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TOPICAL REVIEW

The future of Xenes beyond graphene: challenges and perspective

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Abstract

After more than ten years since the silicene discovery, many Xenes, the class of elemental graphene-like lattices, have now enriched the two-dimensional periodic table of elements. Here, we provide a perspective on the future of the Xenes by briefly summarizing their properties and devices reported thus far. Two main challenges are expected to focus the scientists' attention to bring the Xenes to the next level. To step over the current scenario the Xenes need standardization either in the growth or in the fabrication of devices, aiming at the wafer-scale and the reliability and stability, respectively. The benefits arising from these challenges will enable the concept of hybrid Xenes and hybrid Xenes-based devices, that is a combination of different Xenes with new properties and multifunctional Xenes-based devices, respectively, with potential unexpected fascinating properties to continue the journey.

The existence of two-dimensional (2D) materials was demonstrated by 'slicing' a three-dimensional (3D) crystal in a very simple way [1]. Indeed, peeling a graphite crystal using tape was a funny Friday night experiment carried out in Manchester in 2004 scarcely supported by theoretical background as the Mermim–Wagner theorem stated that 2D materials should not be stable against thermal fluctuations [2, 3]. After the graphene boom, 'discovering' new 2D materials was quite simple as the experimental setup consisted of a van der Waals stacked crystal, a roll of scotch tape, and a lot of patience. In such a way graphene was not alone and single-layer MoS_2 and phosphorene appeared on the stage [4, 5]. The Xenes, the elemental graphene-like crystals, joined the 2D materials family in a different way. In fact, well before the isolation of graphene, Takeda and Shirashi wondered about the possibility to arrange silicon and germanium atoms in a graphene-like fashion by introducing a buckling, i.e. a distortion, in the planar lattice [6]. Their surmise was later confirmed by Cahangirov *et al* showing that low-buckled silicene and germanene are lower in energy than the flat structure and have no imaginary phonon modes in contrast to the lowest energy high-buckled configurations [7]. Despite the positive theoretical background and in absence of a parental 3D crystals to peel off, the experimental realization of silicene (but also germanene) turned out to be more complicated than graphene and MoS_2, until the observation of massive silicene nanoribbons on Ag(110) suggested that the molecular beam epitaxy (MBE) way could have been a suitable methodology to succeed [8]. Eventually, in 2012 the epitaxial growth of silicene on Ag(111) was reported [9]. On the one hand, the epitaxial growth onto supporting substrates makes the Xenes lateral size limited only by the area of the substrate itself. On the other hand, the absence of perfectly lattice-matched surface termination of the substrates gives rise to Xenes reconstruction of the freestanding lattice, whose properties may differ significantly from those theoretically predicted [10–13]. For instance, the observation of Dirac fermions in silicene on Ag(111) was long debated in literature mainly because of the band-folding issues arising from the reconstructed silicene, originating a 4×4 silver superstructure, as a freestanding silicene 3×3 supercell matches the 4×4-Ag(111) supercell [9, 14, 15]. This silicene phase was the first compelling experimental observation of a graphene-like lattice made of silicon atoms and ignited the race to find other Xenes [16, 17]. Following the path of silicene, two key aspects were considered to pursuit the scope. First, the use of MBE was preferred aiming at a precise calibration of the deposited films in ultra-high vacuum (UHV) environment onto lattice-matched substate,

Table 1. Timeline of the synthesis of the Xenes.

YEAR	XENE
2012	Silicene
2014	Germanene, black-phosphorene
2015	Stanene
2016	Borophene, blue-phosphorene, antimonene
2017	Bismuthene, selenene, tellurene
2018	Gallenene, arsenene
2019	Plumbene, violet-phosphorene
2020	Thallenene
2021	Indenene
2023	Molybdenene, beryllene
2024	Goldene

like Ag(111), which turned out to be extremely versatile to accommodate many Xenes like borophene, silicene, germanene, stanene, blue-phosphorene, antimonene, and bismuthene [9, 18–24]. Second, benefiting from the UHV environment, the identification of the Xenes properties was carried out by advanced techniques like scanning probe microscopy (e.g. scanning tunneling microscopy/spectroscopy) and angle-resolved photoelectron spectroscopy for the morphological and electronic characterization [25]. In this framework, the experimental observation of Xenes on substrates flourished and to date, by also considering support from chemical methods, the Xenes family gathers the crystals listed in table 1.

