass loading of electrodes based on 2D inks to commercial levels (10 mg cm^{-2}), further facilitating the practical applications of 2D inks in supercapacitors.

2D materials also show outstanding electrochemical performance in batteries (**Fig. 4a**), where they can serve as anodes[119], cathodes[120], conductive binders[121] and separator modifiers[122]. 3D printing has attracted the most attention among the various deposition methods for the fabrication of battery electrodes owing to its ability to build open and porous electrode structures from 2D inks. Porous electrodes are critical for fast ion transfer kinetics and for a sufficient number of electrochemical reactions[123], and they also favour 'gas breath' in metal–gas batteries[124,125]. In 3D-printed graphene Na-O_2 batteries electrodes, the porous structure enables the access of O_2 across the whole electrode and provides fast and continuous pathways for Na^+ ions diffusion[126]. 3D-printed MXene arrays and graphene lattices were also reported to guide the alkali metal nucleation, resulting in stable and high-rate Li/Na anodes[127,128].

Despite intensive research efforts and considerable progress, several challenges remain. The first is to minimize the stacking of 2D nanosheets caused by van der Waals forces or other interactions, as it reduces the active surface area and thus weakens the electrochemical performance. The second challenge is to simultaneously improve the electrical and ionic conductivities and mass loadings of electrodes. The third challenge is to find fast, scalable and cost-effective ways to produce electrochemical energy storage devices; 3D printing could provide a pathway in this direction.

[H2] Sensors

Sensors are devices that respond to external stimuli and transform them into detectable output signals. Sensitivity, selectivity, speed (response and recovery rate) and stability are four critical factors for sensing devices[129]. Fulfilling these requirements simultaneously is challenging, but can be realized with 2D materials owing to their large surface-to-volume ratios, rich surface chemistry, great biocompatibility and exceptional electrical properties[130,131]. Moreover, the

excellent solution-processability of 2D materials enables fast and scalable manufacturing of portable and flexible sensors.

Chemical sensors based on 2D materials can detect chemical species via physical or chemical interactions between active materials and analytes, including gases (such as organic gases and water vapour), ions (such as alkali and heavy metals) and biomolecules (such as glucose and DNA, **Fig. 4b**)[132]. Generally, these analytes can change the local charge carrier concentration in the 2D material, thus altering its electrical conductivity and generating signal information[133]. For instance, a gas sensor fabricated by drop-casting V_2CT_x inks could sensitively detect both polar and nonpolar gas species through a charge-transfer mechanism[134]. Sensors based on inkjet-printed MoS_2/polyvinyl pyrrolidone[135] exhibited an ultrafast response to humidiy; spray-coated black phosphorus[136] to H^+ ions; and 3D-printed graphene/poly(lactic acid)[137] to heavy metals. In the case of biomolecules, 2D inks also have the advantages of biocompatibility and high sensitivity[138,139]. For example, screen-printed $Ti_3C_2T_x$ microfluidic biosensors were used for the continuous online detection of urea, uric acid and creatinine levels in human blood[140].

Physical sensors capture and monitor various physical stimuli or physiological signals (such as strain, pressure and temperature), and have a wide range of applications, spanning from the detection of human motions and monitoring of health to the creation of artificial sensitive skins for robotic applications[141,142]. MXenes and graphene are two typical 2D materials employed in strain sensors. They enable fast signal transport and easy fabrication of durable devices[143,144]. An example is a $Ti_3C_2T_x$/CNT strain sensor fabricated by one-step spray coating, which could detect both tiny and large deformations (human throat and leg movement) with excellent reliability and stability. Such a sensor is promising for future interactive processing of strain, prosthetic feedback and wearable sensing for comprehensive monitoring in health and motion applications[141]. Another example are spray-coated reduced GO temperature sensors, which can maintain a high sensitivity under different external pressures and surrounding environments, properties suitable for robotic skins[145].

For sensing applications, the high electrical conductivity and large surface area of 2D materials are their main advantages. Remaining challenges include improving the environmental stability of 2D materials, as lots of them (such as MXenes, black phosphorus and silicene) are sensitive to environmental factors such as temperature, oxygen and humidity, and can be oxidized or decomposed under ambient conditions. Forming heterojunctions with other stable materials

would be a promising solution. A second challenge is achieving high selectivity towards different species, especially for analytes with similar properties. A third challenge is integrating multifunctionalities into 2D sensors, to efficiently minimize device sizes and enable multi-scenario applications.

