Research Progress and Prospects of Single-Layer 2D Materials Xenes

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Abstract. Xenes, as a series of single-layer two-dimensional (2D) materials, present emerging properties in biological, electronics, medical and other relevant fields. This review introduces seven main Xenes materials (silicene, phosphorene, borophene, antimonene, stanene, germanene and bimetallene) demonstrating higher conductivity and flexibility and describes their current research works and new findings. Besides, current challenges such as those in stability and quality are concluded, and a prospective view on development of 2D Xenes materials in the future is brought out.

1. Introduction
Since the first fabrication of graphene in 2004, 2D materials have attracted considerable attention from researchers. The outstanding physiochemical properties of 2D materials become a leading focus of materials science all over the world with an exponential growth in the fields of Condensed Matter Physics, Materials Science, Chemistry and Nanotechnology. Recently, global scientists proposed and prepared Mxenes, Organic materials, TMD, Nitrides, and other single-atomic layer 2D materials, such as B, Si, P, Ge, Sn, adjacent to C element. This kind of materials called Xenes expands the members of 2D material family, and has new emerging properties that are completely different from bulk-phase materials. However, most previous research works on 2D materials were focused on growth situation as well as theory calculations. Taking silicene as an example, in 2012, Jing Lu group predicted that silicene have tunable bandgap by using ab initio calculations [1]. Professor Kehui Wu proved the existence of Dirac fermions in silicene [2]. Professor Daniele Chiappe and Alessandro Molle investigated that atomic and electronic structures of silicene grown on Ag (111) via using scanning tunneling microscopy (STM) [3]. The aim of this review is to highlight the current new findings and future prospects of Xenes materials combined with other fields such as electronic engineering and bioengineering. Thus, more creative thoughts and direction for practical applications of Xenes materials in the future can be provided.

2. Researches on Xenes materials

2.1. Silicene
Silicene is a nascent representative of 2D Xenes materials. Three silicon atoms in the six-membered ring are separated from the remaining three on two horizontal planes with vertical displacement, and that means there is a displacement in the vertical direction. Single-layer silicene devices exhibit similar electrical transport characteristics to the same single-layer graphene devices, but present higher gate modulation and electrical diversity (e.g., topological phase transition switching devices). More
significantly, silicene, as the allotrope of monocrystalline silicon, has compatibility advantage that other 2D materials lacking.

From biomaterials perspective, silicene is considered as a promising alternative to silicon-based nanomaterials applied in biomedical engineering. Professor Yu Chen and Jianlin Shi converted traditional 0D nanoparticulate system to 2D material system via reasonable design and wet chemical methods. They synthesized 2D silicene nanosheets (SNSs) which exhibits intriguing physiochemical properties, as well as good biocompatibility and biodegradation [4]. The synthesis and characterization of 2D SNSs are presented in figure 1. They discussed about the potential mechanisms and degradation behaviours of silicene-environment interaction under specific stimulated physiological conditions via combining with DFT-based molecular dynamics (MD) calculations. This work indicates the considerable application prospects of 2D silicene, especially on phototherapy of cancer. Due to the chemical sensitivity of silicene hampering its incorporation in layer stacks, the exploration of electronic devices was impeded as well. Therefore, recently, the University of Twente demonstrated that epitaxial silicene and hexagonal boron nitride (h-BN) have good electrical conductivity [5]. They intercalated silicene below epitaxial h-BN on ZrB2(0001) via using deposition technology at room temperature. Finally, they found it has excellent electronic properties and stability. This is a significant start towards the advancement of layer stacks that support to materials production.

2.2. **Phosphorene**

Phosphorene is a 2D semiconductor material separated from black phosphor which is composed of ordered phosphorus atoms and has a direct band gap. Compared with graphene, phosphorene has a folded structure and a reduced symmetry, resulting in two anisotropic in-plane directions. Phosphorene has a wide range of application prospects of the field-effect transistors, optoelectronic devices, spintronics, gas sensors and solar cells. Initially, professor Xianhui Chen and Professor Yuanbo Zhang reported a 2D black phosphorus field-effect transistor with a thickness of a few nanometres in 2014 [6].