Although this list is hopefully incomplete, as there is plenty of room for new Xenes or new shapes of the Xenes already discovered, hitherto the elements of group IIIA of the periodic table giving rise to the respective Xenes are: boron, gallium, indium, and thallium. These Xenes are light and typically show metallic behavior thus being useful for optically transparent electrodes, highly confined near-infrared and visible plasmons, and contacts for 2D devices applications [26–28]. The elements belonging to the group IVA, for either isoelectronic affinity with carbon or for historical reasons related to the semiconductor industry, attracted enormous interest, and the ones showing a Xene counterpart are silicon, germanium, tin, and lead. These Xenes are probably the most studied ones so far and they are quantum spin Hall insulators (QSHIs), with the exception of plumbene (that needs an electron doping to become QSHI [29]), i.e. the 2D topological phase where an insulating bulk coexists with metallic edges characterized by conduction of charge and spin in gapless edge states without dissipation. The size of the bandgap increases falling from carbon (yes, graphene has a small but nonzero gap!) to tin as the quantum spin Hall insulating state is ruled by the spin-orbit coupling effect (that scales as Z^4, being Z the atomic number) ranging from 1.55 to 73 meV in their freestanding forms [30]. In this framework, finding a topological *knob* to switch on and off the topological properties of the QSHIs is of paramount importance for the applications, e.g. the topological field-effect transistor (FET). Indeed, the transition from trivial to non-trivial topological phase and vice versa can be induced via magnetic and electric fields, chemical functionalization, and strain [31]. Intriguingly, for germanene such a transition has been experimentally demonstrated using the electric field of a scanning tunneling microscopy tip [32]. In light of the previous observations on the modifications induced by the substrates to the freestanding lattices, the Xenes of group IVA turn out to be conceived for a broad range of applications, even if their sizeable bandgaps (either by topology or by engineering) make them prone for (topological) electronic, photonic, biomedical and nanomedicine, photocatalytic, energy storage and conversion, thermoelectric, and spintronic applications [33–37]. The elements of group V like phosphorus, arsenic, antimony, and bismuth probably give rise to the most heterogenous group of Xenes as their properties cannot be simply classified as long as they include thickness-dependent semiconductors like phosphorene (of different colors: black, blue, violet… [38]), arsenene, antimonene, and QSHI like bismuthene [39–42]. In light of the electronic properties of this group, the many applications include, but are not limited to, electronics, optoelectronics, biomedicine, thermoelectricity, photocatalysis, photodetection, batteries, and so forth. Conversely, selenium and tellurium in group VIA can be reduced to Xene correspectives, selenene and tellurene, that are endowed with a (thickness-dependent) semiconducting character, which suggests their use in neuromorphic computing, optoelectronics, thermoelectricity, etc [43]. Out of the columns listed above, recently the synthesis of molybdenene, using MoS_2 as precursor, beryllene, via sonochemical exfoliation, and goldene, through wet-chemically etching away Ti_3C_2 from Ti_3AuC_2, should be considered to date as the farthest Xenes in the periodic table from the forbear carbon [44–46]. On the one hand, the wealth of properties thus far reported on the discovered Xenes makes them appealing to afford the many challenges in nanotechnology (see below), but, on the other hand, the toll to pay for such a versatile scenario is a much more complicated growing and handling of the Xenes in comparison with the more mature 2D materials like graphene and transition metal dichalcogenides (TMDs).

1. Challenges: wafer-scale growth and device standardization

The Xenes listed in table 1 can be grown mostly by physical vapor deposition methods, but also chemical methods have been reported. MBE is the principal synthesis method used for the growth of the Xenes because of its fine tuning of the deposition rate (fundamental in order to growth atomic-thick films) and the UHV environment allowing for clean deposition

