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# Chapter

# Plasmonic 2D Materials: Overview, Advancements, Future Prospects and Functional Applications

Muhammad Aamir Iqbal, Maria Malik, Wajeehah Shahid, Waqas Ahmad, Kossi A. A. Min-Dianey and Phuong V. Pham

#### **Abstract**

Plasmonics is a technologically advanced term in condensed matter physics that describes surface plasmon resonance where surface plasmons are collective electron oscillations confined at the dielectric-metal interface and these collective excitations exhibit profound plasmonic properties in conjunction with light interaction. Surface plasmons are based on nanomaterials and their structures; therefore, semiconductors, metals, and two-dimensional (2D) nanomaterials exhibit distinct plasmonic effects due to unique confinements. Recent technical breakthroughs in characterization and material manufacturing of two-dimensional ultra-thin materials have piqued the interest of the materials industry because of their extraordinary plasmonic enhanced characteristics. The 2D plasmonic materials have great potential for photonic and optoelectronic device applications owing to their ultra-thin and strong light-emission characteristics, such as; photovoltaics, transparent electrodes, and photodetectors. Also, the light-driven reactions of 2D plasmonic materials are environmentally benign and climate-friendly for future energy generations which makes them extremely appealing for energy applications. This chapter is aimed to cover recent advances in plasmonic 2D materials (graphene, graphene oxides, hexagonal boron nitride, pnictogens, MXenes, metal oxides, and non-metals) as well as their potential for applied applications, and is divided into several sections to elaborate recent theoretical and experimental developments along with potential in photonics and energy storage industries.

**Keywords:** graphene, metal oxides, pnictogens, hBN, MXenes, non-metal plasmonics, photonics

## 1. Introduction

1

Plasmonics is the emerging research field, indicating the ability of materials to control light at nanoscale range to examine them for various properties and functions. The plasmonic materials exploit the surface plasmon resonance effects to achieve astonishing optical properties that originate with light-matter interaction and leads to remarkable results. Surface plasmon can confine electromagnetic fields

at very small scales whereas various structures can be employed to control surface plasmons. Previously, Ag, Au, and Al metals were used as plasmonic materials but they did not perform well because of radiative losses, high amount of energy dissipation, and their poor tuneability. To overcome these problems for efficient plasmonic applications, a class of two-dimensional (2D) materials is proposed which presents a significant light-matter interaction phenomenon resulting in efficient quantum confinement effects. A variety of materials including semiconductors, conductive oxides, and dielectric materials have been investigated as plasmonic materials owing to their extra-ordinary plasmonic properties. Considering the advanced properties along with bandgap manipulation and electron transfer, 2D materials got higher attention for plasmonic applications [1, 2].

Graphene was the first 2D material investigated with zero bandgap having exceptional conductivity because of its high electron mobility. Considering graphene's achievements and enormous applications at the laboratory and industry level, researchers have started investigating further 2D materials to explore their potential for plasmonic applications. Currently, almost 150 members of the 2D materials family are serving in elementary and advanced technologies such as light-emitting diodes (LEDs), Field-effect transistors (FETs), environmental applications, sensing applications, and physical catalysis [3–5]. Some important under discussion members of 2D materials, analogous to graphene are; hexagonal boron nitride (hBN), black phosphorene, metal oxides, metal carbides and nitrides (MXenes), metal halides, pnictogens, and non-metals which are being considered as potential plasmonic materials [6–8]. This 2D materials family exhibits a broad electronic and plasmonic characteristic spectrum covering a wide range of properties such as; high surface area, surface state nature, minimum dangling bonds, spin-orbit coupling, and quantum spin Hall effects [9, 10].

On the other hand, stacking of different 2D materials is also the emerging part of the material industry which yields novel heterostructure materials capable of introducing some building blocks in a materials family with enhanced physical and chemical properties. The novel 2D materials such as metal carbides and nitrides, metal oxides and graphene-based materials have mixed properties and can be further tuned by adjusting bandgap that would result in increased light-harvesting efficiency which is the basis to achieve desired optical, electronic, and optoelectronic properties, making them promising materials for plasmonic applications [11, 12]. In addition, the plasmonic efficiency of 2D materials can also be enhanced by injecting plasmonic hot electrons to alter carrier intensity in 2D materials for higher photocatalysis output [13]. The recent extension of plasmonic materials from traditional metals to semiconductors to semi-metal graphene are identified as an ideal materials for surface plasmon resonance in plasmonic structures and their subsequent applications needed to be addressed accordingly. Moreover, the coupling effects between excitons and plasmons for 2D materials are the growing research interests that profound further studies for light-matter interactions to discover novel materials for innovative device applications.

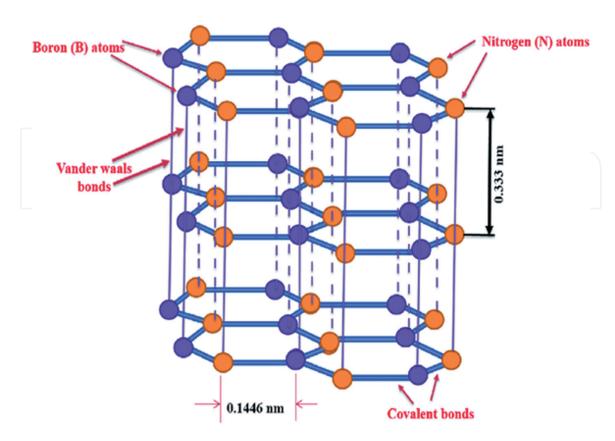
#### 2. Overview of 2D materials

The radiation-matter interaction is more prominent in 2D materials because of their thin sheet structures and significant quantum confinement effects that lead to enhanced electronic and optical properties. Owing to their advanced nature, 2D materials are advantageously evaluated for plasmonic characteristics, and multiple

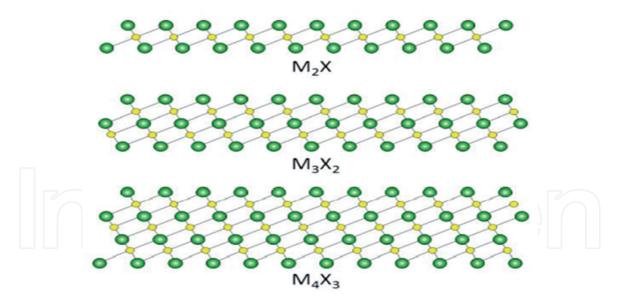
studies have been conducted for hBN to investigate plasmon molecular vibration coupling, plasmon substrate phonon coupling, and graphene plasmon-phonon polaritons coupling [14–16]. The 2D graphene structure exhibits exciting results due to its single-atom thickness and their environmental sensitivity. Other than environmental sensitivity, graphene plasmons can also be tuned with external magnetic and electric fields [17]. The effectiveness of graphene-based plasmonics can be determined by charge carrier density, and heavily doped graphene exhibits high efficiency which is required for plasmonic applications [18]. As a result, graphene is an excellent plasmonic material, and combining graphene with other 2D materials is favorable to obtain optimum efficiency [19].