[H2] Electronics and optoelectronics

2D materials can be insulating (hBN, silicates), semiconducting (TMDs, black phosphorus), metallic (graphene, MXenes) and superconducting (Mo_2C, **Table 1**)[57,146], and cover a wide electromagnetic spectrum, from far-infrared to deep ultraviolet[147]. These properties make 2D inks promising for printed and/or flexible electronics (including transparent conductive films[148], dielectrics[149], thin-film transistors and radio-frequency identification systems[150]), photodetectors[151] and photovoltaic devices[152].

Whereas indium tin oxide (ITO) is expensive and brittle, 2D inks-based transparent conductive films are cheap, flexible, transparent and have tunable conductivity, and are thus attracting increasing attention in modern electronics. Moreover, their fabrication can be up-scaled by depositing conductive 2D inks, and plenty of substrates can be used[148,153]. Flexible $Ti_3C_2T_x$/Ag nanowire transparent conductive films prepared by spray coating on polyethylene terephthalate[154] could not only withstand thousands of bending cycles, but also exhibited higher average transmittance and electrical conductivity than commercial glass-based ITO samples[155]. 2D inks are also attractive for thin-film transistors (**Fig. 4c**[156]). In these devices, hBN is often used as the 2D dielectric material, and TMDs as the 2D semiconductive layers.[157] MoS_2 inks have been used for the fabrication of large-area thin-film transistor arrays on several substrates via solution-processing approaches. The thin-film transistors showed both high room-temperature mobilities and on/off ratios, and enabled the construction of functional logic gates and computational circuits[13]. Moreover, thin, lightweight, flexible and highly conductive films prepared from MXene and graphene inks exhibited excellent data storing and remote reading ability in radio-frequency identification applications[150,158], as well as excellent electromagnetic interference shielding performance[96], comparable or even surpassing that of most commercial metallic materials, such as Cu, Al and Ag. [150,159]

Photodetectors are devices that absorb light and produce electrical signals. They have operational wavelengths ranging from ultraviolet to terahertz[160], and 2D inks, thanks to their diverse bandgaps and photoresponse behaviours, can cover all these ranges[161]. Many 2D

materials show thickness-dependent bandgaps and possess a different bandgap than their bulk counterparts: examples are MoS_2 (1.3 eV for the bulk and 1.8 eV for the monolayer)[162] and β-InSe (1.26 eV for the bulk and 2.11 eV for the monolayer)[163]. This feature extends the response range compared to traditional photodetectors and brings new opportunities to this field. In addition, the solution-processability of 2D inks facilitates the printing of thin photoelectrodes with excellent flexibility, which are much more convenient than fragile silicon and InGaAs used in conventional devices. Examples are organohalide 2D perovskite and MoS_2 inks, which can be printed into high-responsive photodetectors with wide spectral ranges and excellent flexibility[164,35]. Moreover, MoS_2 with electronic structure engineered through the introduction of Mo vacancies defects by pulsed laser deposition achieved an ultrabroadband photoresponse ranging from 445 to 9536 nm at room temperature[165], which is broader than that of commercially available photodetectors based on GaN (<400 nm), silicon (400–1100 nm), InGaAs (800–1600 nm) and HgCdTe (2–5500 nm)[166].

2D inks are also used in photovoltaic cells as transparent conductive electrodes, absorbers, charge transport layers and buffer layers[21]. Graphene[167] and MXenes[168] are mostly employed as transparent electrodes or charge (electron or hole) transport layers. By contrast, TMDs are appealing for buffer and absorber layers owing to their range of bandgaps and the possibility to match their work function with that of other functional layers[169,170]. When employing an UV-ozone treated spin-coated $Ti_3C_2T_x$ MXene as electron-transport layer, the power conversion efficiency of perovskite solar cells reached 17.17%[171]. In another study, a spin-coated 2D MoS_2 buffer layer was found to improve the stability of organometallic–halide perovskite solar cells[152].