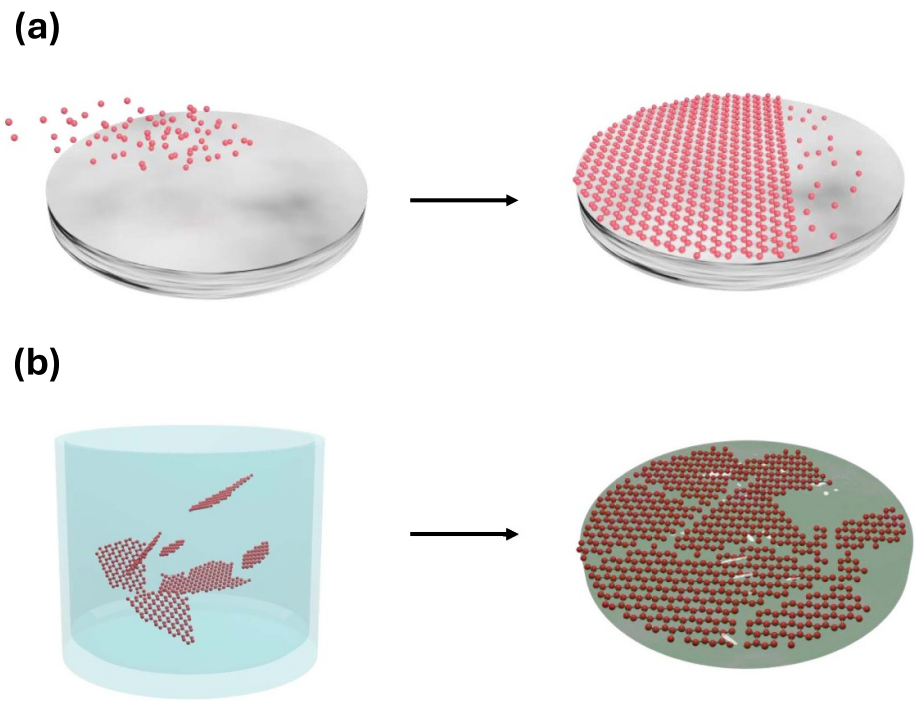

Figure 1. Physical and chemical methods for the large-scale growth of the Xenes. (a) Physical deposition of the Xenes from a solid source on a wafer-scale substrate in a controlled environment to achieve the largest possible size of the high-crystalline Xene with few defects to be used for applications like logic devices. (b) Chemical method for massive production of Xenes flakes with variable (hardly controlled) lateral size to be drop-casted onto a wafer-scaled substrate or embedded into matrices aiming at applications where the high-crystallinity of the Xenes is not requested, like memristors.

and enabling the most used electronic microscopy and spectroscopy investigation tools [25]. Although quite expensive and typically limited to the research environment, MBE allows the growth of the indefinitely scalable Xenes, only limited in size by the dimensions of the system, specifically of the adopted substrate and the solid material's source (i.e. the evaporator of the X element). This methodology therefore is well-suited for the wafer-scale growth of the Xenes challenge (figure 1(a)). Indeed, the large-scale growth of borophene on Cu(111) with single-crystal domains up to 100 μm^2 has been confirmed via low-energy electron microscopy [47]. Also on Cu(111), the synthesis of chiral blue-phosphorene turns out to be limited by the substrate size [48]. The stanene growth on Ag(111), benefitting from a Ag_2Sn buffer layer, shows domains as large as 5000 nm^2 [21]. Even for the silicene growth on top of the Ag_2Sn buffer layer, a 'phase-filtering' is observed resulting in the growth of a single silicene superstructure (i.e. 4×4) at variance with the direct growth on bare Ag(111) where different silicene superstructures coexist (i.e. 4×4, $\sqrt{13} \times \sqrt{13}$, and $2\sqrt{3} \times 2\sqrt{3}$) [49]. It is not quite surprising that the best achievements are to date reported onto metallic substrates that, on one hand, favor the epitaxial growth by MBE and, on the other hand, can be easily accessed by electronic probes. Although the Xenes can be grown also on non-metallic substrates, e.g. MoS_2 or Al_2O_3 [50–53], hitherto a similar approach on the large scale synthesis has not been reported yet. While the physical deposition methodologies described above address the technological challenge of a uniform wafer-scale deposition, chemical-based approaches are considered to directly synthesize Xene nanosheets, and their functionalized forms, in gram-scale quantities with low costs (figure 1(b)). The typical chemical approaches adopted for the synthesis of Xenes are based on the topotactic transformations of the corresponding Zintl precursor [54] or the chemical exfoliation of the nanosheets, by stirring or sonication, in those cases where the layered bulk forms or a powder of the Xene exist [55]. As an illustrative example of the topotactic deintercalation, in the $CaSi_2$ precursor, the silicon atoms are covalently bonded in a puckered honeycomb framework with anionic character, while the calcium atoms act as a cation species in the interlayer spaces. The production of silicene nanosheets proceeds from the deintercalation of the Ca^+ ions in acid solutions at low temperatures (−30 °C–0 °C) for several days [56]. After different process steps, which include filtration and drying, the layered material is reduced in a powder form constituted by flakes (with micrometer scale lateral size) in which a silicon backbone is typically terminated with hydrogen atoms (reports indicate also the presence of O, OH, and alkyl groups as a minor functionalization of the layer) [57]. Inspired by the realization of silicene nanosheets, researchers have turned their