Hexagonal Boron Nitride (hBN) is one of the most intriguing findings in 2D materials for plasmonics, having the unique ability to be fabricated within the host material, and can be used as a promising substrate for graphene-based plasmonic applications because of its graphene-matched crystal structure [18, 20]. The hBN-graphene mixture is helpful to enhance grapheme-plasmon lifetime when compared with other 2D materials and can maintain its bandgap even in varied thicknesses depicting a wide range of plasmonic properties including electro-optic and quantum-optics [21, 22]. Moreover, the point defects in hBN at room temperature demonstrate single-photon emission properties that can be used to integrate plasmonic nanostructures. Despite its wide bandgap, hBN offers high quantum efficiency, optical nonlinearity, and novel plasmonic properties to make it the best choice as 2D plasmonic material [23]. Its structure is shown in **Figure 1** [24].

The MXenes are a new class of 2D materials that contain carbides and nitrides, and they are the biggest family currently available, as seen in **Figure 2** [25]. This family of materials is substantially more stable than graphene with high metallic conductivity, folding and molding properties, and good electromagnetic properties, possessing the unique property of being combined with other materials to tune



**Figure 1.** Schematics of hBN structure [24].



**Figure 2.**MXene sheets with multiple layers where larger spheres represent transient metal, while smaller spheres are C, N, or CN [25].

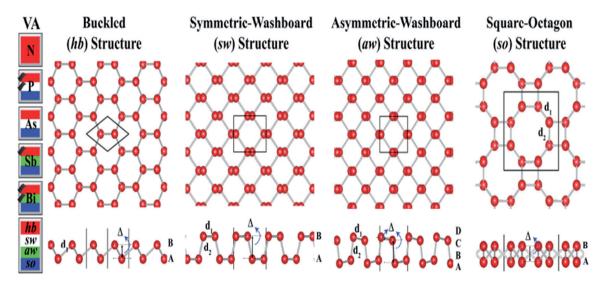


Figure 3.
Pnictogens and their schematic 2D structures [27].

their properties for desired applications. They can be employed in a variety of applications including energy storage devices, photonic-plasmonic structures as well as photocatalytic devices [26], and because of their metallic character along with high conductive nature, they may be used as plasmonic materials equivalent to graphene.

Researchers anticipated the group VA elements such as nitrogen, arsenic, antimony as well as bismuth as single-layer 2D structures with the introduction of 2D materials synthesis, and these elements are referred to as pnictogens and are shown in **Figure 3** [27]. These materials feature a honeycomb, washboard, and square-octagon structure, and they offer outstanding electrical, optical, electro-optical, and plasmonic properties having strong spin-orbit coupling, a narrow bandgap, and band inversion properties, making them ideal for plasmonic device applications [27].

# 3. Theoretical advancements

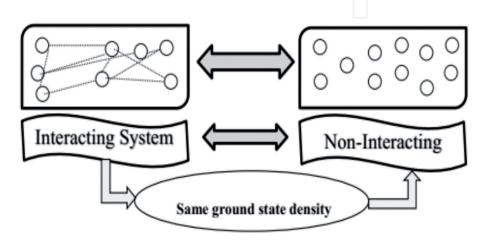
Photonics deals with the light-matter interaction which usually results in the formation of a single electron–hole pair by interacting light photons with free

charge carriers in a metal, whereas in plasmonics, there is a large number of charge Carriers present that leads to collective oscillations which is the fundamental problem in plasmonics because all charge carriers are not part of the solid and can be influenced by structural defects as well as other materials defects such as dislocations. As a result, multi-scale modeling at various structural complexity levels is required for theoretical exploration of these complex models and plasmonic excitations in bulk materials and localized plasmons in metallic structures. To analyze this complicated issue, several theoretical and numerical models have been presented, although only a few of them are described here.

The Drude-Lorentz model which gives a theoretical insight into a material and can be employed in plasmonic applications is an intuitive way to study the underlying dielectric characteristics of solids [28, 29]. The Drude-Lorentz model, also known as the oscillator model, entails representing an electron as a driven damped harmonic oscillator in which the electron is connected to the nucleus by a hypothetical spring with an oscillating electric field acting as a driving force. It also describes the behavior of electrons in terms of their electro-optical characteristics when light interacts with them [30]. The Drude-Lorentz model's predictions are completely supported by the classical oscillator model as well as quantum mechanical features like electronic dipole moments of materials. To justify the microscopic qualities exhibited by classical and quantum techniques using this model, it is necessary to understand the Ehrenfest theorem which shows that quantum mechanical predicted values fundamentally follow classical mechanical conditions [31]. The Kohn-Sham approach is praised for its ease of use in relating a many-body system to a non-interacting system and thereby solving it using Kohn-Sham density functional theory [32]. Figure 4 illustrates such a model [32].

With the developments in computing, new algorithms are being devised to accomplish difficult jobs rapidly and accurately. Different approaches and models for electrical and photonic systems are being explored to accurately anticipate their characteristics, which were previously explored using differential equations. This section discusses the frequency domain approach and the time domain method to have a better knowledge of computational model advancements [33].

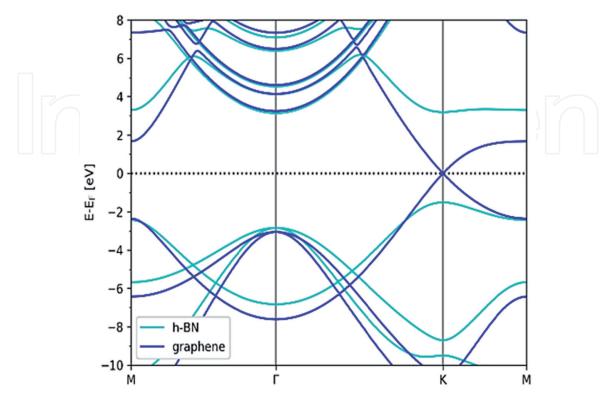
The decomposition of periodic systems into harmonic time-dependent eigenmodes is a basic approach for understanding the optoelectronic and plasmonic characteristics of materials. The frequency-domain approach is a subset of these decompositions that enlarges electromagnetic fields into Fourier eigenmodes which may be used to comprehend optical material properties in the absence of nonlinear effects [34]. This approach is usually started from fundamental photonic systems



**Figure 4.** *Kohn-sham mapping of the interacting and non-interacting systems* [32].

with translational symmetry which produces electromagnetic states and photonic band structures using Maxwell equations and wave Equations [35]. Although the frequency-domain technique is effective for defining material characteristics, but it is an expensive method that restricts its application in numerical models and as a result, the finite-difference time-domain method was presented as an alternative. The time-domain technique is a grid-based method that is linked to several other finite methods. This approach models electromagnetic wave propagation in dielectric media without needing derivation methods, making it easier to be utilized in complicated geometrical simulations, such as non-linear systems, which were previously difficult to manage using the frequency-domain method. Furthermore, in this approach, Maxwell equations are discretized by differences arising from spatial and time derivatives, and the obtained results are solved in a leapfrog fashion on a staggered grid which is a good method being utilized in fluid dynamics [36]. Using the Phyton modules, these simulations can also be used to determine the plasmonic characteristics of materials [37].

