MXene-based electromagnetic wave response

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Abstract

Recently, MXenes stand out as an attractive type of two-dimensional layered material. Their unique deformable surface terminations and rich chemical compositions endow MXenes with adjustable and customizable characteristics, resulting in excellent linear/non-linear electromagnetic wave responses and versatile applications. In order to get more insights in this area, here, we make a comprehensive summarization of the interactions according to the response principles between MXenes and electromagnetic waves, such as absorption, scattering, emission, transmission, resonance, etc. The latest progress of corresponding applications is also introduced in detail, including photothermal conversion, photo-/photoelectro-catalysis, electromagnetic interference shielding, photoluminescence, tumor therapy, transparent electrode, photodetector, surface-enhanced Raman scattering, plasmonic absorption, saturated absorption, etc. Finally, the challenges and opportunities are discussed to look forward to the beautiful future of MXenes and MXene-based electromagnetic wave responses.

1. Introduction

MXenes, a family of two-dimensional (2D) layered transition metal carbides, nitrides and carbonitrides, have been attracting intensive attention since the first report of titanium carbide in 2011 [1]. Such materials share a formula of $M_{n+1}X_nT_x$ fabricated via selective extraction of A element from layered parent carbide and nitrides of $M_{n+1}AX_n$ phases, where M stands for one or more permutations of early transition metal elements (Ti, Mo, Sc, Zr, Cr, Ta, etc.), X is always C and/or N, A denotes A-group element, like Si, Al, Ga, etc, and T is surface terminations (–F, –OH, –O, –Cl, –Se, etc) [2, 3], n is so far 1–3. This structural and chemical versatility allows MXenes to stand out as various nanomaterials. The quickly growing attention on MXenes has led to great progress on their applications of electromagnetic waves [4].

In general, electromagnetic waves appear when energy travels through space that actually consists of a magnetic field and an electric field oscillating perpendicular to one another [5]. The interactions between electromagnetic waves and MXenes can be separated into absorption, scattering, emission, transmission and resonances, etc, leading to wide applications. However, challenges are always springing up during development. It is of great urgency to obtain more insights into the interaction principles between electromagnetic waves and MXenes to support the practical applications.

The first report on electromagnetic waves response of MXenes can be backdated to 2014 as shown in scheme 1 [6]. Scientists used MXenes to absorb the electromagnetic waves ranged from 300 to 600 nm (UV and Vis) to realize photocatalysis reactions [7–9]. Then, with the gradually deepening recognition of distinctive physical and chemical properties of MXene, more and more applications appeared on the basis of the understandings between MXenes and electromagnetic waves. For example, MXenes have been regarded as a high-conductivity material. This characteristic determines the reflectivity and absorption ability of electromagnetic waves [10]. Therefore, in 2016, extended research of electromagnetic wave scattering had been carried out, including electromagnetic interference (EMI) shielding technology in the range of X band (2.5–3.75 cm) [11]. Meanwhile, MXenes had also been employed in the fields of tumor therapy [12], Surface-enhanced Raman scattering (SERS) [13] and transparent conductive film [14] owing to its
absorption, scattering and transmission to the near infrared region (NIR) (800–1100 nm), mid-far infrared region (2.5–50 µm) and visible to infrared region (400–2000 nm), respectively. Based on these results, electromagnetic wave emission of MXenes was achieved in 2017. The photoluminescence (PL) spectrum of Ti$_3$C$_2$ MXene quantum dot (MQD) is excitation-dependent, and corresponding quantum yield reaches about 10% [15]. After constant research, the wavelength range of electromagnetic wave excitation was extended from 300 to 500 nm [16]. There exists research in correlation fields, involving broadband plasmonic absorber [17] (500–2100 nm), plasmonic photodetection [18] (400–800 nm), photonic diodes [19] (300–1000 nm) and femtosecond mode-locked (ML) lasers [20] (1–3 µm).

