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Applications of 2D Materials (MXenes) in Sensors: A Minireview

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MXenes are a class of 2D material produced from the MAX phase structure, e.g., 3D atomic laminate Ti_3AlC_2 ; they have a combination of layered carbides and nitrides. They belong to a distinctive type of structured materials with better conductivity than metals, increased ionic conductivity, flexible mechanical properties, and being hydrophilic. MXenes can be structured to form nanoparticles, multi- and single-layered nanosheets, which exhibit large specific surface areas enhancing their efficiency of sensing in MXene sensors. In addition, they are capable of forming composites with other materials with ease. Their morphology enhances their mechanical flexibility and stretchability enabling them to have wide applications in energy-storage devices, wearable sensors, and for electromagnetic shielding. Considering this, an attempt is made to review the recent advances in MXenes with emphasis on their applications in the area of wearable sensors that include pressure, strain, biochemical, temperature and gas sensing.

Максени — це клас двовимірних матеріалів, виготовлених із МАХ-фазової структури, наприклад, тривимірного атомарного ламінату Ti_3AlC_2 ; вони містять комбінацію шаруватих карбідів і нітридів. Вони належать до особливого типу структурованих матеріалів з ліпшою провідністю, ніж метали, підвищеною йонною провідністю, гнучкими механічними властивостями та гідрофільними. Максени можуть бути структуровані для формування наночастинок, багато- або одношарових нанолістів, які мають великі питомі площі поверхні, що підвищує їхню ефективність зондування в максенових сенсорах. Крім того, вони здатні з легкістю формувати композити з іншими матеріалами. Їхня морфологія підвищує їхню механічну гнучкість і розтягливість (тобто еластичність), що уможливорює широко застосовувати їх у пристроях накопичення енергії, переносних давачах, а також для електромагнетного екранування. У зв'язку з цим робиться спроба розглянути останні досягнення в дослідженнях мак-

сенів з акцентом на застосуванні їх в області переносних давачів тиску та деформації, біохемічних, температурних і газових давачів.

Key words: MXenes, gas sensor, temperature sensor, pressure sensor, biosensor.

Ключові слова: максени, датчик газу, датчик температури, датчик тиску, біосенсор.

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1. INTRODUCTION

MXenes are (2D) two-dimensional nanomaterials first ascertained in 2011 and are pronounced as ‘max-eens’. They are ceramics comprising the big family of 2D materials. MAX phase was the bulk crystal, from which MXenes are made of. Their inherent conductivity and volumetric capacitance is more than other 2D materials. This is due to their structure consisting of molecular sheets derived from the nitrides and carbides of titanium. MXenes are signified for their applications in various sectors like sensing, energy storage and medicine. The main interest in MXenes lies in the fact that this material could feasibly be structured with large millions of possible ordering of transition metals, carbon and nitrogen. We need to investigate stable arrangement. It is reported that still a large number of MXene compounds are likely to be discovered in near future [1]. The discovery of MXene started with ceramics known as MAX phases that consist of layered carbides and nitrides. These ceramics produced 3D materials, which, when substituted with Ti_3AlC_2 powder in hydrofluoric acid, selectively removes aluminium. This chemical process (exfoliation) yield 2D Ti_3C_2 nanosheets called MXene, which is similar to graphene with different properties. MXene was first demonstrated in 2011 by transforming the three-dimensional materials Ti_3AlC_2 representing MAX phase into a 2D material [2]. Figure 1 displays the journey of MXenes during the last decade.

The structure of MXenes emerged them to be distinctive with attractive features such as high conductivity, ionic conductivity and mechanical flexibility as compared to other materials. The size, shape and structure of MXenes can be altered, so that to form nanoparticles, nanosheets of single- and multilayers exhibiting large and specific surface areas, making them favourable for enhanced sensing. In addition, MXenes easily form composites with other materials. The structures of MXenes enhance their mechanical flexibility and stretchability making them feasible for wearable sensors (pressure, temperature, biochemical and gas sensors), energy storage and electromagnetic shielding.