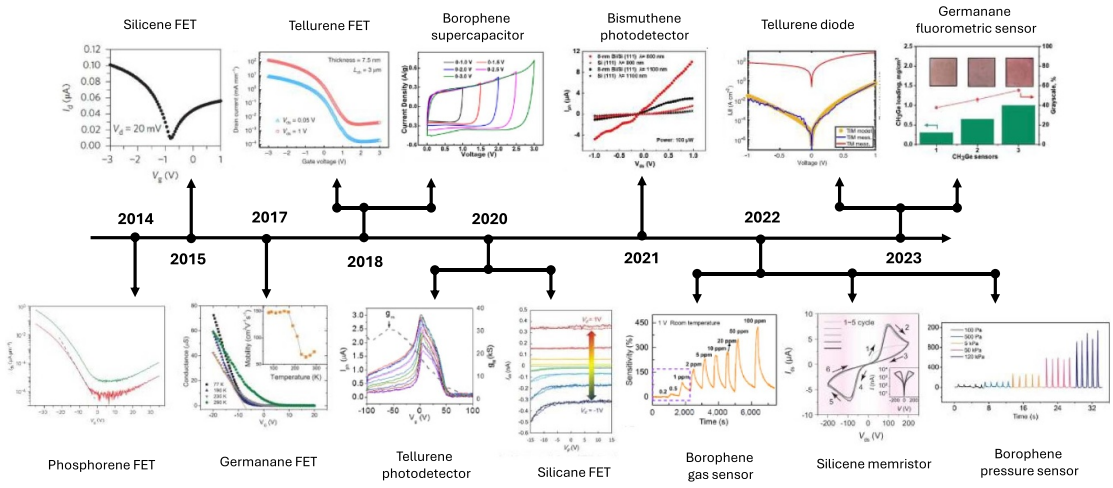

Figure 2. Non-exhaustive timeline of the experimental realization of Xenes-based devices. Reproduced with permission from [63]. Reproduced with permission from [91]. Reprinted with permission from [92]. Copyright (2018) American Chemical Society. Reproduced from [93]. © IOP Publishing Ltd All rights reserved. Reproduced from [66]. CC BY 4.0 [88]. John Wiley & Sons.© 2023 The Authors. Advanced Materials published by Wiley-VCH GmbH. Reproduced with permission from [94]. Reproduced from [65]. © IOP Publishing Ltd CC BY 3.0. Reprinted with permission from [95] Copyright (2020) American Chemical Society [96]. John Wiley & Sons. © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reprinted from [97], Copyright (2022), with permission from Elsevier. Reproduced from [98]. CC BY 4.0. Reproduced from [99], with permission from Springer Nature.

attention to the topotactic intercalation of the Zintl phases of germanium. Indeed, germanium forms a layered puckered honeycomb framework with an electropositive element of the group 2 in the interlayer spacing in $CaGe_2$ precursor [58]. Alternatively, the liquid-phase exfoliation from powders in various solvents has been successfully reported for the synthesis of phosphorene, borophene (from either boron or sodium borohydride), antimonene, beryllene nanosheets [45, 59–62].