The plasmonic material's behavior can be determined by studying the frequency-dependent dielectric factor linked with the excited state of the material. It is essential to analyze both the ground and excited states of material while calculating optical transitions based on material states. For the analysis of material characteristics based on these facts, *ab initio* methodologies like density functional theory (DFT), Hartree-Fock theory, and Green's function method [38–40] are essential. DFT [32] is founded on the concept that, for a quantum mechanical system, ground state charge density provides a complete comprehension of the system's ground state because the charge density of the state is mapped to the total energy of the system. The degree of freedom and functional complexity would be reduced if energy density is properly approximated. **Figure 5** [41] shows the bandgap difference between graphene and hBN, which seems comparable but differs significantly at K-vector space as predicted within DFT (PBE) approximation computed by Warmbier et al. [41]. Green's function method is a quasi-particle approach for



**Figure 5.**Band structure of graphene and hBN computed within DFT (PBE) [41].

improving bandgap findings and reproducing band structures, with Hedin's GW as the most frequent implementation. All of these approaches hold promise for studying plasmonic material characteristics and predicting specific plasmonic device applications.

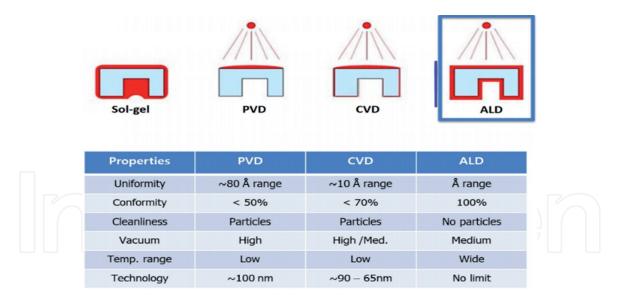
# 4. Experimental progress in the synthesis of 2D materials

The material characteristics such as its dimension, morphology, physical as well as chemical properties, orientation, and crystallinity mainly depend on the material's electronic properties which are impacted by the synthesis technique and experimental conditions. Mechanical exfoliation techniques have been tried in the past, but they have failed due to insufficient van-der-wall forces between 2D material layers, which limit uniformity and quality control, as well as their inability to scale-up [42]. Physical and chemical synthesis methods with controlled structural fabrication can be used with the top-down approach having the disadvantage of poor product yield and sheet restacking, limiting its application, and the bottom-up approach yielding promising results by assembling materials in a substrate using vapor deposition techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition. These are the most often utilized promising ways for fabricating 2D materials with customized thickness, dimensional control, high conductivity, and flexibility for electron transport; all of which are highly sought quantities for plasmonic applications [43].

CVD allows for the controlled synthesis of large areas of 2D materials with the added benefit of step-by-step film synthesis on various substrates and adjustable growth parameters to get the desired output. Metal—organic chemical vapor deposition (MOCVD) is a modified version of CVD that is used to synthesize high-quality, large-area 2D materials for a variety of applications [44]. New research shows that a metal gas-phase precursor might be employed for regulated and uniform thickness instead of a powder precursor, which results in inhomogeneous nucleation and hence uncontrolled synthesis. Furthermore, temperature and pressure have an important impact on deposition uniformity, for example, high temperature and moderate pressure would result in excellent precursor coverage with regulated dimensions while excessively high temperatures might have negative consequences [45]. A comparison of various synthesis techniques is shown in **Figure 6** [46].

Many techniques are available for producing uniform 2D materials and heterostructures with atomic layer deposition (ALD) being a refinement of the vaporbased deposition method in which the self-limiting reaction of the precursor is an essential aspect of ALD and the fact that a self-saturating surface monolayer is created after each precursor exposure distinguishes it from other deposition processes. In addition, ALD allows for the creation of 2D materials with fewer flaws and the synthesis of 2D material heterostructures with a small atom size thickness [47]. As a result of the advancements, ALD has opened up new means of synthesis with decreased interfacial impurities and large area deposition conformity with improved structural properties [48].

Apart from vapor-based synthesis approaches, liquid-phase exfoliation is another good way to get 2D materials in which the surface oxide of liquid metals produces unexpected results from a combination of physical and chemical features of liquid alloys [49]. While interacting with their ambient conditions, liquid metals with electron-rich metallic cores form a natural 2D film; the self-limiting surface oxide film with a thickness of a few atoms [50]. These liquid ingredients serve as host materials for the production of high-quality, one-kind films for innovative applications. The origin to define its development characteristics is the host



**Figure 6.**Comparison of various 2D materials synthesis techniques [46].

materials fluidity, chemical composition, and thermodynamic properties that are the building block for examining the resultant 2D materials [51].

#### 5. Plasmonic materials

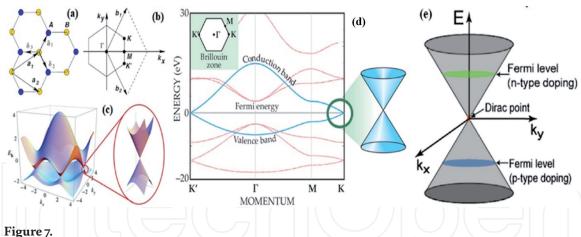
Graphene, graphene oxides (GO), MXenes, pnictogens, and hBN are just a few of the commonly utilized plasmonic materials described in this section.

#### 5.1 Graphene

Graphene is proving itself a revolutionary material for a wide range of applications since 2004 because of its electronic behavior which is responsible for exceptional features including, high mobility charge carriers, optical transmission, and tunable carrier densities [52–60]. The ability of graphene's structure to strongly confine excited surface plasmons in comparison to other materials as well as its ability to tune surface plasmons by manipulating charge densities is remarkable for prospective applications primarily in optoelectronics and plasmonics [61]. Experimental studies [62] show that graphene surface plasmons may be coupled with electrons and photons, allowing them to be used in more promising applications. This graphene coupling is in the form of quasi-particles that hold an intense interest in optoelectronics and condensed matter physics [63]. Surface plasmons in graphene offer a variety of significant advantages over other plasmonic materials, including high confinement, high tuneability, reduced frequency loss, improved electron relaxation time, and high many-body interactions. **Figure 7** shows the structure and band description of graphene [64].