Undoubtedly, 2D materials offer great opportunities for electronic and optoelectronic applications, especially for flexible and wearable devices. Yet, issues and challenges remain. The first challenge is producing high-quality 2D materials on a large scale. Most solution synthesis methods introduce defects and impurities, lowering the conductivity and weakening the signal intensity. The second challenge is improving the linear dynamic range. Compared with conventional linear-response photodetectors (such as those based on Si, Ge and GaAs), most 2D materials suffer from relatively low linear dynamic range, which hampers high-resolution photosensing and video imaging applications[172]. The third challenge is simultaneously improving the stability and photovoltaic efficiency of solar cells based on 2D inks.

[H2] Bioengineering

Their large surface area, tunable surface chemistry, excellent solution-dispersibility, reasonable biocompatibility and biodegradability make 2D materials suitable for bioengineering applications, mainly including regenerative engineering[173] and therapeutic applications.[174,175]

¹⁷⁵Regenerative engineering combines cell biology and materials science to treat and reconstruct defective tissues (such as bone, cartilage and cardiac tissue) or organs by using biomimetic scaffolds. These scaffolds need to have several key properties, including biocompatibility, a complex 3D microenvironment to control and guide cell growth, and the ability to deliver bioactive molecules, to generate chemical and physical signal cues, and to stimulate mechanical properties[176]. Among various 2D materials, graphene and GO, black phosphorus, hBN, MXenes, TMDs and nanoclays (layered mineral silicates)[173,177] have attracted the most attention. Usually they are incorporated into bioscaffolds via direct 3D printing, or are cast onto pre-printed scaffolds. For instance, a GO ink was mixed with a solution of tricalcium phosphate, gelatin and chitosan and 3D printed into composite scaffolds, which displayed improved calcium deposition and enhanced alkaline phosphatase activity compared to the same scaffolds without GO[178]. Efficient acceleration of the in-vivo growth of bone tissue was also achieved by coating bioactive glass scaffolds with Ti_3C_2 MXene inks[179]. Finally, 3D-printed hBN/poly(lactic-*co*-glycolic acid) scaffolds[180] were reported to enhance the viability and growth of human mesenchymal stem cells derived from bone marrow, and 3D-printed GO/collagen/chitosan scaffolds[181] to favour the formation of a cartilage layer.

In therapeutic applications, printed scaffolds containing 2D materials (MXenes, black phosphorus and graphene)[179,182,183] are used to eliminate tumors, in particular breast cancer[184] and osteosarcoma[174], by exploiting photothermal effects (**Fig. 4d)**. For example, a 3D-printed bioactive glass scaffold incorporating Ti_3C_2 inks reached a temperature of 63 °C within 2 minutes of being irradiated by an 808 nm laser, which resulted in the complete removal of bone tumors without recurrence. In addition, this composite scaffold also efficiently accelerated the in-vivo growth of new bone tissue[179]. Similar results were achieved using black phosphorus and graphene-reinforced 3D-printed scaffolds[182,183]. On top of the ability to deliver photothermal therapy, 3D-printed scaffolds containing black phosphorus also exhibited drug delivery functions, which could enhance the efficiency of the therapy[185].

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To conclude, 2D inks have been successfully used in bioengineering applications at the lab scale. Nevertheless, the field is still in its infancy, and many issues remain to be addressed. The first and most important task is to systematically study the biocompatibility and long-term toxicity of 2D materials, which directly determines the applicability of 2D materials in bioengineering. The second task is to widen the applications of 2D inks in bioengineering, as most reported works are limited to bone-related studies. The third task is to develop new deposition methods to meet the complex requirements of biological environments; 4D printing — the fabrication of structures that can adapt and change shape or properties after printing — may be a fruitful direction to investigate.

[H1] Outlook and Future Perspectives

The diversity and advantageous properties of 2D inks present opportunities for many emerging technologies. In fact, research on 2D inks has grown exponentially in the past 20 years, and inks and dispersions have become the main vehicle for the implementation of 2D materials into real-world applications (**Figure 5**). However, issues and challenges remain, some related to scientific questions, others regarding the implementation of 2D inks in commercial applications.

