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Two Dimensional Materials for Military Applications

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ABSTRACT

This paper particularly focuses on 2D materials and their utilization in military applications. 2D and heterostructured 2D materials have great potential for military applications in developing energy storage devices, sensors, electronic devices, and weapon systems. Advanced 2D material-based sensors and detectors provide high awareness and significant opportunities to attain correct data required for planning, optimization, and decision-making, which are the main factors in the command and control processes in the military operations. High capacity sensors and detectors or energy storage can be developed not only by using 2D materials such as graphene, hexagonal boron nitride (hBN), MoS_2, $MoSe_2$, MXenes; but also by combining 2D materials to obtain heterostructures. Phototransistors, flexible thin-film transistors, IR detectors, electrodes for batteries, organic photovoltaic cells, and organic light-emitting diodes have been being developed from the 2D materials for devices that are used in weapon systems, chemical-biological warfare sensors, and detection systems. Therefore, the utilization of 2D materials is the key factor and the future of advanced sensors, weapon systems, and energy storage devices for military applications.

Keywords: 2D materials; Graphene; Sensors; Heterostructured 2D materials; Decision-making

1. INTRODUCTION

Materials have always been fundamental to engineering in constructing and developing applications[1]. Therefore, developing new materials is an important research area for all fields of science[2,3]. Material researches are shaped into the pertinent application field in which they are targeted or needed. Materials used in the air, land, or sea platforms of the military are produced by pure, alloy, or composite forms of metals and non-metallic substances to enhance military capabilities[4]. The durability of the devices or systems, especially under challenging conditions, is directly related to materials and their appropriate utilization. Durability and effective life-cycle of the weapon systems, military vehicles, and electronic devices highly depends on the strength and development level of the materials in the challenging operating conditions[5]. Advanced materials are the source of new technologies that any army requires for improved situational awareness, command-and-control, communication, and sensing to achieve success in the operation field[6].

In military operations, systems consisted of advanced materials have a crucial role in the success of the operation and military organization from tactical to strategic level[7]. For example, some advanced materials are used to reflect or absorb radar emissions and infrared waves, providing stealth or deception for detection and tracking systems[8,9]. Besides, a variety of materials ranging from nano to macro scale are developed for sensor technologies such as detectors, and electronic card components like chips, microprocessors, and diodes[10,11]. Specifically, sensors provide the required data to evaluate or optimize the required decision making in military operations[12,13]. Moreover, advanced electronic devices such as processors or nano/microchips are essential to high-speed data and image processing, computing, and networking, especially to process and optimize big data. The performance of the processors or nano/microchips can be upgraded or novel variants can be developed by using advanced materials. These materials range from nanoscale like 2D materials in one-atom-thickness to macro scales[14]. 2D materials have been one of the most popular research fields of advanced materials over the past decade and the well-known 2D materials are graphene, MoS_2, hBN, WS_2, WSe_2. They can also be combined to create new materials with enhanced thermal, electronic, mechanical, or optoelectronic properties that are named heterostructures[15]. MXenes are other kinds of 2D materials with higher saturable absorption (SA) than the other 2D materials. Having higher SA (up to 50%) provides increased modulation depth for optical isolator applications[16]. This paper mainly focuses on advanced materials, including 2D materials and their utilization in military applications. 2D materials are the future of advanced military systems and 2D material researches are essential to developing novel, long-ranged/high capacity and advanced sensors, weapon systems, and energy storage devices for military applications.

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2. BACKGROUND

Owing to their superior electrical, chemical, optical, thermal, structural, and mechanical properties, two-dimensional (2D) materials have been widely studied in the literature for several engineering applications[17] as shown in Fig. 1. The above-stated properties can be exemplified as follows:

(i) Electrical conductivity: Some 2D materials have high electron carrier capability like a mechanically exfoliated single-layer graphene that has a carrier mobility of 200000 $cm^2/(V.s)$[18].

(ii) Thermal conductivity: The high thermal conductivity property of the 2D materials is the key factor to develop high performance and efficient energy storage, nanoelectronics, and optoelectronics devices[19]. Each 2D material has different lattice thermal conductivity, for example, the thermal conductivity of single-layer MoS_2 is reported to be 84 W/m.K whereas single-layer graphene can present the ultimate thermal conductivity of 4100 W/m. K[20]. This is originated from not only electrons but also phonons that account for the total thermal conductivity[21].