#### 5.2 Graphene oxides (GO)

Graphene oxide (GO) is an amorphous insulator with carbon network bases on the hexagonal rings with both sp<sup>2</sup> and sp<sup>3</sup> hybridization as well as hydroxyl and epoxide groups on sheet sides and carboxyl and carbonyl groups on sheet edges. This kind of morphological structure is responsible for its wide range of technological applications mainly in nano-electronics, nano-photonics, and

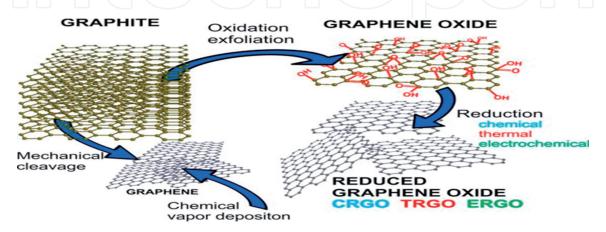


(a) Graphene lattice structure, (b) BZ of graphene, (c) lattice electronic dispersion, (d) graphene electronic structure Bloch band description, (e) Low EBS approximation [64].

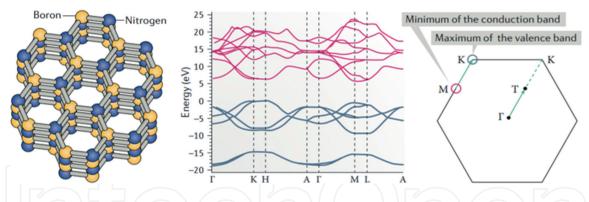
nano-composites. Because of the oxygen functionalities present, GO has a significant benefit when mixed with other polymeric or ceramic materials, resulting in improved electrical and mechanical properties [65]. The GO is in high demand in both industry and academics because of its zero-bandgap feature and excellent flexibility with superior thermal and electrical conductivity. In addition, one of GO's unique properties is the coexistence of its size, shape, and hybridization domains via a reduction mechanism that may eventually control the bandgap and convert GO to a semi-metal form. The main distinction between GO and reduced graphene oxide (r-GO) is that GO has oxygen-containing functional groups, whereas reduced graphene oxide does not [66]. Owing to heterogeneous electrical structure, GO is fluorescent throughout a wide wavelength range, while reduced GO allows quick response in GO-based electronics [67]. The GO is a promising choice for novel photonic materials, solar cells, optical devices, and a range of other applications due to its unique features. **Figure 8** depicts the difference between GO and r-GO [66].

### 5.3 Hexagonal boron nitride (hBN)

The hBN is a traditional 2D heterostructure material that was previously used as a substrate for thin-layered materials but now has the potential to be employed as an active plasmonic material. It is an excellent encapsulant for graphene because it protects it from the environment and increases its electrical mobility, extending the



**Figure 8.**Schematic flow from graphene-to-graphene oxide (GO) and reduced graphene oxide (r-GO) [66].



**Figure 9.**hBN and its band structure properties [70].

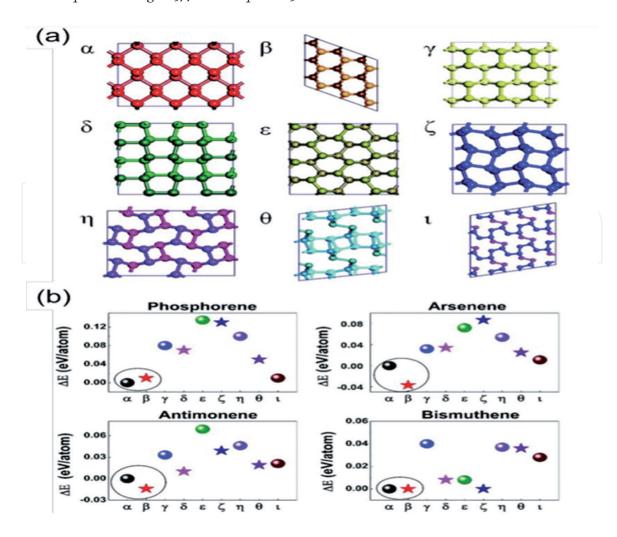
life of surface plasmon polaritons in plasmonic applications [18, 68]. It has a crystal nature and polar bonding, allowing it to perform a wide range of optical, electrical, optoelectronic, and quantum optic functions for device applications. Also, it has a wide bandgap, high internal quantum efficiency, and significant optical nonlinearities that depend on material thickness and is specified by the rotation angle between heterostructure material layers [23, 69]. Its structure and band properties are displayed in **Figure 9** [70].

#### 5.4 MXenes

MXenes are new types of 2D plasmonic materials made up of nitrides and carbides that were discovered in 2011. They are more stable than graphene, can be readily shaped and folded, have superior electromagnetic properties, and can be coupled with other materials to exhibit a wide range of applications in energy storage, supercapacitors, photonics, and plasmonics. The properties of MXenes can be determined by exploring surface termination, composition, doping, or mixing with other materials, resulting in adjustable conductivity that can change the material's properties as a metal or semiconductor [71]. The relative dielectric permittivity of MXenes for plasmonic applications can be studied by inter- and intra-band transitions that define optical parameters such as, absorption coefficient, refractive index, transmittance, and reflectance, and are linked to the material's electrical conductivity, which has already been demonstrated computationally and experimentally to find a place in electronic and optoelectronic applications [72, 73].

# 5.5 Pnictogens

Pnictogens are monolayer stable structures found from elements of group VA (nitrogen, arsenic, antimony, and bismuth) after the discovery of black phosphorene. These materials are named as nitrogen in hexagonal buckled structure, arsenic in hexagonal buckled as well as symmetric washboard structure, antimony, and bismuth in either hexagonal buckled or asymmetric washboard structure, but later on, these elements occurred to have other exotic structures [74]. The pnictogens stability can be depicted using molecular dynamic simulations performed at high temperatures and materials phonon frequencies [75]. Pnictogens, as contrasted with group IV elements, are significantly more stable semiconductor materials with an appropriate bandgap for numerous device applications. Also, in contrast to black phosphorus (BP), they are thermodynamically stable monolayer structures with rhombohedral structural



**Figure 10.**(a) Honeycomb structures, (b) average binding energies of 2D pnictogens [77].

characteristics and interlayer covalent connections which decrease as anisotropy decreases and metallic character increases from arsenic to antimony to bismuth [76]. The 2D monolayer structures of pnictogens exhibit strong directionality in various physical properties that can be implied on plane lateral heterostructures to produce parallel strips of 2D pnictogens with advanced technological applications while the same effect can be observed by a monoatomic chain of group VA elements attached to their monolayers. **Figure 10** represents structures as well as binding energies of pnictogens [77].