The demand for uniformity and defect-free quality along the scalable production generally represent go/no-go steps for the 2D materials to access integration in electronics and photonics. Indeed, many prototypical devices based on 2D materials, including the Xenes, e.g. FETs, diodes, photodetectors, sensors, and so on have been reported thus far (figure 2) [63–68]. The borophene and tellurene cases are instructive because they can be grown by different either physical or chemical methods. This ease of growth in turn enabled the fabrication of the devices without complicated processes, such as for instance those needed for those Xenes grown by MBE. The obvious improvements that will follow up the seminal demonstration of these devices will be anyway purposeless without a continuous effort on the Xenes growth quality. In particular, the outcomes demonstrated that Xenes show multifunctional properties making them suitable for integrated circuits, where, for instance, logic and memory tasks are simultaneously required. In this framework, as recently reported for TMDs [69–71], further advancements are still needed for massive production of integrated circuits based on the Xenes. In addition to large-scale growth, the difficult handling of (most of) the Xenes out of vacuum requires the concomitant development of dedicated processes. The commonly used silicon and/or silicon dioxide wafers to date cannot host the growth of Xenes. Typically, metallic substrates show favorable conditions for accommodating 2D artificial lattices. Among the most adopted templates, silver with surface termination (111) deserves a particular mention as it can accommodate different Xenes. Therefore, a viable route to disclose the large scale growth of the Xenes might be the use of as thin as possible metallic films, e.g. silver, deposited on silicon/silicon dioxide [72]. This wafer-like solution could be subsequently processed using the recently developed transfer methods taking care to avoid deteriorating the as-grown Xene [73–76]. Moreover, in the same growth environment, it is possible to protect the top face of the Xene (the bottom one is in contact with the substrate) by means of protective layers to avoid degradation in ambient conditions (not for all the Xenes). This all-around encapsulation scheme has been proposed for silicene but can be generally extended to all the Xenes [77]. In particular, the choice of an oxide like Al_2O_3, among different options available like graphene or hBN [78, 79], turns out to be interesting in an electronics or photonics context where a gate oxide or a transparent layer might be effective for charge modulation or optical investigation in a broad range of the electromagnetic spectrum, respectively [51, 52, 63, 64]. Even though room temperature amorphous Al_2O_3 proves to protect silicene from oxidation and can be used for accessing its electronic and optical properties, the main issue is however related to the narrow thermal budget that can be provided on top of the Xene, because of its metastable nature, to improve the quality of the deposited oxide, although for many

applications the presence of a crystalline layer is not strictly necessary. For this reason, further research on the growth of Xenes (but generally speaking of 2D materials) in the heterostructures fashion should be aimed at extending the encapsulation process on the wafer-scale as well. One of the main advantages of using chemical synthetized Xenes relies on the relatively easy incorporation of the Xenes flakes into functional polymeric frameworks or solutions [80]. The first challenge to address in these approaches is understanding the specific chemical and physical interactions of the Xenes with the individual constituents of the polymeric frameworks or solution. Indeed, if on one hand, the chemical decoration of the Xene flakes may represent a viable strategy to tune or trigger novel properties (see below), on the other hand the interaction with specific chemical groups may cause the structural degradation of the Xene itself [81]. This constraint has pushed the researchers to undertake non-conventional embedding strategies, which are dependent on the specific Xenes in use or targeted applications [80]. As an example, the creation of Xenes-based inks or solutions, that can be respectively printed or drop-casted on arbitrary substrate at a large scale (figure 1(b)), opened the door to applications where the overall (crystalline) quality of the deposited material can be lower compared to the high-standard quality required in micro- and nano-electronic applications. For instance, this is the case of flexible electronics or catalytic applications, where also the presence of defects (grain boundaries, lattice vacancies, and so on) might be useful to activate mechanism of atom diffusion and charge transfer boosting the performance of the Xenes-based devices. Another explored strategy to embed the flakes into a functional matrix is their integration into complex networks created using synthetic or natural fibroins/polymer (silk, chitosan methacrylate, …) by means of techniques like electrospinning or hydrogel crosslinking [82–85]. These approaches have found their natural field of application into the production of biocompatible composites for biomedicine (tissue engineering, *in-vivo* monitoring and implantation, cancer therapy, etc) [86]. Multiple studies demonstrated that the properties of the Xenes obtained by chemical methods can be dynamically adjusted decorating the nanosheets with different functionalizing groups [87]. Among these, the tunability of the photoluminescence emission has attracted significant attention as a tool for developing real-time sensors of gaseous species or pH levels [88]. In addition, the rapid response to near-infrared radiation (in terms of a strong optical absorption) and the surface chemical reactivity have sparked the interest of researchers towards the application of the Xenes nanosheets in the field of biomedical and theranostic applications [86]. For instance, they have been proposed as carrier medium of selected molecules for targeted delivery of multi-responsive therapeutics to the desired sites. In this framework, the Xenes can boost the development of novel therapeutic methodologies, for example in cancer treatment [89], or in the regenerative medicine with the aim of engineering and restoring various tissues, including bone, cartilage, nerves, muscles, and skin [90]. However, several critical challenges must be addressed in view of exploring the applications of Xenes in biomedical applications. Indeed, their safety and biocompatibility are crucial aspects to be confirmed by specifying the exact chemical composition and functionalization of the produced flakes and thus developing more reliable and robust synthesis processes [57]. At the same time, the development of standardized workflows for the chemical production of Xenes is highly desirable in view of a scale-up of the production from the lab-quantities (gram-scale) to the fab-quantities (kilogram-scale).