(iii) Optical properties: Within the 2D materials family, graphene has good optical transparency higher than 90% therefore, it can be used to develop new detector and sensor technologies[22].

(iv) Mechanical properties: 2D materials have high stiffness and strength properties with approximately one atomic thickness, as well as bending flexibility. Single-layer graphene in one atomic thickness has a hundred times higher strength than steel with 1 TPa elastic modulus[23]. The van der Waals forces between layers determine the mechanical properties such as shear, friction, and fracture characteristics in multilayer 2D materials[24].

(v) Chemical properties: Chemically inert 2D materials can make chemical absorption on their surface that yields a change in the electrical properties of 2D materials, this change is used to detect chemical or biological molecules information for developing sensor devices[25].

2D materials are crystalline materials that consist of a single or a few layers of atoms and are used as superconductors for electronic devices either pure or combined with other 2D materials to improve their desired ability such as thermal and electric conductivity[26]. Furthermore, some of them have good mechanical strength that is suitable for friction and wear reduction, which eventually increases the corrosion resistance in tribological systems[27]. Therefore, 2D materials can be used as solid lubricants for the application in micro and nano-electromechanical systems (MEMS/NEMS), which are used to develop chemical or biological sensors for detection of chemical gasses and biological agents in chemical and biological warfare, identification friend or enemy (FOE) systems, active surfaces, distributed sensor network, micro-robotic electronic disabling systems[28].

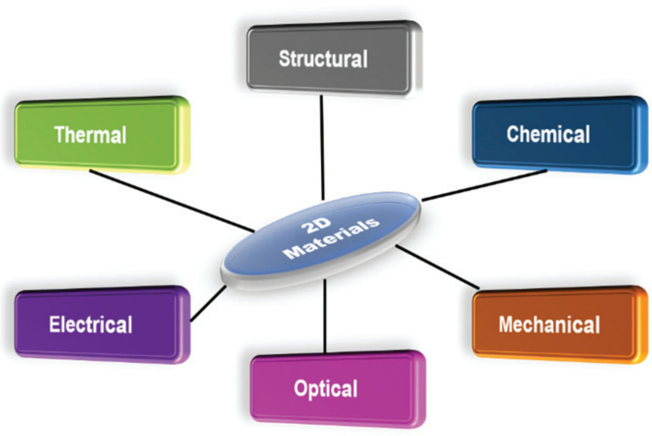

Figure 1. Properties of the two-dimensional (2D) materials.

2D materials have been a strong candidate for optoelectronic device applications such as photodetectors, light-emitting diodes, and photovoltaic devices[29]. The most widely known and the precursor of the 2D materials are graphene, molybdenum disulfide (MoS_2), and hexagonal boron nitride (hBN) with one atom thickness (named single layer) or more than two layers (referred to as multi-layer)[30]. Each of them has different properties that can be used in the different application fields; for example, graphene is found to be an excellent electrical conductor whereas hBN is an insulator with a large bandgap. However, contrary to electric conduction, hBN has better tribological properties than graphene, especially in high temperatures[31]. MoS_2 with different electrical, chemical, biological, and mechanical properties than other 2D materials are used in electronics, catalysis, biomedical, and energy-related fields as nanosheets[32]. Semiconductor MoS_2 can retrieve the weakness of the graphene band gap and is used in optoelectronic applications[33]. 2D materials have great potential for military applications to develop energy storage devices, sensors, electronic devices, and armors. 2D materials can be used to develop cathodes having high power density, long-life and shorter start-up time for thermal batteries which are employed for power delivering to electricity supply, electronic and activation systems of guided missiles, torpedos, and rockets[34]. To date research interest and trends in material science and technology have not only focused on understanding the behavior of these materials at the nanoscale, but also under extreme conditions at the macro-scale[35].

3. TWO DIMENSIONAL MATERIALS AND MILITARY APPLICATIONS

3.1 Graphene

Graphene has been the most attractive 2D material since it was discovered by Geim and Novoselov in 2004[36] and it has been the pathfinder of the 2D materials researches. Graphene consists of two-dimensional hexagonal lattice carbon atoms bonded with *sp2* covalent bonds[37]. With superior properties such as chemical inertness, thermal stability, electrical conductivity, oxidation resistance, and mechanical strength, graphene is the most promising 2D material for all application fields[38]. Graphene can be produced by two main methods that involve mechanically breaking layers of stacked graphite to get a single layer carbon atom, and synthesizing graphene from alternative carbon-containing sources[39,40].