MXenes are derived from MAX phases, whose formula is given as

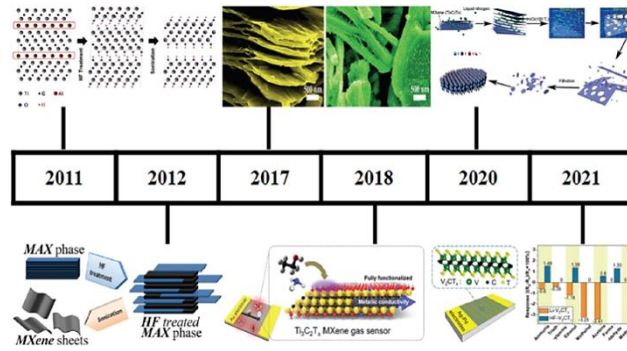


Fig. 1. Journey of MXenes from (2011–2021) by courtesy of Ref. [3].

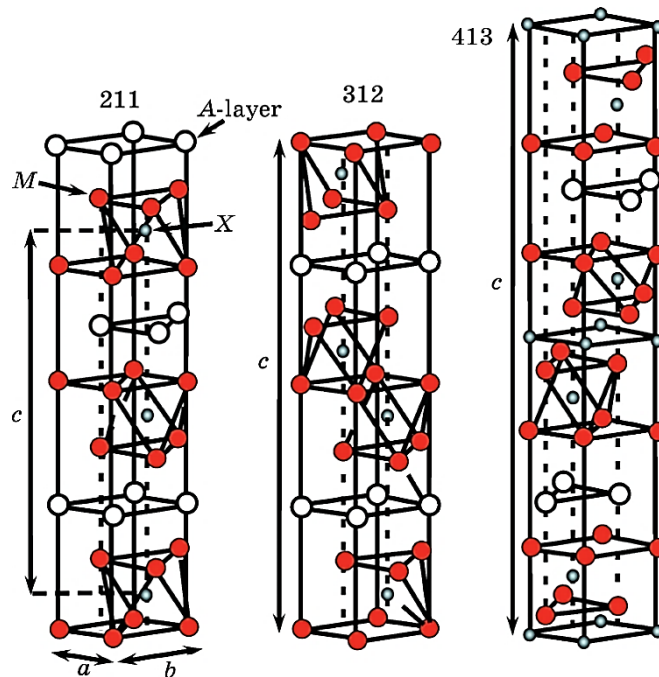


Fig. 2. Crystal structure of MAX phases [5].

$M_{n+1}AX_n$, where $n = 1, \dots, 4$; M is early d -block transition metal; A is main group sp -element (specifically groups 13 and 14); X is N or C atom.

They have edge-sharing structure with distorted XM_6 octahedral loaded by single planar layers of A -group element [4]. Figure 2 displays 3D MAX phase structure.

MXenes can be derived from MAX phases through selective etching of A layers. Synthesis of MXenes effectively controls their mor-

phology, influencing the sensory functions. Different preparation methods of MXenes are reported in Refs. [6, 7]. However, wet etching method is significant in case of sensors [8, 9], where the morphology is altered through varying the quantity of etching solution, time of etching, ultrasonic time [10] and experimental temperature [11, 12]. Using this technique, various compositions of single and multilayered stacks of MXenes are obtained. Apart from various synthesis methods, being used [13–16] wet selective etching is preferred for fabrication of MXenes-based sensors.

2. WEARABLE SENSORS

Wearables are devices embedded into items worn on a body. Information tracking on real time basis is one of the major applications in today's life. They mainly use sensors, which comply with mechanical and sensing capabilities in robotics, monitoring of health and motion detection, *etc.* [18–20]. Based on the complexity of object, flexible devices with accurate electrical output are required during daily movements [21], which might not be achieved with traditional electronic devices. In this regard, many researchers reported various strategies to design microstructured devices instead of external circuit structural design [22].

However, these strategies could not fill the gap between mechanical flexibility and electrical performance leading to develop various wearable applications.

As mentioned, MXenes proved to be favourable as wearable sensors. Figure 3 shows the application of MXenes in various sensors.