In terms of scientific issues, a recurrent problem is tailoring the lifetime of 2D materials to match the requirements of different applications. In most fields (energy storage, sensing, electronics, optoelectronics and photovoltaics), devices are expected to last for decades, but in others, such as bioengineering, they should biodegrade within a short time. Approaches like surface functionalization, heterojunction construction and defect engineering have proven useful to tailor the lifetime of 2D materials[186,187] . Another crucial issue is the biocompatibility and long-term toxicity of 2D materials in living bodies and ecosystems. In the context of sustainability and long-term environmental effects, 2D inks for end-user devices need to be recyclable, and a plan for the management of residues at their end-of-life need to be in place. Graphene has been deeply studied in these regards, and its hazards are relatively well understood[188]. Fortunately, some of this knowledge can be translated to other 2D materials, as several of their interactions with the environment and living bodies are driven by their nanometric size and layered structure.

Other important scientific issues include maximizing the surface area by reducing re-stacking of 2D layers after exfoliation[189] and improving electron transfer in printed devices[190]. These

optimization challenges are important, as device performance will determine whether a 2D material or a competing technology will become the preferred option for a specific application. This race for prominence in the functional ink market does not have a clear winner yet, but there are plenty of contenders[191]: the main competitors of 2D inks are organic polymer-based inks, metallic nanoparticle and liquid metal inks, 1D nanostructured carbon-based inks and nanoparticles solutions. These materials can also be used in combination with 2D inks, forming synergetic hybrids[191], showing that the coexistence of different types of inks is not only possible but also beneficial. The possibility to easily mix materials with very dissimilar properties is one of the greatest advantages of inks.

Other challenges relate to the commercialization of 2D materials. The first one, encountered by early adopters of 2D materials (specifically graphene), is the lack of standardization[192]. Graphene is produced by many manufacturers with very different prices and quality, but advertised under the same name. Poor-quality products generated distrust in 2D materials in general. The second challenge relates to price and mass-production capabilities. Only very niche markets are not price-sensitive, and price and material availability are the first and most common implementation barriers for new technologies. Finally, the third challenge is the compatibility with state-of-the-art processes. If a new material is not compatible with established fabrication processes, its implementation barrier is very high, and needs to be compensated by a clear advantage and good price/performance ratio. For certain markets, the rule of 10 applies[192]: the new material needs to be 10 times cheaper or 10 times better than established materials to successfully enter the market. The value chain of 2D materials is at an early stage and pricewise they cannot yet compete for well-established markets, and will not for the next 5 years at least. Also, although there are some reports of better performance in end applications than commercial materials, usually this good performance does not compensate for the large implementation barrier. Hence, for the time being the market of 2D materials is limited to developing fields where existing technologies are not well established or are underperforming, niche applications in which price is not as important as performance (aerospace, science or health) or devices that offer additional functionalities at a reasonable price for consumers (printed electronics, biocompatible and multifunctional devices for example). 2D inks are mainly used for the latter type of applications, particularly in printed devices (**Figure 5**).

For printed devices, the performance requirements are not as stringent as for CMOS electronics and optoelectronics, where 2D inks struggle to achieve the required conductivity and efficiency, and a low price is an important advantage[55]. The compromise between performance and affordability is one of the strong points of 2D inks, making them ideal for these applications. Additionally, 2D inks are compatible with state-of-the-art printing techniques, which reduces the implementation barrier, and the added functionalities they offer (such as flexibility and form factor) are highly valued by this industry. Because the market for printed devices is just starting to develop, there is a dire demand for new inks to improve overall performance, lifetime, encapsulation and efficiency. Although there are a few competing materials, there is no clear winner yet, creating a gap in the market that 2D inks are in a good position to fill. 2D inks have the advantage that their value chain has experienced fast progress in the past few years thanks to the multimillionaire investments made on graphene (through the graphene flagship for instance)[193]: the market penetration of graphene is opening the doors to other 2D materials. This price advantage, combined with the rapid development of the 2D ink field, the constantly expanding library of 2D materials and their functionalities[27], and the recent emergence of a market for printed devices, has created the perfect ecosystem for 2D inks to take a fundamental role in this field.