In the first method, graphene is obtained via exfoliation of graphite mechanically by using Scotch tape or chemical exfoliation of graphite using as a sacrificial electrode in H_2SO_4-KOH solutions[41]. The second method contains chemical vapor deposition (CVD) that depends on the thermal decomposition of hydrocarbon and further deposition or accumulation on a substrate either in monolayer or multilayer as a Carbon nanosheet[42] as shown in Fig. 2. CVD is the most common method for producing large scale graphene on active metals such as *Cu, Ni, Ru, Pt* and *Cu* either at ambient or vacuum pressure. *Cu* is one of the most commonly used substrates for graphene growth on a large scale due to its low diffusion barrier to carbon[43]. In this method, graphene can be grown using *Ar*, H_2, and precursor Carbon sources like methane and acetylene[44] on copper, nickel in a high-temperature tube furnace (see Fig. 2(a)) at approximately 1000 °C by breaking the *C-H* bonds to form a layer consisted of *C-C* atoms. This layer is then transferred onto any desired surface by polymethyl methacrylate (PMMA)-mediated wet transfer method[45].

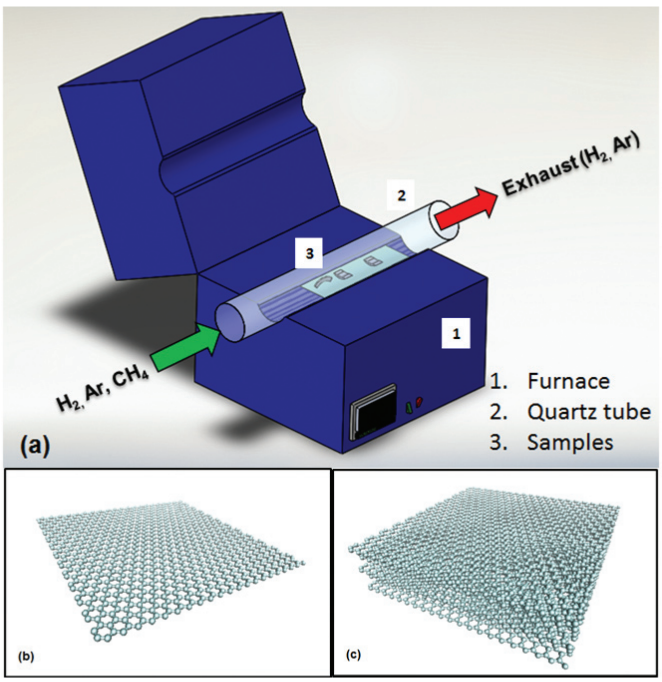

Figure 2. (a) CVD set up for graphene growth, (b) Monolayer graphene nanosheet image, and (c) multilayer graphene nanosheet image.

Molecular beam epitaxy (MBE) is another carbon sourced application of graphene growth. In this application, C_{60} and SiC sources are used to obtain the carbon flux molecular beams for thermally decomposed graphene growth at 1600 °C[46]. Graphene is mostly characterized by Raman analysis using the 532 nm laser wavelength. The typical fingerprint of the graphene is the G and 2D peaks at 1570 and 2670 ± 20 cm^{-1}, respectively as shown in Fig. 3. The intensity ratio of I_G / I_{2D} identifies the layer number of graphene where the ratio increase with layers and $I_G/I_{2D}<1$ indicates monolayer graphene, $1 < I_G / I_{2D} < 2$ and $I_G / I_{2D} > 3$ show bilayer and multilayer graphene[47]. Fig. 3 shows Raman spectroscopy characterization of a large area of mono and multi-layer graphene that is grown by CVD and then transferred on to the AISI 316 steel surface by wet transfer method using PMMA. In addition to Raman spectroscopy characterization, X-ray diffraction, and X-ray photon spectroscopy are also used to characterize graphene.