#### 5.6 Metal oxides

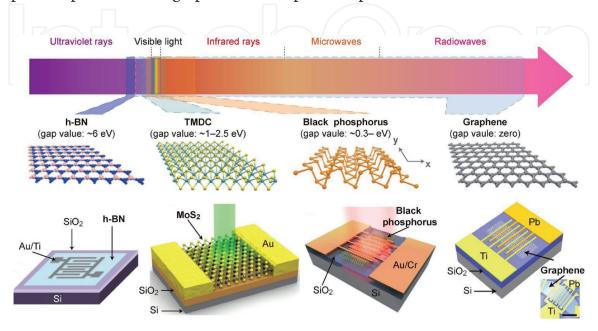
Metal oxides show strong metallic behavior owing to stable charge carrier concentration when doped with various significant dopants such as aliovalent, oxygen vacancies, or interstitial dopants that result in localized surface plasmon resonance and by carefully choosing the host material as well as doped material, these surface plasmonic resonances can be tuned in the range of near- and mid-infrared (IR) region spectrum. The optical modeling of metal oxides illustrates the importance of defects and their impact on charge carrier mobility and the electronic structure of the material which reveals the choice of dopant as an important factor for metal oxides as plasmonic materials. Metal oxides are different from ordinary metals in the sense that they may change their localized surface plasmon resonance by changing their elemental composition, regardless

of material size or shape, and these plasmon resonances can also be adjusted by altering external stimuli, resulting in the unique features of plasmonic materials as a result of crystal and morphological configurations that are useful for a variety of device applications [78].

# 6. Functional applications

The 2D materials can generally be categorized on the basis of electrical and optoelectronic properties in device applications such as flash memories, sensors, tunnel junctions, photodetectors, photonic crystals, optical metamaterials, nanophotonics, and quantum optics. The 2D graphene-based photonic and optoelectronic devices dragged much attention because of their versatile applications in broad fields such as sensing, communication, and imaging technologies [79]. In terms of density of state and band structure, graphene has an adjustable light absorption spectrum and carrier density which may be used in waveguideintegrated graphene photonic devices and molecular sensor detection. Graphene with optical adjustments has also been used for light modulation and detection, and its derivatives are proving to be a feasible alternative for a variety of applications. The GO can be utilized in the manufacture of electrical devices such as FETs and GFETs, LEDs, and solar cells, while r-GO dispersed in solvents may be utilized to replace FTO and ITO electrodes in transparent electrode manufacture; moreover, their large surface area and conductivity allow them to function as energy storage devices for longer periods with a greater capacity [80]. Recent investigations have shown that near-field IR optical microscopy and IR microscopy of graphene are responsible for surface plasmon modeling in plasmonic applications [81]. An overview of 2D plasmonic materials-based devices is shown in **Figure 11** [82].

The hBN has exciting technological applications including, photonics, and its nanostructures feature weak polaritons that interact poorly with light and might be utilized to control the optical angular momentum of hyperbolic phonon polaritons, implying maximum optical density of state and/or improving molecular IR vibrational absorption through surface enhancement [83]. Hybridization of hBN phonon-polariton with graphene surface plasmon-polaritons resulted in the active



**Figure 11.** 2D plasmonic material-based devices for optoelectronic applications [82].

tuning of the polaritons which is a potential characteristic for chip-based nano-photonics [84], photonic devices, modulators, and hyper-lensing [85]. The hBN defects that reduce phonon lifespan have uses in single-photon emitters (SPEs), which have certain appealing properties such as high quantum efficiency, optical stability, linear polarization, and high brightness. In addition, owing to its high efficiency and extended life in device applications, hBN has been utilized to replace AlGaN in deep-UV applications. Another method for incorporation of hBN is to link emission with plasmonic resonator-based structures in which localized surface plasmons cause broad field confinements throughout a wide range of emission, resulting in substantial Purcell amplification for dipole emission coupled to these resonators. When compared to uncoupled devices, the hBN quantum emitter coupling with plasmonic arrays has previously been demonstrated, with studies revealing PL enhancement and lifespan reduction with a quantum efficiency of around 40% and enhanced saturation count rates [86].

MXenes plasmonics is a relatively new field with a wide range of possible applications, including surface-enhanced Raman spectroscopy, conductive substrates, and plasmonic sensing [72]. Nonlinear optical applications based on the nonlinear absorption process by plasmonic illumination near plasma frequency have been suggested for MXenes, and these nonlinear applications include ultrafast lasers, optical switching, and optical rectification devices like optical diodes. At near-infrared frequencies, arrays of two-dimensional titanium carbide ( ${\rm Ti}_3{\rm C}_2{\rm T}_{\rm x}$ ) MXene nanodisks exhibit strongly localized surface plasmon resonances, which have been exploited to produce broadband plasmonic metamaterial absorber [87]. MXenes are also used as super-absorbers in broadband plasmonic metamaterials, and these super-absorbers may be used for photodetection and energy harvesting. **Figure 12** shows an MXenes super-absorber [88] with configurable nano-aperture width for broadband applications.

Pnictogens with a 2D structure are in great demand for high-performance device applications, since they have a midrange tunable bandgap and unparalleled mobility, allowing them to be employed in FETs for more efficient response than other materials. Because 2D materials lack a suitable bandgap, photodetectors are a major challenge, but pnictogens direct and tunable bandgap has solved this problem acting as a bridge between narrow and wider bandgap materials, attracting a lot of interest in photodetectors with improved photo-responsivity



**Figure 12.** *MXene broadband super-absorber* [88].

for telecommunication applications. The BP has an intriguing direct bandgap from visible to IR, making it a potential material for optoelectronic applications [89], while ultra-thin BP FETs have been described as effective NO<sub>2</sub> gas sensors with remarkable stability of pnictogens-based FETs during sensing [90, 91]. The 2D metals and metal oxide semiconductors, whether conducting or insulating, are useful for thin-film transistors and numerous device applications, where they can be employed in any component such as the source, drain, gate, electrodes, or gate dielectrics. Metal oxides are also useful in p-n junction device fabrications for diode rectifiers, solar cells, and organic photovoltaic applications, where they operate as a charge extracting interfacial layer to improve power conversion efficiency.

# 7. Future challenges and prospects

Plasmonics has advanced to the forefront of science due to technical advances in the experimental and computational fields as well as contributions to scientific applications. These contributions also confront some challenges that must be addressed in the future for effective plasmonic applications. To begin with, plasmonic nanostructures of controlled size and features cannot simply embed in their surroundings because they change the dielectric function of the surrounding medium, affecting plasmonic switching and hence plasmonic applications. Another problem is optical pumping, which has the potential to deliver ultrafast plasmonic switching but has the drawbacks of destructive heat accumulation and high-power consumption. A major shortcoming of plasmonic materials is that self-tuned plasmonic structures lack effective plasmon coupling control abilities. Also, it is difficult to fabricate colloidal metal nano-crystals in controlled symmetry for plasmonic device applications on a large scale, even though lithography techniques performed well but had some drawbacks such as high cost, long-time consumption, and difficulty with damped plasmonic properties on a large scale [92].