In the emerging ecosystem of printed devices, we also need to critically consider the limitations of the current printing techniques. We discussed how printing and coating techniques offer a reliable route for depositing 2D materials in a controllable way, but significant challenges remain in achieving consistent, high-resolution printing for large-scale fabrication in a commercial setting. In particular, for printed electronics with multilayer structures, high printing accuracy and spatial resolution are needed. Among deposition methods, ink-jet printing is the most commonly used because of its high printing accuracy and ease of prototyping. However, its large-scale application is limited by the complicated printing setting and low printing speed. Although the printing speed of inkjet printers with multiple heads can reach 30–60 m/min, their throughput is still much lower than that of roll-to-roll techniques (gravure, flexographic and screen printing), which are well-established in the industrial framework. Unfortunately, these methods are currently less studied in academia because of the high prototyping cost, moderate printing resolution and need for large ink volumes. This creates a barrier in the development of devices based on 2D inks, as extra work is required to adapt inks and procedures to the large-scale roll-to-roll setting. Despite this issue, there are already

commercial roll-to-roll printed devices [MPS please insert link https://haydale.com/products/inks/] based on 2D material inks (such as pressure sensors, RFID tags and biomedical test strips)[194], and as the sector gets more experience with 2D inks, the implementation barrier for all 2D materials will be lowered.

To conclude, 2D inks are an exciting alternative for emerging flexible and wearable technologies for daily life applications. Their further development and implementation are still plagued by issues with production standardization and compatibility with currently available manufacturing approaches. These shortcomings may make it difficult for devices based on 2D inks to enter very competitive markets. However, it is clear that 2D inks are set to occupy technological and market niches in which low production costs are more relevant than high performance.

Table 1. 2D materials and their ink-based applications. SOC: spin-orbit coupling QSH: quantum spin Hall effect, FET: field-effect transistor, PL: photoluminescence, ECL: electrochemiluminescence; GO: graphene oxide; LPE: liquid-phase exfoliation; RP: Ruddlesden–Popper; RT: room temperature; TMDs: transition metal dichalcogenides; MOFs: metal–organic frameworks; TMOs: transition-metal oxides.

Material	Structure	Solution processing	Properties	Ink-based applications
Single elemental				
Graphene	Carbon with a honeycomb structure	• LPE[3] by sonication, ball milling, high-shear mixing or microfluidisation • Ion intercalation • Reduction of GO	• Excellent mechanical properties, tensile strength of 130 GPa.[27] • Transparent, opacity of 2.3% [195]. • High conductivity: Intrinsic conductivity of 10^8 and 10^4 S/m in ink-based devices[196,197]. • Semimetal with zero band gap, shows photoluminescence and electroluminescence[198].	Printed supercapacitors[108]; flexible electronics[153]; printed photodetectors[199]; catalysis[200]; sensors[137]; wearable sensors[201]
Group IV Xenes (e.g. silicene, germanene)	Group IV elements with buckled honeycomb structure[202].	Exfoliation by etchants[203].	• High SOC and QSH at accessible temperatures[28]. • Zero bandgap but tunable with external fields and functionalization.[28] Predicted up to 0.4 eV. • Unstable under ambient conditions.[203] • Easy to modify by functionalization, decoration and doping [202].	Energy storage[203]
Group V Xenes (e.g. phosphorene)	Group V elements with buckled or puckered honeycomb structure.[27]	LPE by sonication[204] or high-shear mixing[205]	• High anisotropy.[27] • Bandgap changes with the number of layers[27] (for phosphorene from 0.3 eV in bulk to 2 eV in monolayer). • High carrier mobilities: up to 5000 $cm^2V^{-1}s^{-1}$ for black phosphorous at RT.[206] • Unstable under ambient conditions[204].	Printed energy storage devices[207]; biosensors[208]; catalysis[209]; printed optoelectronics[58].
Bi-elemental				
hBN	B and N atoms alternate in a single-plane honeycomb configuration	LPE[3]: sonication, ball milling, high-shear mixing[3]	• Large bandgap (5.97 eV) with strong photoluminescence in the UV.[27,29] • Good mechanical properties[27,210] with a tensile strength of 70 GPa. • Electric insulator and transparent. • Very stable. Highly resistant to oxidation and corrosion, and thermally stable up to 1000 C.[210]	Printable FETs [211]; insulator for solution-processed electronics[212]; electrochemical sensing[213].