Although the development of a MXene-based electromagnetic wave response is still in its early stage, related research works have greatly increased during the last six years. It is significant to present a comprehensive summary of the recent advancement of MXene in this field. Here, we emphasize the interactions between MXenes and electromagnetic waves. First, the interaction principles between MXenes and electromagnetic waves are briefly summarized. Then the latest developments in the applications of MXene-based electromagnetic wave responses are introduced in detail, mainly including photothermal conversion, photo-/photoelectro-catalysis, EMI shielding, transparent conductor, plasmonics, photodetectors, SERS, and saturable absorption. Finally, we try to find out the challenges and opportunities that still exist in this field. We believe this review offers a unique perspective to understand comprehensively MXene-based electromagnetic wave responses, and further provides valuable guidelines for the utilization of MXenes in future.

2. Electromagnetic wave response of MXenes

The interactions between materials and electromagnetic waves (absorption, scattering, emission, transmission, resonance, etc.) can be determined by reflection coefficient $F$, transmission coefficient $T$ and refractive index $n$. According to Maxwell’s electromagnetic wave theory, electromagnetic waves are incident perpendicularly from vacuum to materials. The reflection coefficient $F$, transmission coefficient $T$ and refractivity index $n$ is given by [21]:

$$ F = \frac{\sqrt{\mu_1 \varepsilon_1} - \sqrt{\mu_0 \varepsilon_0}}{\sqrt{\mu_1 \varepsilon_1} + \sqrt{\mu_0 \varepsilon_0}}, \quad T = \frac{2 \sqrt{\mu_1 \varepsilon_1}}{\sqrt{\mu_1 \varepsilon_1} + \sqrt{\mu_0 \varepsilon_0}}, \quad n = \frac{\sqrt{\mu_1 \varepsilon_1}}{\sqrt{\mu_0 \varepsilon_0}} $$

where $\mu_0$, $\mu_1$, and $\varepsilon_0$, $\varepsilon_1$ are the magnetic permeability and complex dielectric constant of vacuum and materials. The dielectric function can be described by [22]: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\omega$ is the angular frequency.
Scheme 2. Summarized the regulation of MXene structure parameters for optimizing their electromagnetic interactions and related applications.

...frequency of electromagnetic waves. The real part $\varepsilon_1(\omega)$ represents the phase modulation or dispersion, and the imaginary part $\varepsilon_2(\omega)$ represents the amplitude modulation or loss/gain. The imaginary part $\varepsilon_2(\omega)$ is dependent on the intrinsic electrical conductivity ($\sigma$) and inversely proportional to the $\omega$ of the electromagnetic waves. $\sigma$ can be expressed as: $\sigma = \frac{C e^2}{2m^* \tau}$, where $C$ is free carrier density, $e$ is the charge, $m^*$ is effective mass, $\tau$ is relaxation time. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ obey the rule of the Kramers–Kronig transformation [23]. In other words, the refractivity, reflectivity, and absorption or extinction coefficients can be obtained using such equation after confirming the value of the dielectric function $\varepsilon(\omega)$.

Generally, electromagnetic wave responses are mainly the interactions between electromagnetic waves and free electrons. So the electronic structures are critical to the dielectric functions of MXenes, which are varied with structural parameters, such as termination composition, strain and morphology etc. Various approaches, including surface termination [24], elemental composition [25], ion intercalation (e.g. Li, Na) [26], defects [27], doping [28], and post-treatments [29] (such as Ar-atmospheric annealing), have been proved to realize the modulation of the electronic structure of MXenes and associated electromagnetic wave responses (scheme 2). MXenes can be thus varied from a highly conductive metallic state [26] to half-metallic [30], semiconducting [31] and insulating states [32].