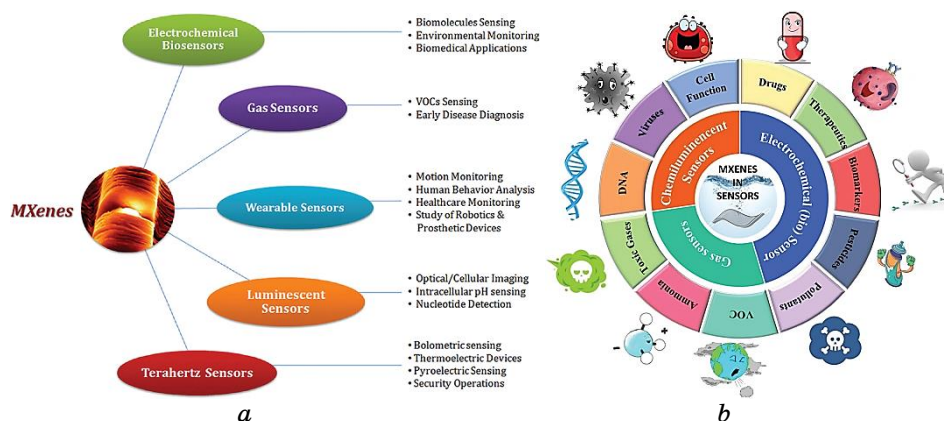


Fig. 3. (a) MXenes-based sensors [17]; (b) MXenes in various sensors including their area of applications [23].

2.1. Physical Sensors

A device capable of sensing physical quantities (pressure, temperature, *etc.*), converting it into a signal that can be analysed by an observer is known as physical sensor. It is evident that different nanostructured materials are used to construct various physical sensors. This include nanowires, nanoparticles, nanoribbons, nanotubes and graphene. However, MXenes prepared by chemical liquid etching are found to be superior as compared to graphene with excellent properties and ease in chemical modification [24]. MXenes are being used in stress sensors for detection of tiny shaped variables. Their accordion-like shaped structure can be used in piezoresistive sensors. As mentioned earlier, enhanced sensor performance, due to mixing with other materials, make MXenes more significant as physical sensors.

2.2. Strain Sensors

A device capable of converting the applied force into variable resistance is known as strain sensor. It can be used to convert force, pressure, tension, weight, *etc.* into a variable resistance and can be measured [25]. Application of external force on the sensor cracks the internal conductive materials, causing the electrical characteristics to change accordingly. These materials are made of closely stacked 2D sheets with van der Waals forces existing between adjacent sheets. On application of an external stress, the sheets get large cracks whose dimensions are proportional to applied stress. Blockage of conductive on application of large force limits the stability and sensing range. To avoid this drawback, different phases of 3D materials with different dimensions are added into 2D materials. This could achieve a sensitivity of 64.6 for 0–30% strain and 772.60 for 40–70% strain. Similarly, silver nanowire combined with $Ti_3C_2T_x$ with introduction of dopamine and nickel ions lead to strain sensor [26]. This yielded a sensor with GF 256.1, 433.3, 1160.8, 2209.1, and 8767.4 in strain ranges of 0–15%, 15%–35%, 35%–60%, 60%–77% and 77%–83%, respectively. It is reported that highest sensing range is above fifty percent with sensitivity greater than 200, which exceeds many of the reported strain sensors [27]. It is reported that one-dimensional materials if used to connect MXenes sheets, make the device enhance sensitivity and strain sensing range [28]. In a similar way, composite films with $Ti_3C_2T_x$ nanosheets derived from $Ti_3C_2T_x$ MAX phase through MXenes and poly [29] reported conductivity up to 2000 S/m. By altering the morphology of $Ti_3C_2T_x$ materials through alteration of etchant, etching time and ultrasonic time, $Ti_3C_2T_x$ nanoparticles and

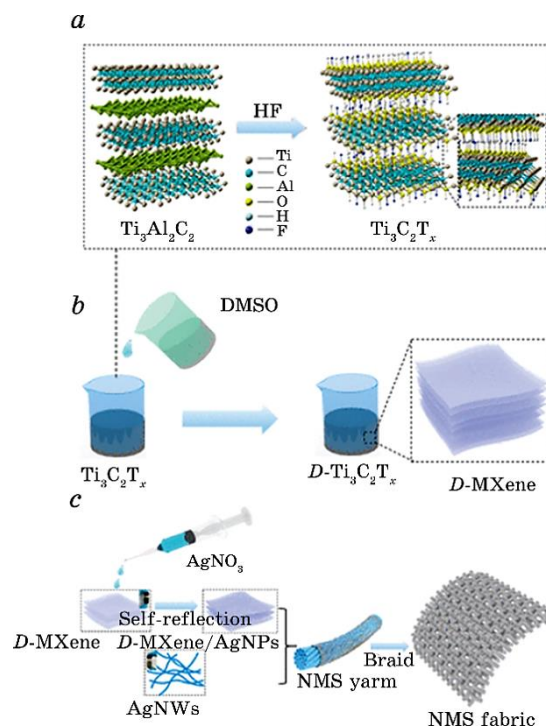


Fig. 4. Experimental process of HF etching [32].