Carbon nitrides	Structure changes with carbon proportion. C_3N has a honeycomb structure, C_2N, CN and C_3N_4 have a porous single-plane structure.	- LPE by sonication[30] and ion intercalation[214] - Exfoliation by etchants[30]	Due to their different structure, carbon nitrides with different carbon proportions show different properties: • Mechanical properties are better for higher C content. (C_3N has a tensile strength of 100 GPa, C_2N of 60GPa) • Thermal conductivity is higher for higher C content. • Bandgap is higher for lower C content. Most have a high electronic density of states at the band edges (useful for catalysis)[27] and some show ferromagnetic properties[215].	Photoelectrochemical cells[216]; 3D-printed structures for solar wastewater remediation[217]; solution-processed ECL immunosensors[218]
TMDs	Each TMD layer consists of one hexagonally packed transition metal layer in between two chalcogen layers. Each TMD can crystallize with different crystal structures.[16]	LPE[3]: sonication, ball milling, high-shear mixing, ion intercalation.	• Stiffness decreases with increasing chalcogen atomic number; also depends on the TMD phase (1T or 2H)[27] • Layer-dependent properties: Mo and W TMDs show an indirect-to-direct band gap transformation when the number of layers is reduced.[27] • Sizeable band gap in semiconducting TMDs[219] (for example the bandgap of MoS_2 increases from 1.3 eV in bulk to 1.8 eV in the monolayer). • Most are redox active.	Printed photodetectors[35]; solution-processed electronic devices[13]; solution-processed organic solar cells [220]; photoelectrochemical electrodes[221]; energy storage [34]
Others				
MXenes	The general formula is $M_{n+1}X_nTz$; with M a transition metal, X C and/or N, and T surface terminations, n= 1 to 4. M can be a single transition metal or a combination of two in a solid solution or segregated layers.[189].	Exfoliation by etchants and sonication.[36,222]	• Surface terminations add new functionalities, for example MXenes with -O surface terminations behave as TMOs and are redox-active.[38] • Good mechanical properties but depends on the compound. $Ti_3C_2T_x$ has a Young's modulus of 333 GPa and a tensile strength of 17.3 GPa.[38,223] • Negative Z potential allows to form inks of stable colloidal solutions.[38] • Metallic behaviour, but some are predicted to be semiconductors under certain surface terminations,[38] for example, $Ti_3C_2(OH)_2$ can be a narrow-bandgap semiconductor. • High conductivity, for $T_3C_2T_x$ up to 15000 S/cm[117].	Energy storage[89,127]; biosensors [140]; optoelectronics[224]; electromagnetic shielding[96]; wearable sensors[141,143]

2D MOFs	Periodic structures composed of metal nodes linked by organic ligands.	- LPE by soaking[225], sonication[225], solvothermal [225], microwave[225], ball milling [226], ion intercalation[226] - Freeze-thaw[226]	• Compositional diversity; the wide selection of metallic clusters and linkers provides different functionalities[40] • Ligands and clusters can be substituted after synthesis, increasing their versatility [40].	Catalysis[227]; gas sensing[228]; biomedical sensors [229]; regenerative medicine[230]; electronics
TMOs	Can be layered or non-layered; layered TMOs are more common for solution processing and ink formation.	- LPE[43] by intercalation, sonication, heating[43] - Synthesis on washable templates[231]. - Self-assembly[232] - Hydrothermal[42] - Solvothermal[42] - Microwave-assisted liquid-phase growth.[42]	• Many feature reversible redox reactions. [43] • Excellent chemical and thermal stability. [43] • Some show ferroic behaviour.[233] • The oxygen termination facilitates functionalization.[43] • Oxygen vacancies allow the adjustment of certain properties (e.g: MoO_3 bandgap can be adjusted between 2.8 and 3.6 eV[234])	Printed electronics [235]; energy storage[95]
Perovskites	2D perovskites can be categorized into three sub-families[48]: organic–inorganic mixed halide perovskites, inorganic halide perovskites and RP perovskites.	- LPE by sonication[49] - Colloidal synthesis[49]	• High structural and compositional tunability[49]; by changing the anions and cations in their building blocks new materials can be obtained. • Tunable bandgap by small compositional changes.[49] • High PL quantum yield[48], up to 53% in colloidal 2D RP microdisks. • High optical absorption coefficient.[236]	Photovoltaics[237]; light-emitting diodes[238]; printed photodetectors [164]