![Figure 1. Synthesis and Characterization of 2D Silicene nanosheets [4].](image)
For electrode materials, ionic transport plays a significant role in the rate of rechargeable battery and energy efficiency. Recently, professor Litao Sun from Southeast University dynamically observed the transport of sodium ion between phosphor nanosheets and single crystal nanostructures via using transmission electron microscopy (TEM) technology, and they directly found that the ionic transport between few-layer phosphorene is unimpeded and reversible [7]. Moreover, the transport mechanics of sodium ions also were pointed having intimate relationship with interface orientation and the contact between solid electrodes can inhibit dendrite growth. Finally, professor reported the unique transport behaviour of sodium ion from phosphorene, demonstrating a variety of its transport route at the interfaces with atomic spatial resolution. Meanwhile, black phosphorous also can be applied in biosensing field. Professor Su Chen introduced a new electrochemical actuator based on black phosphorous/carbon nanotubes (BP-CNTs), which, compared with conventional electrode materials, presents higher electromechanical properties and biomimetic values, such as low power consumption and high energy densities [8]. The synthesis and structural characterization of BP-CNTs are shown in Figure 2. More importantly, he exhibited in his paper that ordered layered structure, high redox activity and electrochemical capacitance are key causes of high performance. This found would prompt substantial development of electrochemical actuators in the future.

Figure 2. Synthesis and structural characterization of BP-CNTs [8]
2.3. **Borophene**

Borophene is a 2D planar structure composed of boron elements. Its unique 2D hexagonal honeycomb structure results in Dirac cone energy band structure and relevant quantum effect. Unlike graphene, borophene’s research started from computer instead of laboratory. Theoretical calculations show that honeycomb borophene cannot exist stably in the free state due to the absence of electrons. Previous research works prepared several planar boron clusters; however, it is still hard to fabricate the planar grid structure of pure boron. In 2014, based on the evolutionary algorithm and the first-principles calculation, professor Xiangfeng Zhou and professor Huitian Wang predicted a unique 2D boron structure [9]. In the same year, Lai-sheng Wang and Jun Li synthesized planar hexagonal B36, which was named borophene [10].

Recently, researcher Adrian Gozar from Yale University and his group reported the synthesis of borophene monitored in situ via STM et.al characterization technologies, as well as simulated by ab initio theory. They found that the single-crystal domains of the borophene grown on the Cu (111) is up to 100 µm2, and the crystal structure of borophene is an innovative triangular network as figure 3 shows. Their experimental data combined with the first-principles calculations inferred that there is a charge transfer coupled with the substrate [11]. This research work paved a path for the fabrication of borophene-based devices and confirmed that borophene can be used as an advanced model for artificial 2D materials.

![Figure 3. Growth dynamics of the borophene on the Cu (111) surface [11]](image)

2.4. **Antimonene**

Antimonene is a new type of 2D semiconductor material which is composed of the fifth main group (nitrogen group) element antimony. The first-principles calculation predicts that antimonene has a
good stability and excellent photoelectric performance. The single-layer antimonene is an indirect bandgap semiconductor with high carrier mobility and attractive thermal conductivity. Moreover, the indirect bandgap can be transformed to direct bandgap via strain induction. In 2015, professor Haibo Zeng from Nanjing University of Science and Technology theoretically predicted antimonene material with a wide bandgap and superb stability [12], and discussed its electron mobility [13]. In 2016, Julio Gómez-Herrero obtained a single-layer antimonene via mechanical isolation [14].

Currently, 2D magnetic materials cannot satisfy the practical application due to its low Curie temperature. Nonmagnetic dopants produce sp electron magnetism with a large spin exchange constant and correlation length. Therefore, professor Han Zhang from Shenzhen University cooperated with professor Yujia Zeng and proposed the high-temperature ferromagnetism of 2D F-antimonene materials. As shown in figure 4, F-antimonene demonstrated superior magnetic properties compared to pure antimonene. The sample fabrication utilizes previous electrochemical depilation and synchronous fluorination [15]. This study paves a way to 2D atomic layer-based spin devices. On the other hand, as antimonene is a semiconductor material with fascinating stability, Professor Haobo Zeng, Shengli Zhang and Harald Fuchs selected Cu (111) and Cu (110) as substrates to prepare the high-quality monocrystalline antimonene via MBE technologies. They observed the epitaxial growth of two types of antimonene after spontaneous formation of surface alloys on two substrates via STM, which showed a hexagonal lattice. Finally, they reported that different substrate-induced strain and stress are able to improve electronic properties [16].

![Image](image)

Figure 4. Magnetic properties of F-antimonene and pure antimonene [15]

2.5. Stanene

Theoretical calculation indicates that stanene is a quantum spin hall effect insulator with a large energy gap and can be converted into a 2D topological superconductor. Stanene crystal has significant potential application in the fields of electron non-dissipative transport, spin current generation, high
performance thermoelectricity, optoelectronic devices and topological quantum computation. In 2013, professor Shouchen Zhang initially proposed that the stanine material could achieve 100% conductivity at room temperature [17]. Professor Dong Qian fabricated 2D stanene crystal film via molecular beam epitaxy (MBE) technology and predicted the existence of it theoretically [18].