Taking surface termination functionalization of MXenes as an example, unterminated MXenes are intrinsically metallic with substantial electronic states crossing the Fermi level, while the surface of widely-used MXenes is always electronegative and hydrophilic because of rich surface terminations. This characteristic brings multiple electronic structure modulation and electronic transmission of MXenes resulting from mutative free carrier density and effective mass. It is well-known that surface terminals are bonded to the external M layers that contribute more on electronic distributions than the inner M layers. Therefore, the electronegative terminals can draw valence charge from the external M layers, resulting in a new energy level below the Fermi surface [33]. As one representative MXene, bare Ti$_3$C$_2$ is metallic. The band structure can be adjusted to semi-conductive state by surface functionalizations. Differences in electronegativity of terminals [1, 31], such as –OH and –F, are able to vary the band gaps from 0.05 eV to 0.1 eV. Besides, the free electron states near the Fermi level can provide a non-scattering channel for electron transmission [34–37]. Such changes of electronic structure and electronic transmission are attributed to diverse dielectric responses of MXenes. In UV range, functional terminals can simultaneously promote the ability of the absorptivity and reflectivity. In visible range, the absorption coefficients of Ti$_3$C$_2$ with –F and –OH terminated surfaces are smaller than those of the pristine ones. And thus it is highly promising to tune the responses upon UV–Vis–IR regions by controlling functional groups at the surface. On the other hand, if
the surface terminals are removed by annealing in vacuum or inert gas, the carrier movement can be promoted in ten times, leading to improved conductivity $\sigma$ [29].

The rich tunability of compositions, like element composition [24], ion intercalation (e.g. Li, Na) [26], doping [28] of MXenes can also devote to the adjustment of electronic structures and energy band, which leads to alter the dielectric function. For example, the transition between centered honeycomb and honeycomb lattices can be controlled by altering the annealing temperature and pressure [38, 39] by altering the atomic packing order of the M atoms, which will affect the transmission of electrons. The energy band gap of MXenes can be changed by altering the element composition, which affects the transmission of electrons, such as in $M_2\text{CO}_2$ solid solution, the band gap is adjustable from 1.25 to 1.80 eV [40]. Balci et al found that the band gap of the original $\text{Sc}_2\text{OF}_2$ is 0.96 eV, and when C atoms are further replaced by other elements, like B, N, etc, the band gaps can be varied to 0.24 ~ 0.55 eV [41]. N-type and p-type doping both contribute to enhancing the electric conductivity of MXenes [28]. Besides, smaller metal ion intercalation (such as Li and Na) can generate a higher carrier density of MXenes, and thus improve the conductivity [22]. However, due to the increase in the distance between layers and the increase in resistance, large-size ion molecular intercalants such as tetrabutylammonium may induce the transition from metal to semiconductor [24].

The band gap of MXenes can also be engineered by applying external strain [42–44] and extra electric fields [11, 45, 46]. For instance, when MXene is applied with a 2% external biaxial strain, the electric structure of a single layer of $\text{Sc}_2\text{OF}_2$ MXene is changed from indirect nature to direct nature, and the band gap varies from 1.39 to 1.82 eV [43]. Employing insulating polymers (such as polyvinyl alcohol [11] and polystyrene [47]) as supporters will increase the inter-chip resistance and thus inescapably affect the conductivity of the entire samples. For example, in the MXene-based cooperative polymer composites, the dielectric constant is increased up to $10^5$, because of the accumulated charges upon the electric fields between MXene and polymer [48].

Besides, morphology engineering can strongly affect the relaxation time $\tau$. Size and packing of MXenes have been proved to optimize the dielectric function. For example, aligned MXenes can minimize the carrier scattering among flakes and improve the conductivity of $\sigma$. More based on these MXene-based electromagnetic wave responses have been utilized according to interaction principles between electromagnetic waves and MXenes, like absorption, scattering, emission, transmission and resource as shown in scheme 2. MXene-based absorption has been used for photothermal conversion, bioimaging and photocatalysis, etc, increasing the absorption or extinction coefficients of MXenes from UV to IR to improve the absorption efficiency. Improved transmission coefficient $T$ allows MXenes applied as transparent conductive films, while reduced transmission coefficient $T$ contributed to effective EMI shielding. MXene-based emission and scattering can be used for PL and SERS, respectively. Moreover, joint interactions are able to create more applications. For example, absorption and transmission can be used together for saturable absorbing. Absorption and scattering of MXenes for electromagnetic waves are helpful for EMI shielding. All the applications will be introduced in detail with the classification of linear and non-linear responses.

3. Applications of MXene-based linear response

As a rising family of 2D materials, MXenes exhibit fascinating physicochemical properties for the use of electromagnetic waves. In this section, we will focus on the applications of MXene-based linear responses, such as absorption, scattering, emission, transmission and resonance.