Plasmonics must control light at the nanoscale with minimal losses, and to do so, light localization must be pushed to new heights without jeopardizing its propagation nature. Similarly, advances in topological plasmons must be incorporated in nanophotonic circuits by maintaining plasmon propagation stability and improving manufacturing techniques. For the experimental process to be effective, theoretical models must be improved to acquire the nonlinear and nonlocal physics of plasmonic devices. In short, both light and matter quantization are required to make a fine path toward a better understanding of light-matter interactions for advanced large-scale applications. The numerical approaches outlined are strong tools in terms of computing but they have conceptual limitations and their validity range becomes inefficient when a heterogeneous system is studied. To tackle plasmonic multi-scale challenges, the validity of numerical models must be improved by combining them with other numerical tools which is not well understood at this time and requires future considerations.

#### 8. Conclusions

We have briefly addressed 2D plasmonic materials and their active properties in this chapter that are responsible for their wide range of applications in the electrical, photonic, and optoelectronic fields such as, FETs and GFETs, LEDs, and solar cells, modulators, hyper lensing, metamaterial absorbers, super-absorbers as well

as nonlinear applications including ultrafast lasers, optical switching, and optical rectification devices like optical diodes. The synthesis techniques employed for 2D plasmonic materials have also been reviewed, with pulsed laser deposition (PLD) and CVD being the most extensively used and promising approaches for more controlled and conformational film growth. Also, these techniques have the advantage to provide desirable results by tuning their functional parameters such as temperature, pressure, substrate angles, and deposition time. Computational models have to be examined to carry out a successful experiment, and there is a need to update simulation approaches to address problems in achieving desired plasmonic device features. Finally, we have outlined new prospective applications of 2D plasmonic materials and their significance in the industry as well as the drawbacks of materials that prohibit them from performing properly while providing the possible directions for future research.

# **Conflict of interest**

There are no conflicts of interest to declare.

#### Note

US spelling with serial comma.





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# References

- [1] Geim AK, Novoselov KS. The rise of graphene. In: Nanoscience and Technology: A Collection of Reviews from Nature Journals. Singapore: World Scientific; 2010. pp. 11-19
- [2] Novoselov KS, Morozov SV, Mohinddin TMG, Ponomarenko LA, Elias DC, Yang R, et al. Electronic properties of graphene. Physica Status Solidi. 2007;244(11):4106-4111
- [3] Late DJ, Huang YK, Liu B, Acharya J, Shirodkar SN, Luo J, et al. Sensing behavior of atomically thin-layered MoS<sub>2</sub> transistors. ACS Nano. 2013;7(6):4879-4891
- [4] Zhang Y, Chang TR, Zhou B, Cui YT, Yan H, Liu Z, et al. Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe<sub>2</sub>. Nature Nanotechnology. 2014;**9**(2):111-115
- [5] Pospischil A, Furchi MM, Mueller T. Solar-energy conversion and light emission in an atomic monolayer p–n diode. Nature Nanotechnology. 2014;**9**(4):257-261
- [6] Nair RR, Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, et al. Fine structure constant defines visual transparency of graphene. Science. 2008;**320**(5881):1308-1308
- [7] Wrachtrup J. Single photons at room temperature. Nature Nanotechnology. 2016;**11**(1):7-8
- [8] Liu Y, Weiss NO, Duan X, Cheng HC, Huang Y, Duan X. Van der Waals heterostructures and devices. Nature Reviews Materials. 2016;**1**(9):1-17
- [9] Tang Q, Zhou Z. Graphene-analogous low-dimensional materials. Progress in Materials Science. 2013;58(8):1244-1315
- [10] Butler SZ, Hollen SM, Cao L, Cui Y, Gupta JA, Gutiérrez HR, et al. Progress,

- challenges, and opportunities in twodimensional materials beyond graphene. ACS Nano. 2013;7(4): 2898-2926
- [11] Zu S, Bao Y, Fang Z. Planar plasmonic chiral nanostructures. Nanoscale. 2016;8(7):3900-3905
- [12] Zhu H, Yi F, Cubukcu E. Plasmonic metamaterial absorber for broadband manipulation of mechanical resonances. Nature Photonics. 2016;**10**(11):709-714
- [13] Cheng F, Johnson AD, Tsai Y, Su PH, Hu S, Ekerdt JG, et al. Enhanced photoluminescence of monolayer WS2 on Ag films and nanowire–WS<sub>2</sub>–film composites. ACS Photonics. 2017;**4**(6):1421-1430
- [14] Yang X, Kong XT, Bai B, Li Z, Hu H, Qiu X, et al. Substrate phonon-mediated plasmon hybridization in coplanar graphene nanostructures for broadband plasmonic circuits. Small. 2015;**11**(5):591-596
- [15] Rodrigo D, Limaj O, Janner D, Etezadi D, De Abajo FJG, Pruneri V, et al. Mid-infrared plasmonic biosensing with graphene. Science. 2015;349(6244):165-168
- [16] Brar VW, Jang MS, Sherrott M, Kim S, Lopez JJ, Kim LB, et al. Hybrid surface-phonon-plasmon polariton modes in graphene/monolayer h-BN heterostructures. Nano Letters. 2014;14(7):3876-3880
- [17] Yan H, Li Z, Li X, Zhu W, Avouris P, Xia F. Infrared spectroscopy of tunable Dirac terahertz magneto-plasmons in graphene. Nano Letters. 2012;**12**(7):3766-3771
- [18] Woessner A, Lundeberg MB, Gao Y, Principi A, Alonso-González P, Carrega M, et al. Highly confined low-loss plasmons in graphene–boron

- nitride heterostructures. Nature Materials. 2015;**14**(4):421-425
- [19] Yeung KY, Chee J, Yoon H, Song Y, Kong J, Ham D. Far-infrared graphene plasmonic crystals for plasmonic band engineering. Nano Letters. 2014;14(5):2479-2484
- [20] Caldwell JD, Novoselov KS. Midinfrared nanophotonics. Nature Materials. 2015;**14**(4):364-366
- [21] Dai S, Ma Q, Liu MK, Andersen T, Fei Z, Goldflam MD, et al. Graphene on hexagonal boron nitride as a tunable hyperbolic metamaterial. Nature Nanotechnology. 2015;**10**(8):682-686
- [22] Tran TT, Bray K, Ford MJ, Toth M, Aharonovich I. Quantum emission from hexagonal boron nitride monolayers. Nature Nanotechnology. 2016;11(1):37-41
- [23] Ni GX, Wang H, Wu JS, Fei Z, Goldflam MD, Keilmann F, et al. Plasmons in graphene Moiré superlattices. Nature Materials. 2015;**14**(12):1217-1222
- [24] Kumar A, Malik G, Chandra R, Mulik RS. Bluish emission of economical phosphor h-BN nanoparticle fabricated via mixing annealing route using non-toxic precursor. Journal of Solid State Chemistry. 2020;288:121430
- [25] Jakšić Z, Obradov M, Jakšić O, Tanasković D, Radović DV. Reviewing MXenes for plasmonic applications: Beyond graphene. In: 2019 IEEE 31st International Conference on Microelectronics (MIEL). Washington, DC, USA: IEEE; 2019. pp. 91-94
- [26] Anasori B, Lukatskaya MR, Gogotsi Y. 2D metal carbides and nitrides (MXenes) for energy storage. Nature Reviews Materials. 2017;2(2):1-17
- [27] Ersan F, Keçik D, Özçelik VO, Kadioglu Y, Aktürk OÜ, Durgun E, et al.