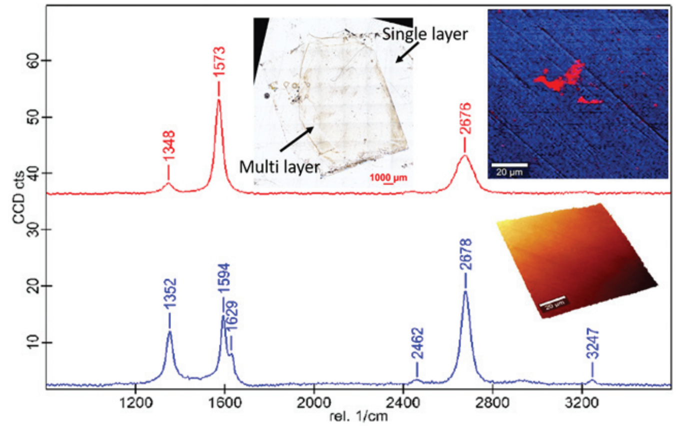

Figure 3. Raman mapping of a larger area monolayer and multilayer CVD grown graphene on a steel surface (Blue area with blue Raman spectrum is monolayer graphene and red area with Raman spectrum shows multilayer graphene on steel surface).

Single-layer graphene that is grown on the *Cu* sample shows no graphitic (002) peak whereas multilayer graphene shows the (002) graphitic peak at 26.5° indicating graphitic lattice spacing of 0.335 nm. *C1s* peak at a binding energy of 284.5 *eV* is attributed to typical *sp2* hybridized carbon atoms of graphene[48].

Mechanical characteristics of graphene were identified by AFM nanoindentation, scratching tests, and wear, friction behavior of graphene was evaluated via ball on disk tribometer tests. From the tribological aspect, graphene acts as a strong solid film with higher than 1 TPa reported elastic modulus between the sliding surfaces that reduces the friction and wear of the tribological system[49]. Meanwhile, graphene nanoparticles have been added to the engine oil and tested against base oil in recent studies, where significant friction and wear reduction have been reported[50]. However, there hasn't been any commercial tribological application of graphene in the military yet. Figure 4 demonstrates nanoscale friction force evaluation by atomic force microscopy of mono and multilayer graphene on the steel surface. A significant friction force reduction was observed for graphene at 50 nN loads.

Due to its higher mechanical strength than steel (tensile strength=0.4 GPa) with 130 GPa tensile strength, graphene has the potential to be a light ballistic armor material[51]. In the case of the application of multi-layer graphene, on-body armors will increase the mobility of the soldiers in the operation field. On the other hand, recent researches reported that hydrophobic graphene increases the corrosion resistance of the surfaces. Parasai[52], *et al.* reported that graphene significantly reduces the oxidation of the metals and it is the thinnest corrosion protective coating.

Kousalya[5], *et al.* reported that synthesized graphene on the copper surface can be an oxidation and corrosion protective coating for refrigeration systems that run in the liquid or liquid-vapor phase of refrigerant. Graphene has not been a commercial corrosion protection application yet due to the difficulty of large scale production and transfers to the desired surface. However, researches on large scale graphene coating or directly graphene growth on metals has still been continuing with different growth