3.1. Absorption

3.1.1. Photothermal conversion

Photothermal conversion can directly transfer electromagnetic waves into thermal energy (heat) [45]. An ideal photothermal material needs sufficient absorption across the Vis–IR region and an efficient photothermal conversion. To date, MXenes have been demonstrated for highly efficient photothermal conversion. They can efficiently absorb photons from electromagnetic radiation (i.e. light) and eventually convert the electromagnetic radiation into heat [46]. Hence, MXenes with outstanding absorption and utilization of the electromagnetic radiation results are attractive where temperature is the main status. More and more scientists have devoted themselves to this field and contributed to great progress about MXene-based photothermal conversion, especially in solar energy utilization and biomedical areas.

So as to solar energy utilization, $\text{T}_{1\text{C}}\text{C}_2$ and $\text{T}_{1\text{C}}\text{C}_2$-based composites are widely reported to harvest the inexhaustible solar energy on the planet [45, 49–52]. One presentive work is solar steam generation reported by Luo’s group [53]. The configuration is shown in figure 1(a). The MXene film is placed on the top of the ionic solution. When the light illuminates on one side of the MXene film, MXene can successfully pump...
water through the nanofluidic channels and convert such asymmetric light irradiation to an asymmetric evaporation. This device can keep working and generating current under natural sunshine (figure 1(b)). It fully demonstrates the potential of MXene to realize solar energy utilization.

In addition, MXenes are hydrophilicity and biocompatibility, and thus absorption of MXenes can be utilized within the biomedical areas, like photothermal therapy (PTT) and photoacoustic (PA) imaging. Regarding tumor treatment, MXenes can use photon energy to heat the tumors locally, resulting in necrosis of cancer cells through hyperpyrexia. Several MXenes, such as Nb$_2$C [55, 56], Ta$_4$C$_3$ [57, 58], Ti$_3$C$_2$ [12, 59] and V$_2$C [54, 60], have been used as PTT and PA imaging agents. Zada et al [54] reported that 2D V$_2$C is suitable for photothermal cancer therapy of MCF-7 tumor in IR biowindows (figure 1(c)) guided by PA imaging. Corresponding photothermal conversion efficiency reaches up to 48%. The temperature rising range of solution (200 $\mu$g ml$^{-1}$) increases from initial $\approx$25 to $\approx$58 $^\circ$C after IR laser irradiation (0.48 W cm$^{-2}$) for 10 min (figures 1(d) and (e)). So treatments with V$_2$C under 808 nm irradiation was effective in suppressing the tumor growth, leading to completely ablation of tumor after 12 days (figures 1(f) and (g)).

Although many reports about photothermal conversion and MXene-based photothermal are still at the primary stage, related mechanisms are strongly dependent on the response types to electromagnetic radiation [61] and look forward to further exploration.

3.1.2. Photo-/Photoelectro-catalysis
Photo-/Photoelectrocatalysis has been regarded as scalable and efficient energy conversion approaches to realize sustainable economy. Such approaches can generate chemical products and clean fuels from abundant resources, like H$_2$O, CO$_2$, N$_2$, O$_2$, organic molecules, etc, but their developments are limited by unsatisfied catalysts [62, 63]. Hence, looking for suitable photo-response catalysts becomes more and more significant.

MXenes stand out as promising candidates due to their unique merits, such as adjustable electronic structure, high electrical conductivity, satisfied carrier mobility, rich terminations and associated hydrophilic surface, etc, resulting in facilitated redox reactions. MXenes are shown to function either individually or synergistically in the form of composites with other materials. Theoretically, bare metallic MXenes are not able to favor photocatalytic reactions alone because their zero band-gap nature cannot realize light harvesting [64]. Benefiting from termination functionalization and element composition adjustment, some MXenes can be varied to semiconductors to absorb specific light. Based on abinitio calculations, Sun et al...
investigated 48 types of MXenes with different elements and surface functional groups. Zr$_2$CO$_2$ and Hf$_2$CO$_2$ with suitable electronic structures serve as possible individual photocatalytic candidates for water splitting as shown in Figure 2(a). Barsoum and Gogotsi et al. have successfully demonstrated the degradation of organic pollutants, like cationic methylene blue (MB) and anionic acid blue 80 under UV light [6].