- Two-dimensional pnictogens: A review of recent progresses and future research directions. Applied Physics Reviews. 2019;**6**(2):021308
- [28] Hulst HC, van de Hulst HC. Light Scattering by Small Particles. New York, USA: Courier Corporation; 1981
- [29] Bohren CF, Huffman DR. Absorption and Scattering of Light by Small Particles. Weinhein, Germany: John Wiley and Sons; 2008
- [30] Mohammed F, Warmbier R, Quandt A. Computational plasmonics: Theory and applications. In: Recent Trends in Computational Photonics. Cham: Springer; 2017. pp. 315-339
- [31] Sen D, Das SK, Basu AN, Sengupta S. Significance of Ehrenfest theorem in quantum–classical relationship. Current Science. 2001;80(4):536-541
- [32] Iqbal MA, Ashraf N, Shahid W, Afzal D, Idrees F, and Ahmad R. Fundamentals of Density Functional Theory: Recent Developments, Challenges and Future Horizons. UK: IntechOpen; 2021
- [33] Taflove A. Review of the formulation and applications of the finite-difference time-domain method for numerical modeling of electromagnetic wave interactions with arbitrary structures. Wave Motion. 1988;10(6):547-582
- [34] Johnson SG, Joannopoulos JD. Block-iterative frequency-domain methods for Maxwell's equations in a planewave basis. Optics Express. 2001;8(3):173-190
- [35] Joannopoulos JD, Johnson SG, Winn JN, Meade RD. Photonic Crystals: Molding the Flow of Light. 2nd ed. Princeton, New Jersey: Princeton Univ; 2008
- [36] Smith GD, Smith GDS. Numerical Solution of Partial

- Differential Equations: Finite Difference Methods. New York, USA: Oxford University Press; 1985
- [37] Mohammed F, Warmbier R, Quandt A. Computational plasmonics: Numerical techniques. In: Recent Trends in Computational Photonics. New York City, USA: Springer; 2017. pp. 341-368
- [38] Hohenberg P, Kohn W. Inhomogeneous electron gas. Physical Review. 1964;**136**(3B):B864
- [39] Becke AD. A new mixing of Hartree–Fock and local densityfunctional theories. The Journal of Chemical Physics. 1993;**98**(2):1372-1377
- [40] Hedin L. New method for calculating the one-particle Green's function with application to the electron-gas problem. Physical Review. 1965;139(3A):A796
- [41] Warmbier R, Mehay T, Quandt A. Computational plasmonics with applications to bulk and nanosized systems. In: Active Photonic Platforms X. Vol. 10721. San Diego, California, United States: International Society for Optics and Photonics; 2018. p. 107211V
- [42] Wei Z, Hai Z, Akbari MK, Qi D, Xing K, Zhao Q, et al. Atomic layer deposition-developed two-dimensional α-MoO3 windows excellent hydrogen peroxide electrochemical sensing capabilities. Sensors and Actuators B: Chemical. 2018;**262**:334-344
- [43] Xu H, Akbari MK, Zhuiykov S. 2D Semiconductor nanomaterials and heterostructures: Controlled synthesis and functional applications. Nanoscale Research Letters. 2021;**16**(1):1-38
- [44] Kang K, Xie S, Huang L, Han Y, Huang PY, Mak KF, et al. High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. Nature. 2015;520(7549):656-660
- [45] Yu J, Li J, Zhang W, Chang H. Synthesis of high quality

- two-dimensional materials via chemical vapor deposition. Chemical Science. 2015;**6**(12):6705-6716
- [46] Xu H, Akbari MK, Kumar S, Verpoort F, Zhuiykov S. Atomic layer deposition–state-of-the-art approach to nanoscale hetero-interfacial engineering of chemical sensors electrodes: A review. Sensors and Actuators B: Chemical. 2021;**331**:129403
- [47] Leskelä M, Ritala M. Atomic layer deposition chemistry: Recent developments and future challenges. Angewandte Chemie International Edition. 2003;42(45):5548-5554
- [48] Brun N, Ungureanu S, Deleuze H, Backov R. Hybrid foams, colloids and beyond: From design to applications. Chemical Society Reviews. 2011;40(2):771-788
- [49] Daeneke T, Khoshmanesh K, Mahmood N, De Castro IA, Esrafilzadeh D, Barrow SJ, et al. Liquid metals: Fundamentals and applications in chemistry. Chemical Society Reviews. 2018;47(11):4073-4111
- [50] A de Castro I, Chrimes AF, Zavabeti A, Berean KJ, Carey BJ, Zhuang J, et al. A gallium-based magnetocaloric liquid metal ferrofluid. Nano Letters. 2017;**17**(12):7831-7838
- [51] Caturla MJ, Jiang JZ, Louis E, Molina JM. Some Issues in Liquid Metals Research. Switzerland: MDPI; 2015.
- [52] Britnell L, Gorbachev RV, Jalil R, Belle BD, Schedin F, Katsnelson MI, et al. Electron tunneling through ultrathin boron nitride crystalline barriers. Nano Letters. 2012;**12**(3):1707-1710
- [53] Pham VP, Jang H-S, Whang D, Choi J-Y. Direct growth of graphene on rigid and flexible substrates: Progress, applications, and challenges. Chemical Society Reviews. 2017;46: 6276-6300

- [54] Pham VP, Kim KH, Jeon MH, Lee SH, Kim KN, Yeom GY. Low damage pre-doping on CVD graphene/Cu using a chlorine inductively coupled plasma. Carbon. 2015;**95**:664-671
- [55] Pham VP, Kim KN, Jeon MH, Kim KS, Yeom GY. Cyclic chlorine trap-doping for transparent, conductive, thermally stable and damage-free graphene. Nanoscale. 2014;6:15310-15318
- [56] Pham VP, Kim, Nguyen MT, Park JW, Kwak SS, et al. Chlorinetrapped CVD bilayer graphene for resistive pressure sensor with high detection limit and high sensitivity. 2D Materials. 2017;4:025049
- [57] Pham PV. Hexagon flower quantum dot-like Cu pattern formation during low-pressure chemical vapor deposited graphene growth on a liquid Cu/W substrate. ACS Omega. 2018;3:8036-8041
- [58] Pham PV, Mishra A, Yeom GY. The enhancement of Hall mobility and conductivity of CVD graphene through radical doping and vacuum annealing. RSC Advances. 2017;7:16104-16108
- [59] Pham PV. Cleaning of graphene surfaces by low-pressure air plasma. Royal Society Open Science. 2018;**6**:172395
- [60] Pham VP et al. Low energy BCl<sub>3</sub> plasma doping of few-layer graphene. Science of Advanced Materials. 2016;**8**:884-890
- [61] Fang Z, Wang Y, Liu Z, Schlather A, Ajayan PM, Koppens FH, et al. Plasmon-induced doping of graphene. ACS Nano. 2012;**6**(11):10222-10228
- [62] Fei Z, Rodin AS, Andreev GO, Bao W, McLeod AS, Wagner M, et al. Gate-tuning of graphene plasmons revealed by infrared nano-imaging. Nature. 2012;487(7405):82-85