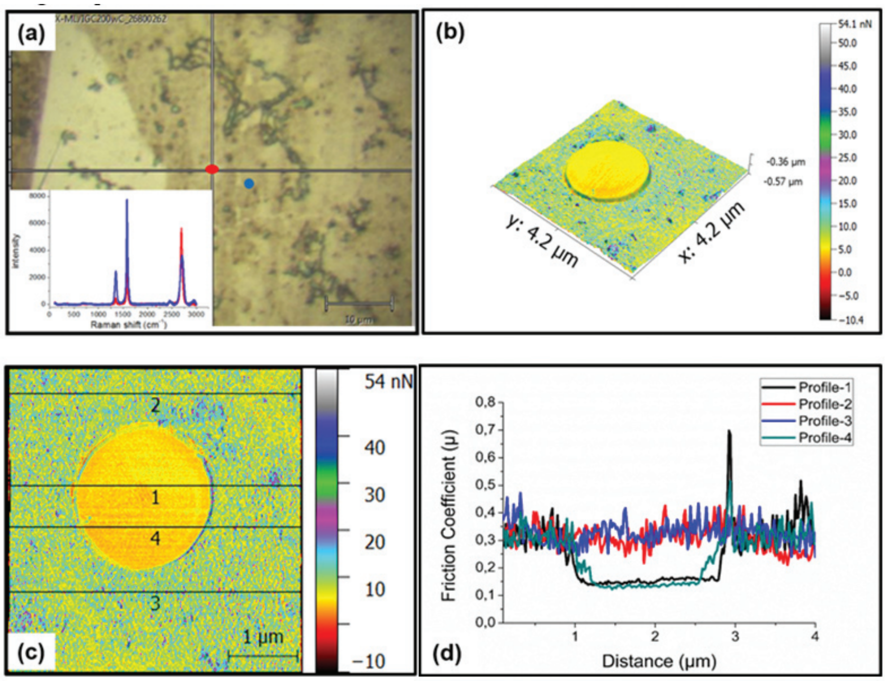

Figure 4. (a) Raman analysis of graphene on the steel surface showing monolayer (red dot and spectra) graphene and multilayer (blue dot and spectra) graphene, (b) friction force measurements of graphene overlayed topography image of graphene, (c) friction force profile extraction, (d) friction coefficients of extracted profiles.

methods[54]. With the high corrosion resistance, graphene can be used to protect critical parts of the mechanical or electronic systems from the corrosion that are used especially in naval operations, e.g. unmanned aerial vehicles (UAV) or air/surface radars, aircraft. Due to its superconductivity, graphene can be used in electric/electronic applications as computer processors, antennas, and solar cells[55]. On the other hand, quantum confinement and edge effects of graphene have been reported to cause photoluminescence (PL). Besides, by using quantum confinement effects, the fabrication size of quantum dots can be controlled to adjust the graphene bandgap and these dots have potential applications in a new generation of detection and microelectronics devices, biomedicine production[56]. Its superior electrical property with low noise makes graphene an excellent sensor candidate that can be used in military applications such as pressure and humidity sensors[57].

The higher level of electrical conductivity and optical transmittance opens a path to graphene use in screens, liquid crystal displays, organic photovoltaic cells, and organic light-emitting diodes (OLEDs)[58]. Especially, shatter-resistant graphene-made screens and touch panels can be used in military applications in hard operating conditions. A very specific surface area with high conductivity is the desired characteristic to develop electrodes for novel energy storage and batteries. Graphene has a very high specific surface area of 2675 m^2/g compared to metals[59].

Graphene is a supercapacitor material with a specific surface area of 925 m^2g^{-1}, the pore size of mainly 3-15 nm, and a specific capacitance of 117 Fg^{-1} in H_2SO_4 electrolyte[60]. Therefore, graphene is used as an electrode material for lithium-ion batteries enhancing the anode's conductivity in diverse phases of the charge-discharge cycle and capacity[61] of the battery up to 1500 $mAhg^{-1}$. Therefore, graphene increases battery storage capacity, which means longer battery life for handheld radios used by units in the operation field[62]. Graphene was used to produce infrared (IR) transparent windows that can be used in IR guided missiles. On the other hand, owing to higher than 85 % IR transmittance, graphene is used as an IR sensor/detector for IR cameras or missile detectors as shown in Fig. 5 with desired electromagnetic (EM) shielding properties[63].

3.2 Hexagonal Boron Nitride

The two-dimensional hexagonal lattice boron nitride (2D-hBN) has a similar structure as graphene and is named as white graphene which is an electrically insulating, chemically, and thermally stable ceramic material[64]. The bond length of *B-N* is 1.44 Å in hBN whereas the bond length of *C-C* is 1.45 Å in graphene as shown in Fig. 6[65]. Single-layer h-BN can be synthesized on *Pt* and *Cu* foils via ambient/ low-pressure CVD by using a precursor-like borazine and ammonia-borane at 1000 °C or it can be produced from bulk crystalline h-BN exfoliation[66]. The typical XRD peaks at 2θ = 26.3, 41.4, 43.5, 54.7, and 75.7 are identified as (002), (100), (101), (004), and (110) planes respectively of the hexagonal phase of BN (see Fig. 7(a))[67]. The FT-IR spectrum of hBN

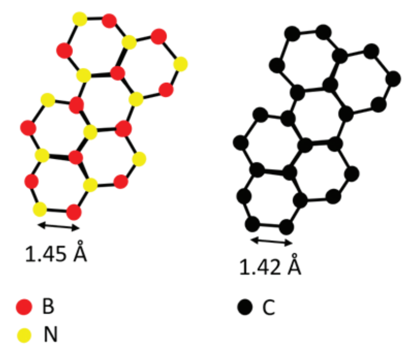

Figure 5. Structure of the IR seeker of the missile.