On the other hand, most studies pay more attention to MXene-based composites due to more enhanced photocatalytic efficiencies than their individual components [65]. The secondary materials, like oxides (TiO$_2$ [66], Nb$_2$O$_5$ [67], Cu$_2$O [68], etc.), sulfides (CdS, ZnS, Zn$_x$Cd$_{1-x}$S [62], In$_2$S$_3$ [69]), C$_3$N$_4$ [70, 71], polymers, etc. can be deposited on MXenes through the in-situ conversion of MXenes, direct chemical growth and/or deposition [64]. Considering the function of MXene during photocatalysis, first, MXenes can offer a large-area conductive and structural skeleton [65]. Second, MXenes can be used to improve photo-generated carrier utilization by modulating the electronic structure through the Schottky barrier or lattice strain at the interfaces. Such changes can avoid electron accumulation and fasten the separation/migration of photo-generated carriers. Figure 2(b) exhibits that Ti$_3$C$_2$T$_x$ together with CdS photo-absorbers can realize 136.6 times higher photocatalytic H$_2$ evolution under visible light than that of bare CdS. MXenes here facilitate electron migration toward enhanced photocatalysis [62]. Similar contributions can also be found in many other composites, like Cu$_2$O and Ti$_3$C$_2$T$_x$ hybrids during catalyzing the conversion from CO$_2$ to CH$_3$OH [68], C$_3$N$_4$ and Ti$_3$C$_2$T$_x$; TiO$_2$ and Ti$_3$C$_2$T$_x$/Nb$_2$CT$_x$/Ti$_2$CT$_x$ for photocatalytic H$_2$ evolution [66, 70, 71], etc. Third, MXenes benefit for suppressing hole-mediated photocorrosion during photocatalysis. Taking Ti$_3$C$_2$T$_x$/CdS catalysts as examples (figure 2(c)), Ti$_3$C$_2$T$_x$ can strongly absorb Cd$^{2+}$ that are generated during photocatalysis. So that the dissolution of CdS can be inhibited, giving rise to promoted photo-stability of CdS and long-term stability of photocatalysis [72].

Besides binary composites, ternary composites have also been widely used. Su et al. realize Nb$_2$O$_5$/C/Nb$_2$C composites through partially oxidizing the Nb$_2$CT$_x$ with CO$_2$ as the mild oxidant [67]. With the suitable oxidation duration, optimal C interfacial junction between Nb$_2$CT$_x$ and Nb$_2$O$_5$ contributes to maximum separation/migration of photo-generated carriers. Hence, the H$_2$ evolution efficiencies of the
ternary composites are 4 times enhanced than those of bare Nb$_2$O$_3$ as shown in figure 2(d). Another typical example is sandwich ZnIn$_2$S$_4$–Ti$_3$C$_2$T$_x$–ZnIn$_2$S$_4$ composite. Efficient carrier modulation resulting from Schottky junction and structural superiorities of ultrathin 2D nature contribute synergistically to the promoted photocatalytic H$_2$ evolution and excellent stability.

3.2. Scattering

3.2.1. EMI shielding

Modern electronic devices (like hearing aids and cardiac pacemakers) are sensitive to electromagnetic interference, so the protection of equipment from electromagnetic pollution is of significance [73, 74]. Thus, the more scientists devote to inhibiting undesirable electromagnetic radiations. Since a breakthrough discovery in 2016 of Ti$_3$C$_2$T$_x$ [11], MXenes have become a series of leading lightweight EMI shielding materials.

Several possible mechanisms have been put forward for interactions between incident electromagnetic radiation and compact MXenes films, in which attenuation of electromagnetic radiation occurs through reflection, absorption, and multiple reflection [75, 76]. Since reflection always caused by the interference between MXenes and other propagation media due to different impedance or refractive indexes, introducing additional interfaces within the MXene would be helpful to promote shielding ability. Besides, additional internal scattering or multiple reflections resulted from mismatching impedance characteristics can also enhance absorption loss interfaces. Third morphology engineering provides additional extra interfaces with abundant internal scattering during shielding. The interactions between MXene and electromagnetic radiation can be enhanced in a layer-by-layer film [77, 78], porous structure and segregated structure by extending the propagation path length of electromagnetic waves [79].