nanosheets increased the synergistic effect. The maximum sensing range of the sensor is more than fifty percent and suitable for the whole body [30]. To obtain the MXenes for strain sensing, combination of $Ti_3C_2T_x$ with hydrogels is used and leads to antifreeze, self-healing and high-sensitivity ($GF = 44.85$) [31].

Apart from that we discussed above, zero dimensional silver nanoparticles were loaded on two-dimensional MXene nanosheets and are compounded with one-dimensional silver nanowires. This method is reported to ensure high GF and continuity at large strain of yarn (200%). Figure 4 represents process, in which aluminium is etched directly by hydrofluoric acid (Fig. 4, a), adding DMSO solution to delaminate MXene nanoblocks into nanosheets (Fig. 4, b) and silver nanoparticles [32].

2.3. Pressure Sensors

A device capable of sensing pressure and converts it into an electric signal proportional to the applied pressure. Various pressure sensors are developed for transient electronic skins, flexible displays, intelli-

gent robotics, real-time sensing performance decreasing electronic waste and environmental impact. However, the real challenge in achieving a high sensitivity and high range of sensing, quick response, durability was intact. Apart from conventional techniques, sensors developed with MXenes are proved to exhibit high GF values. A sensor with GF 180.1–94.8 and 94.8–45.9 in the range of 0.19–0.82 and 0.82–2.13% was reported [33]. This sensor was used to explore human activities like throat swallowing, eye blinking, *etc.* The sensor has a shape of musical instrument accordion when multiple layers of MXenes were used. It is a piezoresistive sensor, in which the applied pressure on the device is converted to by material deformation. In a similar way, high sensitive degradable pressure sensor with low detection limit, broad range, fast response (11 ms), low power consumption and excellent degradability was fabricated. This is used to monitor the health of patients duplicating E-skin in clinical diagnoses, personal healthcare monitoring and artificial skins.

Figure 5 demonstrate the steps involved in fabricating MXene

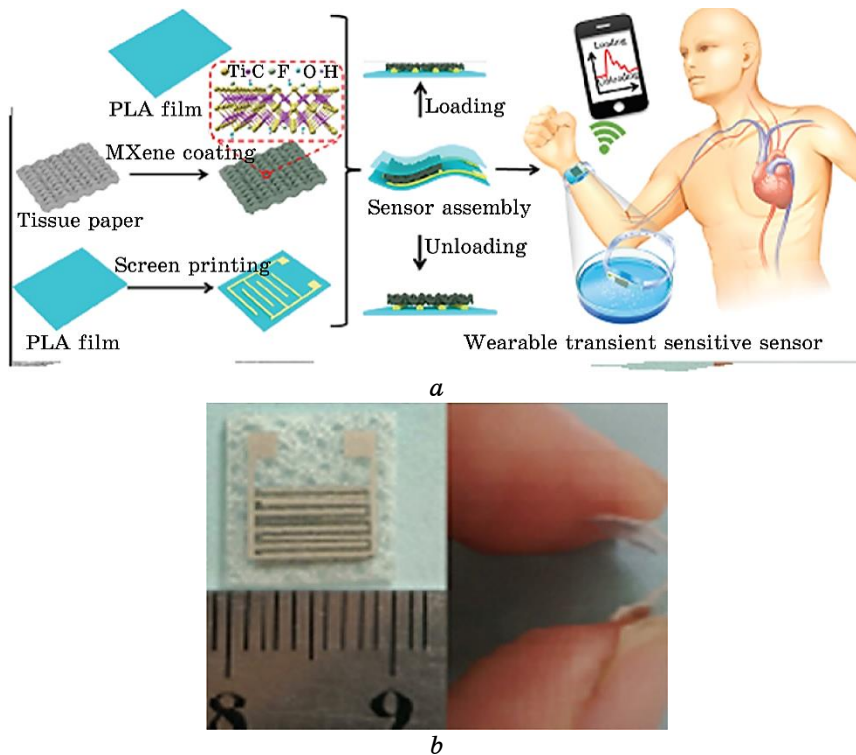


Fig. 5. (a) Steps involved in fabrication of flexible wearable transient pressure sensors with MXene nanosheets [34]; (b) flexible wearable transient pressure sensor [34].

nanosheets into flexible wearable transient pressure sensor (Fig. 5, *a*) and its photograph (Fig. 5, *b*).