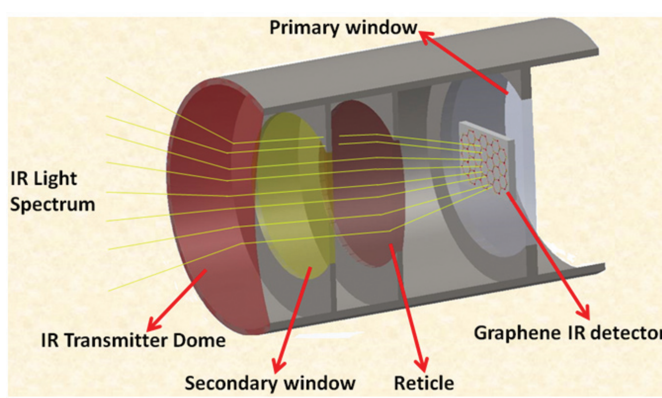

Figure 6. Structure and bond lengths of hBN and graphene.

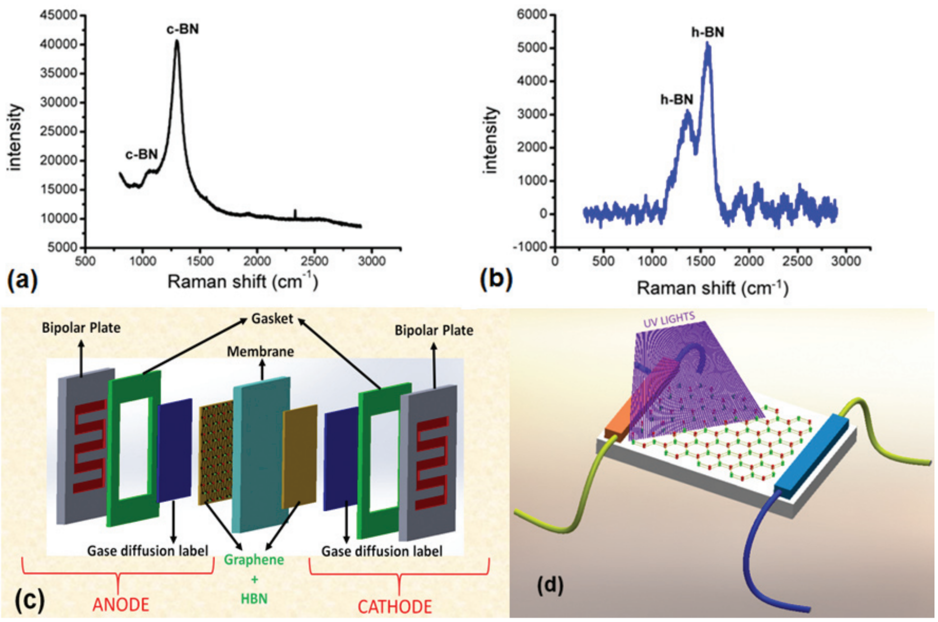

Figure 7. (a) Raman spectra of cBN, (b) Raman spectra of hBN, (c) Graphene-hBN heterostructure fuel cell, and (d) UV-photodetector.

shows two typical peaks at 1380 cm^{-1} and 805 cm^{-1} described as *B–N* stretching vibration. In the XPS identification, *B1s* peak at a binding energy of 190.2 *eV* is assigned to *B-N* bonds of hBN[68].

The 2D hBN is characterized by Raman analysis with the determination of a typical sharp peak at 1360-1370 cm^{-1} wavelength in Raman spectra as shown in Fig. 7(b)[69] that arises from the E_{2g} phonon[70].

When looking at the mechanical properties of the 2D hBN, the tensile strength of the 2D hBN is reported to be 120-165 GPa, and Young's modulus was found to be 0.8-1± 0.1 TPa by AFM indentation measurements[71]. Due to this high mechanical strength and lower friction coefficient, it has been used as a solid lubricant in tribological systems[72] or added into base oil as a nano additive in which it reduced wear approximately[73] 50 %. The thermal conductivity of the few-layer 2D hBN nanosheet was measured to be 100-270 W/m.K, which is a good heat spreading material for novel electronic devices[74]. With these findings, it has been reported as a new material candidate against SiO_2 used in transistors[75]. Although 2D hBN is an insulator material, it can be activated by graphene in fuel cells (see Fig. 7(c)) enhancing the cell performance up to 50%[76]. On the other hand, with the high band edge absorption coefficient, it can be utilized to develop UV photodetectors as shown in Fig. 7(d)[77].