Another interesting report by Yun et al has studied the effect of multireflections on the shielding of nanometer thickness MXene films [80]. The monolayer (1 l) and multilayer MXene films were produced by assembling and repeated stacking of MXene nanosheets. The 1 l Ti$_3$C$_2$T$_x$ film with the thickness of 2.3 nm possesses higher than 90% transmittance and a thin layer resistance of 1056 $\Omega$. The increase of absorption and a thin layer resistance decreased with the increasing layers of Ti$_3$C$_2$T$_x$ MXene (figure 3(a)), while the EMI shielding gradually increases (figure 3(b)). A five layer (5 l) film offered 10 dB, while a 24 layer film offered 20 dB. In addition to single phase film, two-phase assembling with different impedance results in scattering at interface and acids attenuation of electromagnetic waves. Ti$_3$C$_2$T$_x$ and Ag nanowire decorated with silk fabricated by vacuum-assisted layer-by-layer spray coating [81]. This composite possesses a leaf-like morphology with Ti$_3$C$_2$T$_x$ nanosheets exhibiting the conductive layers and Ag nanowires as highly conductive veins (figure 3(c)). MXene can protect Ag nanowires again from oxidation. The leaf-like hydrophobic film results in an outstanding EMI shielding efficiency of 42 dB in 8–12 GHz (figure 3(d)), while retaining its highly sensitive humidity responses and permeability (figure 3(e)).

3.2.2. SERS

SERS is able to identify small quantities of molecules with the merits of highly efficient and noninvasive nature [82, 83]. MXenes are one typical type of the substrates of SERS [84–86]. Ti$_3$C$_2$ substrates without precious metals were created to identify Rhodamine 6G, gentian violet and acid blue. The mechanism of signal enhancement may be due to interband transitions of empty vitality states of the surface termination of MXenes, take after toward a charge exchange of the adsorbed molecule [84]. By modifying Ti$_3$C$_2$ with Al oxyanions, the intrinsic fingerprint features could be maintained and the high molecular detection sensitivity could be obtained [85]. In addition, Ti$_2$N MXene could also be used as the substrate material of SERS, the enhancement factor of Ti$_2$N for Rhodamine 6G arriving 10$^{12}$ larger than that of Ti$_3$C$_2$

3.3. Emission

The typical application of MXene-based emission is PL. The intrinsic PL of 2D MXene nanosheets is low, so their biological applications receive certain restrictions. In order to improve MXene-based emission, scientists have tried many optimization approaches. Morphology engineering seems promising, such as reduced size of the nanoscale. For example, 0D QDs [15, 16, 87–90] would enhance the PL by the help of the quantum confinement, large surface area and edge effects. Monolayered Ti$_3$C$_2$ MXene quantum dots (Ti$_3$C$_2$ MQDs) of 2.9 nm have been fabricated through hydrothermal treatments [15]. Their quantum yield of excitation-dependent PL was around 10%. This value is high enough for optical applications. Geng et al have created ultra small MXene with a lateral dimension of 2–8 nm, which exhibits bright fluorescence around 507 nm [91]. Strong quantum confinement endows N-doped Ti$_3$C$_2$ MXene quantum dots with quantum yields of up to 18.7% [90]. Besides, the functionalization of MQDs is another effective approach. Ti$_3$C$_2$@PEG QDs show pH-dependent blue PL [92].
All the above-mentioned Ti$_3$C$_2$ MQDs show blue emission. To realize efficient white emission, Lu et al [16] synthesized Ti$_3$C$_2$ MQDs (figure 4(a)) with an absolute photoluminescence quantum yield of 9.36% and 220 nm full width at half maximum under 360 nm excitation (figure 4(b)). The two-photon fluorescence luminescence intensity has quadratic dependence on the excitation power (figures 4(c) and (d)). Huang et al [89] reported V$_2$C MXene QDs with the size of 4.13 nm (figure 4(e)) through a hydrothermal process. MXenes with fewer atomic layers are more sensitive to external passivation due to the Coulomb blockade effect [93]. The absorption or PL region of the MQDs was successfully broadened to red light by passivation (figures 4(f) and (g)). Under the 355 nm excitation, the absolute quantum yield reaches 15.88%. The PL of V$_2$C MQDs covers the cutoff edge up to about 700 nm, rather than around 600 nm of Ti$_3$C$_2$ QDs [15].