2. Future directions: hybrid-Xenes and hybrid Xenes-based devices

On top of the above-mentioned challenges, further efforts should be devoted to pursuit the following research directions. In a materials science framework, the Xenes are an open playground for the manipulation of matter at the atomic scale and order. The possibility to explore different Xenes phases changing their properties via interaction with the supporting substrates makes them versatile materials for further engineering or functionalization more than other 2D materials [100]. The idea here is to engineer hybrid materials whose properties are more than the sum of each component (figure 3(a)). Moreover, combining different Xenes together in a heterostructure fashion add a further degree of freedom, even considering the outcomes in twisted graphene layers [101]. Although controlling the twist angle in an epitaxial framework is not so trivial, it cannot be ruled out that one can take benefit from different matching layout with substrates, and eventually gives rise to radically new hybrid configurations as those recently demonstrated by van der Waals epitaxy [102]. However, this represents a stimulating opportunity to synergistically merge the physical and chemical methods in a new subject. Indeed, it is possible to consider the epitaxial growth of a first Xene on a substrate on which a second Xene, obtained by chemical method, is drop-casted thereby allowing for tuning the twist angle in a Xene-based moiré lattice. This scenario requires a specific environment to work, thus being also a technological challenge beyond the scientific one. Organizing these hybrid systems into ordered structures poses several challenges in terms of reproducibility, scalability, processability and structural integrity of the different constituents. For instance, taking into account the reproducibility, variations in the production process can lead to differences in the

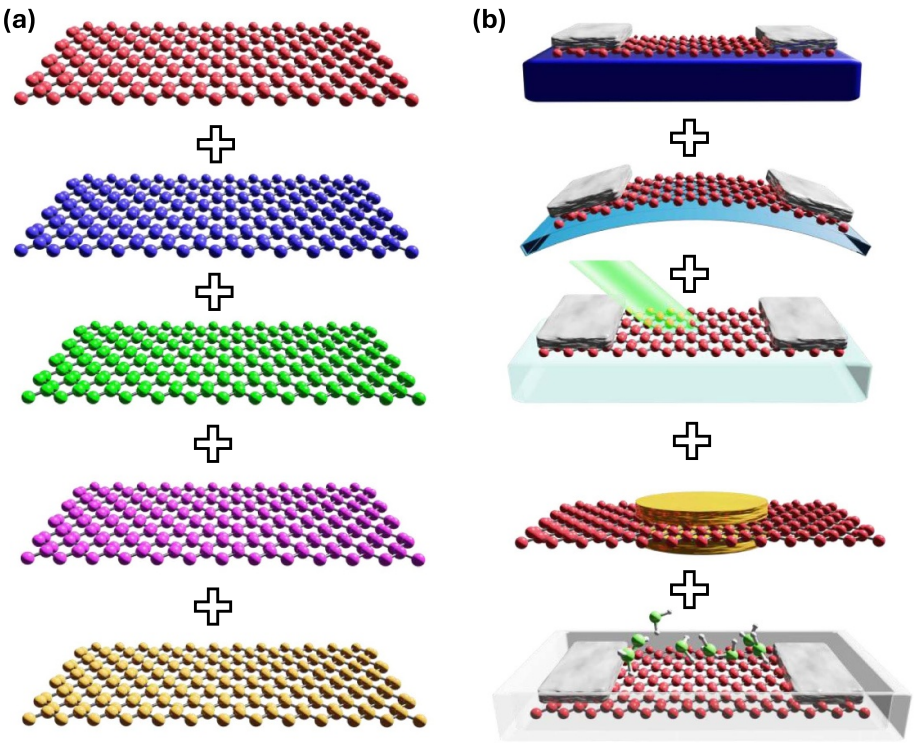

Figure 3. Sketch for the hybrid Xenes and hybrid Xenes-based applications. (a) From top to bottom different Xenes (represented in different colors for graphical purpose) can be combined together aiming at the formation of new materials with unprecedented properties. (b) From top to bottom different Xenes-based applications that include, but not limited to, electronics (e.g. FET), flexible (e.g. bendable membrane), optoelectronics (e.g. phototransistor), memory (e.g. resistive switch or atomristor), catalysis, energy, biodetection and biosensing (e.g. hydrogen evolution reaction). All these applications can be combined in the formation of hybrid devices capable of multifunctional tasks.