3.3 Molybdenum Disulfide

The other popular 2D material is molybdenum disulfide (MoS_2) with unique electrical, physicochemical, biological, and mechanical properties[78]. It can be produced by exfoliation of geological MoS_2 crystals, chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD), and pulsed laser deposition (PLD) and then transferred onto the desired sample[79]. MoS_2 consists of trigonal prismatic structure *S-Mo-S* bonds (see Fig. 8(a))[80] with van der Waals interactions and typical Raman characterization show 2D MoS_2 peaks between 380-390 and 400-410cm^{-1} at Raman spectra[81].

2D MoS_2 has been used to develop ultra-fast field-effect transistors (FETs), optical devices, and flexible electronic devices[82]. Besides, the hybrid heterostructure MoS_2 combined with graphene showed a good ability to sense gases[83]. Thus, 2D MoS_2 can be used to produce low-powered, high-performance gas sensors to detect and monitor explosive and chemical gases for land and marine units, especially, in chemical warfare[84]. The 2D MoS_2 has been used to develop phototransistors (see Fig. 8(b), flexible thin-film transistors, and electrodes for lithium-ion batteries[85]. For the tribologic applications, single and multilayer MoS_2 nanosheets were added into a base oil and tested with a ball on the disk tribometer. It was reported that multilayered or two-dimensional MoS_2 nanosheets can be a commercial nano additive for the paraffin oil to improve friction and wear resistance properties[86]. Besides, 2D MoS_2 was reported to be a good solid lubricant for relatively sliding mechanical components[87].

3.4 MXene 2D Materials

2D transition metal carbides, nitrides or carbonitrides have been introduced as MXene with a chemical formula of $M_n + 1YnTx$, where *M* is the transition metal (such as *Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn*), Y is the carbon or nitrogen, *T* is the functional groups such as *=O* or *-OH* (*n*=1-3). They are produced by extracting the *Y* element from three-dimensional (3D) *MYT* phases with acidic chemical reactions[88]. They have great potential to develop photothermal conversion, field-effect transistors, topological insulators, optoelectronic properties, sensors, and hydrogen evolution reactions[89]. Furthermore, they have better saturable absorption (SA is up to 50%) than other 2D materials such as graphene and MoS_2 (SA is up to 20%), which is used to increase modulation depth for optical isolator applications in fiber-based femtosecond lasers. Therefore, they can be used in weapon systems such

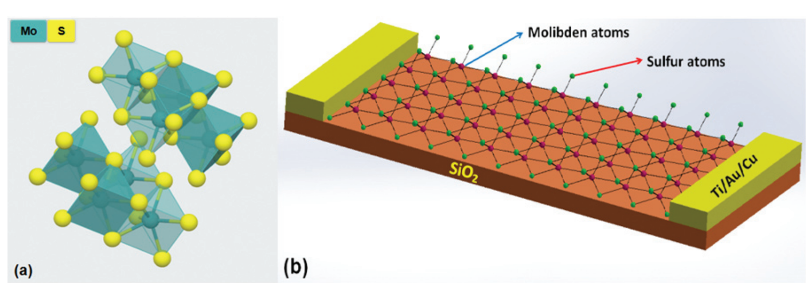

Figure 8. (a) Structure of MoS_2 and (b) Schematic view of the fabricated multi-layer MoS_2 phototransistor.

as FLIR cameras, targeting pods, especially they could be a solution to overheating of the laser power supply of targeting pods that cause missiles to fall into ballistic guidance[90]. Moreover, recent studies have been reported higher effective Young's modulus of 330 ± 30 GPa than 2D MoS_2, GO, r-GO, however, lower than graphene and hBN. This high elasticity suggests protective coatings, membranes, and nanoresonators for military applications[91].