Table 2. Methods for depositing 2D inks and their main features. R2R: roll-to-roll; *Z*: inverse Ohnesorge number; *G*': elastic modulus; *G''* viscous modulus.

Technique	Resolution	Substrate	Deposition thickness	Throughput /Speed	Ink requirements	Ink modifications	Features
Methods for printing 2D films							
Drop casting	-	No particular requirements	No particular limits	Low–medium	No particular requirements	Forming azeotropic mixtures[74]; inert gas purging[75]; creating a saturated solvent environment[76]	Pros: low cost; simple. Cons: Low film quality; lack of control.
Spin coating	-	Plastic, silicon	>1 nm[239]	Low	No particular requirements	Using high-quality, thin 2D sheets[79]	Pros: Low cost; high-quality and

		wafer/glass, metal					ultrathin film fabrication. Cons: limited deposition area and thickness; material losses.
Spray coating	>100 μm (determined by shadow masks)	Plastic, silicon wafer/glass, paper, fabric, metal	5 nm–30μm[150,240]	Medium – high (0.3–20 m/min)[241,242]	Low solid content; low viscosity (1–100 mPa·s); solvents with high boiling point	Using two-solvent systems[100], using additives (surfactants, polymers)	Pros: relatively high throughput; uniform coverage; ultrathin film manufacturing. Cons: material losses; masks needed.
Screen printing	Typically 100 μm (<50 μm can be achieved)[243]	Plastic, glass, paper, metal	0.1–125 μm[117,243]	Medium–high (70–100 m/min in R2R mode)[85]	Relatively high viscosity (500–10000 mPa·s)[84,85]; shear thinning; medium shear yield stress; solvents with low volatility	Adding binders (mainly soluble polymers)[9]; inducing gelation	Pros: high throughput; high compatibility with various inks and substrates Cons: relatively high prototyping cost.
Gravure and flexographic printing	Typically 100–200 μm (<30 μm can be achieved)[86]	Plastic, paper, metal (highly flexible substrates)	<5 μm[86,88]	Ultrahigh (>100 m/min)[3]	Medium viscosity (50-2000 mPa·s); solvents with low boiling point	Adding binders[86]	Pros: ultrahigh throughput. Cons: high set up and prototyping cost; large ink quantities required.
Methods for printing 2D films and 3D architectures							
Ink-jet printing	Typically > 20 μm[69,92,94] (<10 μm can be achieved)[244]	Plastic, silicon wafer/glass, paper, fabric, metal	>5 nm[4]	Low-medium (1-10 m/min)[242]	Very low viscosity: 4 - 30 mPa·s[84]; Appropriate Z values: 1 – 14; Appropriate sheet size (< 1/50 of nozzle diameter)[97]	Adding additives (surfactants, binders, stabilizers)[245]; Solvent exchange or two-solvents systems[20].	Pros: digitally controlled direct writing; minimal material waste; low prototyping cost. Cons: relatively complex ink formulation; low throughput.
Extrusion printing	>5 μm [246]	Plastic, silicon wafer/glass, paper, fabric, metal	> 1 μm[247]	Medium (<4 m/min)[248]	High viscosity (> 10^2 Pa·s)[249]; Distinct shear thinning; High G' (>100 Pa) and appropriate ratio of G'/G'' (>1 at lower frequencies), high shear yield stress[79,81]	Adding additives/binders[105]; Using larger 2D sheets[79,104]; Inducing gelation[108]; Functionalizing 2D sheets[106]	Pros: capable of generating complex hierarchical structures; minimal material waste; low prototyping cost. Cons: complex ink formulation