Stanene as a promising 2D material is expected to be applied in next generation quantum devices. Based on density functional theory (DFT), professor Shunfang Li and Yu Jia from Zhengzhou University explored the growth mechanism of stanene grown on Bi2Te3(111) substrates via the first-principle calculation. The calculation results demonstrated that Sn atoms deposited on the surface of substrates present obvious repulsion interaction in the initial growth stage [19]. More importantly, the film of Bi (111) atomic layer grown on Bi2Te3(111) as a substrate (Bi-Bi2Te3(111)) provides a place for nucleation and growth of deposited Sn atoms, and it is conducive to the stanene crystal. This work will be involved in producing high quality stanene massively with appealing physical properties.

2.6. Germanene

Germanene is a kind of 2D atomic crystal material derived from germanium, hence it has become marvellous research specializations all over the world due to its planar crystal structure of single atom thick, unique physiochemical characteristics and huge potential application value. As a germanium-based counterpart of graphene, germanene has been predicted of its existence and excellent properties which are similar to graphene.

Recently, a novel approach of germanene exfoliation has been presented. The research group of Zdenek Sofer used germanene (Ge6H6) as a stable original material for the fabrication of germanene derivatives, and proposed a creative method of germanene chemistry. They reported the technology of deprotonation, followed by functionalization with pinitrobenzyl bromide. Moreover, they discussed about the ability of alkali metal (Li, Na, K, Cs) to reduce naphthalene, as well as explored specific behaviours of other aromatic hydrocarbons when reacted with sodium [20]. On the other hand, this kind of materials can be applied in intelligent substance of micromachines due to their self-propelled and automatic system. However, micromachines are still facing the obstacle of tracking delivering molecular cargo. Professor Martin Pumera studied the high-stability fluorescent labels of 2D germanene derivatives based on chemical modification. Different fluorescence characteristics makes targeted micromotor can be discriminated under UV irradiation. Figure 6 demonstrates that these microrobots with 2D germanene derivatives remain traceable, which provides a multiple detection of self-driven micromachines [21]. In summary, this new methodology will pave the way to identification of functionalized micromachines in multiple surroundings.

![Figure 5. Tubular microrobots with outer layers functionalized with 2D germanene derivatives][21]
2.7. Bimetallene

Bimetallene is a new type of highly buckled bimetallic nanosheet with sub-nanometre thickness. In 2019, professor Shaojun Guo at Peking University prepared a highly buckled conformation, sub-nanometre-thick bimetal palladium molybdenum (PdMo) alloy nanosheet material, which is named "bimetallene" due to its graphene-like structure. The morphology, structure and composition of PdMo bimetallene are as shown in Figure 7. The density functional theory calculations show that the alloy effect, the strain effect and the quantum size effect modify the electronic structure, and sequentially enhance the oxygen binding on the catalyst surface [22]. As a valuable electrocatalyst for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) in alkaline electrolytes, PdMo bimetallene can improve the properties of Li-air batteries and demonstrate higher mass activity and stability.

![Figure 6. Characterization of the morphology, structure and composition of PdMo bimetallene](image)

3. Perspective of Xenes Materials

Compared with bulk-phase materials, the atom utilization rate of single-layer 2D material has improved significantly because of its almost completely exposed surface. Single-layer 2D materials are easier to regulate the energy band structure and electrical properties via thickness control and element doping, such as silicene and phosphorene.
Although above Xenes materials are extremely promising new member of 2D materials family, a number of challenges impede the potential application progress. For instance, so far there is no practical way for improvement of the overall quality and mass production of 2D Xenes materials. Additionally, Xenes materials with high oxidation cannot be characterized easily. Therefore, the fabrication methods need to be explored continually to solve difficulties in device cost and stability. The reaction activity needs to be prevented through several encapsulation stages. Apart from several discussion in the previous section, overall, Xenes are expected to develop nanoelectronics devices thanks to low power consumption in device operations, and they also can be exploited in energy field due to their robust thermoelectric properties and high ion storage performances.

4. Conclusion
In summary, although not all of research works are reported in this review, several classic and experimental progress of Xenes materials are briefly introduced. Moreover, a wide range of practical research works were presented, such as silicene materials with considerable prospects of cancer phototherapy and advancement of layer stacks, phosphorene applied in the ionic transport of rechargeable battery as well as antimonene magnetic materials of 2D atomic layer-based spin devices. It is expected that this series of functional 2D materials would make a significant progress such as energy storage and smart devices compared with conventional functional materials lacking of outstanding conductivity properties. Meanwhile, they are still facing several challenges in stability and massive production.

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