properties of the hybrid systems which can significantly affect their performance when integrated into devices. At the same time, the integration of hybrid 2D materials into existing manufacturing processes and commercial devices requires them to be easily processable. This includes compatibility with techniques like wet and dry etching, lithography, spray coating, inkjet printing and so forth. Additional technical challenges to afford will rely on the thermodynamic growth conditions for the epitaxial growth of the Xenes, e.g. substrate temperature, as well as their flakes size variability when obtained by chemical methods. Clearly, strong support from *ab initio* calculations is necessary to determine the interesting configurations of Xenes on substrates, Xenes heterostructures, and twisted Xenes heterostructures. In a different direction, hybridization of Xenes with other 2D materials leads to custom and/or additional functionalities, like—to say a few—chemical/structural stabilization, mechanical flexibility, bandgap opening and electronic bandstructure design, non-conventional optical absorption and responsivity, *ad hoc* catalytic performance or chemical reactivity, non-trivial topological character, etc. Xenes-based hybrids consist of combinations of Xenes with other 2D materials, including graphene (silicene–graphene, phosphorene–graphene [103, 104]), hexagonal boron nitride (e.g. hBN/phosphorene [105]), TMDs (phosphorene-TMDs [106]), and can be made by direct Xene growth (silicene/MoS_2 [107], germanene/MoS_2 [53]) or Xene transferring onto a 2D materials template (silicene/MoS_2 [73]), or by encapsulating the Xene with a 2D material cap (graphene/silicene [79]). Therefore, designer Xenes hybrids with tailored structural order, precise chemical compositions, and controlled interlayer coupling, is a new path to gain synergistic or completely novel properties that would not be available at the single Xene stage. On the other way around, individual Xene may serve as 2D template to build up unconventional 3D materials with radically new properties from the conventional 3D bulk. For instance, stanene is the precursor for the growth of slightly distorted α-Sn nanosheets on InSb displaying topological insulating or topological Dirac semimetal character in case of compressive or tensile epitaxial strain, respectively [108]. Similarly, silicon grown from a silicene template is observed to display completely different electronic character [64] and optical responsivity up to a certain thickness threshold in

the nanoscale regime [51]. Concomitantly, in a nanotechnology framework, the demonstration of Xenes-based devices has been reported showing promising advantages in specific fields of applications (figure 2). Yet again, the use of the hybrid Xenes with improved integration protocols might undoubtedly bring substantial advantages in electronics, photonics, neuromorphic computing and so on, even beyond the contribution of the single Xene. However, on the basis of the engineered Xenes properties, it would be of paramount importance to pursuit the manufacture of hybrid devices capable of multiple functionalities (figure 3(b)). Examples of increasing complexity are the fabrication of MoS_2-based memtransistors [109, 110], graphene-based moiré synaptic transistors [111], and most importantly, asymmetric van der Waals heterostructure devices that can function as a diodes, transistors, photodetectors and rectifiers [112]. Hitherto similar evidences have not been reported on Xenes-based devices, even if the recent findings on bendable silicene membranes proved that cooperation between stanene and silicene turns out to improve the sensitivity of silicene to the application of strain making the realization of a silicene-based piezoresistor possible (with a third electrode also a transistor) [68]. As per other 2D materials, today it is unlikely that Xenes could start a new industrial revolution by themselves and therefore a progressive integration with the current silicon technology should be sought at first [113, 114].

3. Conclusion

In summary, the future of the Xenes, after more than ten years-long unstoppable research, is at a turning point. Many Xenes have been discovered and prototypical devices have been reported. On these aspects, two important challenges related to the wafer-scale high-quality growth and the standardization of devices will likely attract the efforts of the scientists in this field. Given the extreme versatility of the Xene in the 2D materials framework, the main advantages coming from addressing these challenges will rely on plenty of room in both the materials engineering and the functionalized Xene-based or -related devices. Indeed, as they do not exist *per se* and must be artificially created, they represent a stage where the creativity of the human intellect is the only limit under certain boundary conditions. After twenty years since graphene isolation, the expectations about its impact on our lives perhaps were overestimated as few products on the market truly exploit its properties (mostly the mechanical ones). In this light, the Xenes beyond graphene might team up in the race on both fundamental tabletop physics and lab-to-fab transition.

Data availability statement

No new data were created or analysed in this study.

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