Due to fragility of MXenes, they cannot sustain high pressure. This drawback can be overcome by mixing them with high strength materials that supports stress on the sensor. MXenes based flexible piezo-resistive sensors are mainly of two types given by aerogel and elastic matrix sensors. Aerogels exhibit high porosity and super elasticity, which signify them for fabrication of flexible piezoresistive sensors. In this context, various pressure sensors with this principle have been reported [35–39].

2.4. Chemical Sensors

These are devices capable for converting the property of a particular analyte into a measurable signal, which is proportional to analyte concentration. It is capable for recognizing the molecule of the analyte through selection by converting the response into an electrical signal. These sensors are capable of measuring and analysing chemical compounds. The property of MXenes being hydrophilic in nature made them significant to be used in wearable sensors. They can adsorb biomolecules and gas molecules by controlling the morphology and surface modification, hence bringing a change in their electrical properties. In MXenes, *M*-layer elements are transition metals that include Ti, Nb, Ta, *etc.*, which are inert to biological organisms. This characteristic of inertness equips compounds of MXenes excellent biocompatibility. It is shown that MXenes can be eliminated from mice through degradation [40].

2.5. Gas Sensors

These are devices, which detect the presence and concentration of hazardous vapours and gases that include explosive gases, VOCs, humidity, *etc.* Gas sensors are essentially required to sense environmental parameters, which is a challenging task in wearable sensors [41]. MXenes has a suitable surface structure for adsorption of different gas molecules, which affects its overall conductivity [42]. MXenes-based composite in sensing of gases such as H₂, O₂, CO₂, CH₄, NH₃, *etc.* was demonstrated [43]. First principles simulation was used to infer that Ti₂C monolayer with O₂ termination was more suitable for NH₃ than other gas molecules. Similarly, reaction between NH₃ and O terminated semiconducting MXenes with different charge states was reported using the same principle [44]. TiC₂T_x embedded flexible polyimide platforms using solution-casting method lead to high performance sensor for detection of NH₃. Ti₃C₂T_x–

graphene hybrid fibres made by scalable wet-spinning process exhibited excellent mechanical and high electrical conductivity improved NH_3 sensing significantly [45]. $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes films as metallic channels for volatile organic compounds (VOCs) gas sensors were demonstrated with high signal-to-noise ratio [46]. Flexible polyimide substrate with V_2CT_x solution formed a gas sensor with high sensitivity toward non-polar gas [47].

It is reported that literature related to MXenes based gas sensors was limited. Generally, MXenes in combination with certain gas-sensitive materials forming composite material can be used as gas sensors with high performance. These sensors contain vacant spaces in the middle layers of MXenes, which adhere to gas molecules [48].

Table shows the gas sensitivity exhibited by various MXene-based composite materials.

Different types of gas sensors using MXenes were reported such as hydrogen peroxide (H_2O_2) sensor up to a concentration of 0.7 nM with response time of nearly 10 seconds [50]. In a similar way, a Pt/PANI/MXene nanocomposite was used to fabricate H_2O_2 sensor, which demonstrated a magnified current response and low detection of 1.0 μM [51]. Similarly, NH_3 gas was sensed with the help of MXene-based sensors. The reaction between NH_3 and O-terminal MXenes with various charges was studied to know the adsorption of NH_3 molecules on M_2CO_2 with evident electron transfer [52]. In this context, sensors reported for detection of ethanol, acetone along with NH_3 are of importance [53]. Even though merging of MXene materials with other gas-sensitive materials lead to development of

TABLE. Gas sensitivity exhibited by various MXene-based composite materials [49].