- [63] Zayats AV, Smolyaninov II, Maradudin AA. Nano-optics of surface plasmon polaritons. Physics Reports. 2005;**408**(3-4):131-314
- [64] Cui L, Wang J, Sun M. Graphene plasmon for optoelectronics. Reviews in Physics. 2021;**6**:100054
- [65] Mokhtar MM, Abo-El-Enein SA, Hassaan MY, Morsy MS, Khalil MH. Mechanical performance, pore structure and micro-structural characteristics of graphene oxide nano platelets reinforced cement. Construction and Building Materials. 2017;138:333-339
- [66] Rowley-Neale SJ, Randviir EP, Dena ASA, Banks CE. An overview of recent applications of reduced graphene oxide as a basis of electroanalytical sensing platforms. Applied Materials Today. 2018;**10**:218-226
- [67] Cao Y, Yang H, Zhao Y, Zhang Y, Ren T, Jin B, et al. Fully suspended reduced graphene oxide photodetector with annealing temperature-dependent broad spectral binary photoresponses. ACS Photonics. 2017;4(11):2797-2806
- [68] Kretinin AV, Cao Y, Tu JS, Yu GL, Jalil R, Novoselov KS, et al. Electronic properties of graphene encapsulated with different two-dimensional atomic crystals. Nano Letters. 2014;**14**(6): 3270-3276
- [69] Kim CJ, Brown L, Graham MW, Hovden R, Havener RW, McEuen PL, et al. Stacking order dependent second harmonic generation and topological defects in h-BN bilayers. Nano Letters. 2013;13(11):5660-5665
- [70] McCreary A, Kazakova O, Jariwala D, Al Balushi ZY. 2D Materials. 2020;**8**(1):013001-013018
- [71] Dillon AD, Ghidiu MJ, Krick AL, Griggs J, May SJ, Gogotsi Y, et al. Highly conductive optical quality solutionprocessed films of 2D titanium carbide.

- Advanced Functional Materials. 2016;**26**(23):4162-4168
- [72] Hantanasirisakul K, Gogotsi Y. Electronic and optical properties of 2D transition metal carbides and nitrides (MXenes). Advanced Materials. 2018;30(52):1804779
- [73] Liu Z, Alshareef HN. MXenes for optoelectronic devices. Advanced Electronic Materials. 2021;7(9):2100295
- [74] Ersan F, Aktürk E, Ciraci S. Stable single-layer structure of group-V elements. Physical Review B. 2016;**94**(24):245417
- [75] Özcelik VO, Aktürk OÜ, Durgun E, Ciraci S. Prediction of a two-dimensional crystalline structure of nitrogen atoms. Physical Review B. 2015;**92**(12):125420
- [76] Gusmão R, Sofer Z, Bouša D, Pumera M. Pnictogen (As, Sb, Bi) nanosheets for electrochemical applications are produced by shear exfoliation using kitchen blenders. Angewandte Chemie. 2017;129(46):14609-14614
- [77] Yua X, Lianga W, Xinga C, Chena K, Chena J, Huangd W, et al. Rising 2D pnictogens for catalytic applications: Status and challenges. Journal of. 2018;6(12):4883-5230
- [78] Agrawal A, Johns RW, Milliron DJ. Control of localized surface plasmon resonances in metal oxide nanocrystals. Annual Review of Materials Research. 2017;47:1-31
- [79] Tong L, Huang X, Wang P, Ye L, Peng M, An L, et al. Stable mid-infrared polarization imaging based on quasi-2D tellurium at room temperature. Nature Communications. 2020;**11**(1):1-10
- [80] Li F, Jiang X, Zhao J, Zhang S. Graphene oxide: A promising nanomaterial for energy and

- environmental applications. Nano Energy. 2015;**16**:488-515
- [81] Low T, Avouris P. Graphene plasmonics for terahertz to mid-infrared applications. ACS Nano. 2014;8(2):1086-1101
- [82] Wang H, Li S, Ai R, Huang H, Shao L, Wang J. Plasmonically enabled two-dimensional material-based optoelectronic devices. Nanoscale. 2020;12(15):8095-8108
- [83] Autore M, Li P, Dolado I, Alfaro-Mozaz FJ, Esteban R, Atxabal A, et al. Boron nitride nanoresonators for phonon-enhanced molecular vibrational spectroscopy at the strong coupling limit. Light: Science and Applications. 2018;7(4):17172-17172
- [84] Iqbal MA, Ashraf N, Shahid W, Awais M, Durrani AK, Shahzad K, Ikram M. Nanophotonics: Fundamentals, Challenges, Future Prospects and Applied Applications. UK: IntechOpen; 2021
- [85] Caldwell JD, Vurgaftman I, Tischler JG, Glembocki OJ, Owrutsky JC, Reinecke TL. Atomicscale photonic hybrids for mid-infrared and terahertz nanophotonics. Nature Nanotechnology. 2016;**11**(1):9-15
- [86] Nguyen M, Kim S, Tran TT, Xu ZQ, Kianinia M, Toth M, et al.
  Nanoassembly of quantum emitters in hexagonal boron nitride and gold nanospheres. Nanoscale.
  2018;10(5):2267-2274
- [87] Chaudhuri K, Alhabeb M, Wang Z, Shalaev VM, Gogotsi Y, Boltasseva A. Highly broadband absorber using plasmonic titanium carbide (MXene). ACS Photonics. 2018;5(3):1115-1122
- [88] Aydin K, Ferry VE, Briggs RM, Atwater HA. Broadband polarizationindependent resonant light absorption using ultrathin plasmonic super

absorbers. Nature Communications. 2011;2(1):1-7

[89] Liu H, Du Y, Deng Y, Peide DY. Semiconducting black phosphorus: Synthesis, transport properties and electronic applications. Chemical Society Reviews. 2015;44(9):2732-2743

[90] Chen C, Youngblood N, Peng R, Yoo D, Mohr DA, Johnson TW, et al. Three-dimensional integration of black phosphorus photodetector with silicon photonics and nanoplasmonics. Nano Letters. 2017;17(2):985-991

[91] Abbas AN, Liu B, Chen L, Ma Y, Cong S, Aroonyadet N, et al. Black phosphorus gas sensors. ACS Nano. 2015;**9**(5):5618-5624

[92] Shao L, Tao Y, Ruan Q, Wang J, Lin HQ. Comparison of the plasmonic performances between lithographically fabricated and chemically grown gold nanorods. Physical Chemistry Chemical Physics. 2015;**17**(16):10861-10870