3.4. Transmission

Transparent conductive electrodes (TCEs), with high transparency and conductivity, are key components in optoelectronic devices (e.g. touch panels and photovoltaic light-emitting diodes) [94]. MXenes have very good metal conductivity corresponding to a very large potential for application in the field of TCEs. Compared with other transparent conductive oxides, MXenes have the advantages of high flexibility and
dispersibility in water. It has broad application prospects in high performance TCEs and photodetectors [95, 96].

Many research groups have reported that MXene films possess above 90% of broadband transmittance of electromagnetic waves under Vis–IR range [26, 97]. It is noteworthy that the transmittance of Ti$_3$C$_2$Tx MXene film is as high as 98%, contributing to flexible and high volumetric transparent capacitors [26]. Large ionic interaction (e.g. NMe$_4$OH) with increased c-axis can also increase the transmittance [98]. The transmittance of 97% in the Vis region need been acquired in a 1.2 nm spin coated Ti$_3$C$_2$Tx MXene into a film around glass, quartz and polyetherimide substrates [99].

MXenes with a tunable electromagnetic wave response and electrical characteristics allow devices to regulate the generation, transport and restriction behavior of charge carriers to utilize in optoelectronic applications. Within the case of 2D MXenes, Ti$_3$C$_2$Tx/n-Si heterostructures can be used for self-powered photodetectors [100]. The temporal photosresponse is inspected beneath the 405 nm laser light with 15.17 mW cm$^{-2}$, conveying a photoresponsivity with 26.95 mA W$^{-1}$ and an on/off ratio up to $\approx 10^5$. Given the great electromagnetic wave transmittance and metallic conductivity, Ti$_3$C$_2$Tx works as both Schottky contacts and transparent electrodes for the heterostructure photodetectors. MXenes can be integrated with III–V semiconductors [101], like Ti$_3$C$_2$Tx–GaAs–Ti$_3$C$_2$Tx (MX-S-MX) photodetectors. This device works well in the Vis–NIR range.
3.5. Resonance

The resonant interaction between electron undulations near the surface of the MXenes and the electromagnetic field of the electromagnetic waves creates the surface plasmons (SP). The plasmonics of MXene are applied in SERS [13], broadband plasmonic metamaterial absorber [17, 102] and plasmonic photodetection [18, 103]. The SP resonance response of spherically silver and gold@MXene emerges in Vis range, and realize the detection of diluted ($10^{-6}$ M) MB by SERS (figure 5(a)) [13]. In addition to the SP mode of MXene hybrids, Ti$_3$C$_2$T$_x$ assemblies have been used for wide wavelength window ($\sim$1.55 $\mu$m) (figure 5(b)) and effective absorbance ($\sim$90%) (figure 5(c)) applications [17]. In addition to the existing Ti$_3$C$_2$T$_x$, MXene, Mo$_2$CT$_x$ is also used for plasmonic photodetection, which exhibits broad photo responses in Vis–NIR range with high responsibility and reliable photoswitching properties at 660 nm [18]. Electron energy-loss spectroscopy (EELS) of Mo$_2$CT$_x$ shown in figure 5(d) fully convinces the existing plasmonic resonance.