Material	Gas	Operating temperature, °C	Response time	Gas response, R_g/R_a
$\text{Ti}_3\text{C}_2\text{T}_x$	acetone	RT	NA	0.125/200 ppm
$\text{W}_{18}\text{O}_{49}/\text{Ti}_3\text{C}_2\text{T}_x$	acetone	300	4.6 s/20 ppm	11.6/20 ppm
$\text{CuO}/\text{Ti}_3\text{C}_2\text{T}_x$ MXene	toluene	250	270 s/50 ppm	11.4/50 ppm
MXene/ SnO_2	NH_3	RT	36 s/50 ppm	40/50 ppm
MXene/ TiO_2	NH_3	RT	60 s/10 ppm	3.1/10 ppm
Li- V_2CT_x	NH_3	RT	41 s/50 ppm	3.41/500 ppm
HF- V_2CT_x	CH_4	RT	169 s/500 ppm	1.49/500 ppm
Cl- $\text{Ti}_3\text{C}_2\text{T}_x$	NH_3	RT	98 s/500 ppm	13.2/500 ppm
$\text{Co}_3\text{O}_4@/\text{PEI}/\text{Ti}_3\text{C}_2\text{T}_x$	NO_x	RT	27.9 s/30 ppb	N/A
MXene/ Co_3O_4	HCHO	RT	83 s/10 ppm	9.2/10 ppm
$\text{SnO}-\text{SnO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	acetone	RT	18 s/100 ppm	12.1/100 ppm
$\text{Ni}(\text{OH})_2/\text{Ti}_3\text{C}_2\text{T}_x$	NH_3	RT	78 s/50 ppm	6.2/10 ppm

high-performance gas sensors, they are less and limited to NH_3 detection and certain VOC gases.

2.5. Biosensors

These are devices capable of measuring chemical or biological reactions through signal generation proportional to analyte concentration. They measure and characterize organic materials. These sensors include enzyme sensors and DNA analysis systems. Recently, MXenes are proved as strong intracellular pH sensors. pH-sensitive Ti_3C_2 quantum dots were fabricated [54] and used to develop a ratio metric photoluminescence probes that monitor intracellular pH. This can be applied to develop wearable fluorescent nanosensors. Apart from intracellular pH monitoring, MXenes can be used to detect glucose and phenol molecules. A biosensor made from gold and MXenes composite for detection of glucose was reported [55]. The device exhibited good range of glucose detection from 0 to 18 mM. Three-dimensional porous composite of MXenes for non-enzymatic glucose sensor was fabricated and reported in Ref. [56]. Similarly, MXenes/DNA/Pd/Pt material was used for developing sensitive DA sensor [57]. A mediator free biosensor was fabricated through TiO_2 - Ti_3C_2 nanocomposite of accordion shape that disable haemoglobin was developed [58]. A sensing platform was formed by loading TiO_2 nanoparticles on Ti_3C_2 substrate suitable for enzyme immobilization [59]. Studies on electrochemical response of MXenes for detection of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} for new platform were proposed to detect heavy metal ions [60]. Apart from detection of heavy metal ions, MXenes nanosheets are capable of removing heavy metals like copper, lithium, sodium, *etc.* [61].

3. CONCLUSION

MXenes and their applications in the field of wearable sensors were reviewed. The ease, with which the morphology of MXenes is controlled, makes them significant in the field of wearable sensors. Their mechanical properties, conductivity and hydrophilicity play key role in their applications. Different sensors with MXenes proved to be exhibiting high sensing performance with good GF values. Reviewing the lead taken by MXenes in the field of sensors, new sensing devices may be fabricated with combination of various materials and MXenes. This combination may improve synergistic effect between various materials and MXenes leading to efficient sensors with more response range and sensitivity. At the same time, it is noteworthy to realize the role of MXenes based sensors in med-

ical detection, wearable devices and electronic skin as many problems persist. Synthesis of MXenes poses toxicity to environment, which need to be addressed. In addition, human body will be affected due to HF etching. In view of this, safety measures need to be considered. As linear induction cannot be realized for high strain in practical MXenes-based sensors, it affects sensors program setting. Hence, the microstructures of MXenes need to be redesigned in improving the linearity of the sensor. Literature shows that MXenes used in biomedical applications are biocompatible but no references of systematic evaluation. Hence, lot of understanding the surface chemistry of MXenes and its synthesis and their applications in wearable sensors is essential. Hence, it is of prime importance to explore ways to improve the role of MXenes for further exploration.

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