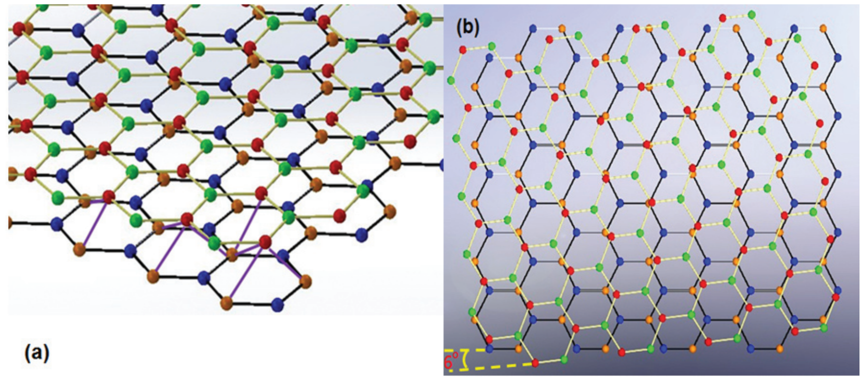

Figure 9. (a) Structure of 2D mono-layer $MoS_2/MoSe_2$ and (b) Top view of $MoS_2/MoSe_2$.

3.5 Heterostructured 2D Materials

Graphene derived from exfoliation of the graphite is the flagship of the 2D materials researches and has also accelerated researches on heterostructure 2D materials which are carried out directly stacking individual monolayers of 2D materials such as WSe_2, $MoTe_2$, WS_2-MoS_2, WSe_2-SnS_2, hBN-graphene, MoS_2-graphene. The combination of these 2D materials forms heterostructures that enable excellent electron transfer. They also have specific properties that open new paths to novel researches for military applications including transistors, photodetectors, chemical, and biological sensors, and nanoelectromechanical systems. For example, the combination of graphene and black phosphorus provides rich novel light-substance interaction phenomena, like photothermoelectric, and various other optoelectronic effects which have the great potential to develop new IR detectors for military applications[92]. Development of the flexible gas sensor by using MoS_2/graphene heterostructure material was reported by Cho[93], *et al.* With this sensor, hazardous/toxic gases can be detected and it has potential usage in chemical gas detection systems for military applications. Heterostructured 2D materials researches on developing energy storage systems have been significant in recent years to replace lithium-ion batteries with a new energy storage technology that has the ultimate fast charge capacity and long effective life[94]. Graphene-based Na^+, K^+, Mg^{2+}, and Al_3^+ electrodes are in the scope of this researches. Graphene-based silicene, borophene, phosphorene 2D heterostructures are new electrode candidates for future energy storage devices[95]. The development of new energy storage devices can lead to an upgrade in the diesel-electric submarine propulsion system. Thanks to 2D heterostructure wearable sensing systems, flexible/stretchable electronics devices and novel sensors (pressure, humidity, etc.) could be developed for military applications to be used in infantry units[96]. The Moire patterns (an involvement pattern produced by overlaying similarly structured monolayer materials, but slightly rotated in any direction) are formed by 2D mono-layer van der Waals stacking materials such as $MoS_2/MoSe_2$ as shown in Fig. 9. These materials with high electron mobility are reported to have great potential for the development of nanodevices[97]. Therefore, the production of vertical or lateral heterostructures from two-dimensional materials opens a gate to quantum-engineered transistors which will be the alternative silicon technology for sensors, electronic devices, and computers[98].

Additionally, MXenes/graphene heterostructures have been explored for battery cathodes and their positive effects on capacity compared to functionalized MXenes have been reported[99].

4. CONCLUSION

Advanced materials are going to be key for the future of the state of the art device developments, where 2D materials have an important role in this development process. Sensors, MEMs, electronic devices that use diodes, chips, transistors; and energy storage systems such as batteries and fuel cells will be more effective by using 2D materials than conventional ones. With the large application field, 2D materials have many advanced technological benefits to the military for critical applications such as thermal batteries for missile systems. Advanced 2D material based sensors and detectors will give a significant opportunity to attain correct data that is needed for planning, optimization, and decision-making which are the main factors in the command and control process in the military operations. Development and commercialization of advanced 2D materials require models including materials and systems. In the material model, the nanostructure is the output of the application field. The system model includes requirements and environment as inputs where performance, costs, safety, reliability, and durability are the outputs. To achieve any product based on advanced 2D materials robust optimization between these models is needed. Therefore, interdisciplinary work must be conducted between the fundamental sciences, and respective engineering fields; i.e. mechanical, electrical, electronic, and industrial engineers in developing advanced 2D materials based systems for military applications.

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