Figure 1. Structure of selected 2D materials. For each materials family, the top and side view of a representative material are shown. (a) Graphene, (b) group IV Xenes, with silicene as an example, (c) group IV Xenes, with phosphorene as an example, (d) hexagonal boron nitride (hBN), (e) carbon nitrides, with C_3N as an example, (f) transition metal dichalcogenides (TMDs), with MoS_2 as an example, (g) MXenes, with Ti_3C_2 as an example, (h) 2D metal–organic frameworks (MOFs), with Zn(1)(DMF) as an example (DMF is dimethylformamide), (h) 2D Ruddlesden–Popper perovskites with chemical formula $L_2A_1B_2X_7$, where L is the long chain molecular cation, A and B are cations and X an anion, and (j) transition-metal oxides (TMOs), with V_2O_5 as an example. Panels a, d, f and g are reproduced with permission from ref. [1] (Nicolosi et al.); panels b, c, e and j from ref. [27] (Liu et al.); panel i from ref [48] (Lan et al.); panel h from ref. [250] (Foster et al.).

Figure 2. Ink preparation by liquid-phase exfoliation. (a) Schematic representation of the main categories of liquid-phase exfoliation (LPE) processes. (b) Purification of 2D materials dispersions obtained by LPE. The inset shows a TEM micrograph on an exfoliated flake of MOS_2 (c) Examples of 2D materials inks. Reproduced with permission (b)[1] (Nicolosi et al.) and (c)[251] (Smith et al.).

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Figure 3. Techniques for depositing 2D inks. Schematics of different deposition and printing techniques: (a) drop casting; (b) spin coating; (c) spray coating; (d) screen printing; (e) gravure printing; (f) flexographic printing; (g) ink-jet printing (CIJ: continuous inkjet; DOD: drop-on-demand inkjet. Note that DOD is the mostly used technology); (h) extrusion printing. (i) Overall comparison of achievable resolution, throughput, rheological requirements, prototyping cost and film deposition thickness of the different printing techniques (more details are listed in Table 2). Modified screen printing in flatbed automated and roll-to-roll modes can have very high throughput, up to 70–100 m/min[84,85]. Panels b, c, and g adapted from ref. [12] (Bonaccorso et al.), Wiley. Panels d, e, and f adapted from ref. [3] (Hu et al.), Royal Society of Chemistry. Panel h adapted from ref. [103] (Ahn et al.), AAAS.

Figure 4. Applications of 2D inks. (a) Electrochemical cells: 2D materials can work as cathodes and/or anodes: ions intercalate in or are extracted from the 2D layers[252]. (b) Chemical sensors: 2D materials are responsive to various chemical species, such as biomolecules, ions and gases. These species change the local charge carrier concentration in the 2D material, altering its electrical conductivity and generating signal information. (c) Electronics: in liquid-gated thin-film transistors, transition metal dichalcogenides MS_2 (M = Mo, W and Re) can act as channels. V_{ds}, source–drain voltage, V_G, gate voltage [156]. (d) Bioengineering: when irradiated with near-infrared laser light, MXenes (Ti_3C_2 in this example) generate heat, and can hence act as photothermal agents for cancer therapy[179]. The near-infrared light is less harmful to normal cells and tissues away from the MXenes. Panel a adapted from Ref. [252] (Bonaccorso et al.), c from Ref. [156] (Ippolito et al.), d from Ref. [179] (Pan et al).

Figure 5. Technology Readiness Level (TRL) of applications using 2D inks. The scale ranges from 1 (basic principles observed) to 9 (full commercial application). The bottom timeline indicates when each application might become commercially available. Applications outlined by a dashed line involve printing techniques. PV: photovoltaic; TCFs: transparent conductive films. Data come from the Graphene Flagship annual reports [253,254], Graphene flagship Technology and Innovation Roadmap[192]; for structural materials from Refs.[255–257]; for coatings and liquids from Ref.[257]; for energy storage and generation from Refs.[170,258–260] and from https://www.skeletontech.com/ultracapacitor-technology and https://bedimensional.com/applications/; for sensors from Refs.[85,261–263] and from https://www.dropsens.com/en/screen_printed_electrodes_pag.html.

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Author Contributions

All authors contributed equally to the writing of the manuscript.

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