4. Applications of MXene-based nonlinear response

Nonlinear optical response occurs under the intense light, and the response is nonlinear relative to the magnitude of the electromagnetic field. Researches of MXenes in nonlinear optics are merely found, mainly focused on the saturated absorption of MXene. Saturable absorption is always dependent on the simple two-level mode. MXenes stand out as saturable absorbers have been applied to photonic diodes [19] and femtosecond ML pulse lasers [20, 104]. Jiang group investigated those broadband saturable absorption properties for Ti$_3$C$_2$T$_x$ in IR regions utilizing the essential Z-scan strategy (figures 6(a) and (b)) [105]. The maximum modulation depth of saturable absorbers of MXenes reach 40%, but the linear light decay is just 2%, which largely limits the modulation depth. Moreover, multiphoton absorption can be prompted under
intense light illuminations, which prompts those diminished from optical transmission. If Ti$_3$C$_2$T is used as the saturable absorber, it is possible to realize ML laser operations in fiber resonators. Experimentally, the devices manifest a gradual expansion for transmittance with expanded illumination intensities. Ti$_3$CNT$_x$ with a modulation depth of 1.7% serves as an excellent saturable absorber by ultrafast ML and Q-switched operations in 1.56 µm and 1.78 µm, respectively (figures 6(c) and (d)) [20].

5. Conclusions and perspective

Since Ti$_3$C$_2$T debuted in 2011, MXenes have achieved disruptive success in various technical fields. Here, we systematically review the progress of MXene-based electromagnetic wave responses, the relationship between electromagnetic wave responses and the structure of MXenes, and the latest achievements and developments in related applications. Because of the excellent absorption ability in ultraviolet, visible and infrared range, MXenes serve as a photothermal conversion reagent in biology and energy fields. The high conductivity of MXenes makes it unique when interacting with electromagnetic waves for EMI shielding, SERS, etc. Direct band gap transitions produce high PL quantum yields, ensuring that MXenes can be used for PL-based stoichiometry, white-light laser generation, and bioimaging. MXenes with special transmission from visible light to infrared light can be used for TCEs. Its excellent nonlinear saturation absorption characteristics allow ultrafast lasers with pulse durations of only 100 fs.

In despite of these achievements, there are still some remaining questions about MXenes.

Firstly, although plenty of MXenes have been predicted theoretically, nevertheless, only a small part of MXenes could be successfully achieved. The rational synthesis of MXenes still needs systematic research. Various MXene types need further exploration. Up to now, ‘M’ is a little limited. A large amount of transition metals (such as Fe, Mn, Co, Nd, Eu, Er) are also worth detailed exploration. Besides, compared with transition metal carbides, their nitrides or carbonitrides are also attractive. Related reports are rarely found about the nitride and carbonitrides families. We believe that the attractive new types can widely enable the MXenes’ functionalization and expand novel applications. In particular, in order to cater to the increasingly stringent requirements of various applications, multi-theoretical predictions of types are becoming increasingly significant to MXenes.
Secondly, it is urgent to develop an appropriate response theory. For example, currently, the photothermal conversion of MXenes is mainly determined by LSPR effects of metal characteristics. Nevertheless, it is worth pointing out that not all MXenes are metallic and that further exploration and universal understandings of photothermal principles are urgently necessary. The composition and understanding of surface termination for electronic properties should also be impressive.

Thirdly, we deem that it is also an extraordinarily fertile field to combine different electromagnetic wave responses to realize multifunctional applications. For example, MXenes have excellent photothermal conversion abilities. Since the chemical reaction is temperature-dependent, if MXenes are used in photocatalytic environment, it would be expected to change local temperature and adjust the related reaction kinetics. So, more combinations will create more surprises in future.

Fourthly, nonlinear responses of MXenes and MXene-based composites is significant, but lack detailed theoretical and experimental studies. Theoretically speaking, it is probable to further explore the hybrid quantum/molecular mechanics method to fully illuminate the complex heterogeneous environment and establish the structure performance relationship. Now, limited experimental studies primarily focus on saturable absorbers generated by ultrafast ML and Q-switched lasers. It remains an opportunity and challenge to expand the systematic observations about MXene-based nonlinear optical properties and the structure-property relationships, like the influences of structural and morphological parameters.

Overall, a MXene-based electromagnetic wave response is expected to develop more and more breakthroughs. The future of MXene-based electromagnetic wave responses is very attractive. We look forward to more innovations in this field in the near future.

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