Novel hierarchical structure of MoS₂/TiO₂/Ti₃C₂T_x composites for dramatically enhanced electromagnetic absorbing properties

Heng DU^{a,b,†}, Qipeng ZHANG^{a,†}, Biao ZHAO^c, Frank MARKEN^d,
Qiancheng GAO^c, Hongxia LU^a, Li GUAN^c, Hailong WANG^c,
Gang SHAO^c, Hongliang XU^c, Rui ZHANG^{a,e}, Bingbing FAN^{a,*}

^aSchool of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

^bKey Laboratory of Functional Molecular Solids, Ministry of Education,
Anhui Normal University, Wuhu 241000, China

^cHenan Key Laboratory of Aeronautical Materials and Application Technology,
Zhengzhou University of Aeronautics, Zhengzhou 450046, China

^dDepartment of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

^eSchool of Materials Science and Engineering, Luoyang Institute of
Science and Technology, Luoyang 471023, China

Received: January 26, 2021; Revised: April 17, 2021; Accepted: April 17, 2021

© The Author(s) 2021.

Abstract: In order to prevent the microwave leakage and mutual interference, more and more microwave absorbing devices are added into the design of electronic products to ensure its routine operation. In this work, we have successfully prepared MoS₂/TiO₂/Ti₃C₂T_x hierarchical composites by one-pot hydrothermal method and focused on the relationship between structures and electromagnetic absorbing properties. Supported by comprehensive characterizations, MoS₂ nanosheets were proved to be anchored on the surface and interlayer of Ti₃C₂T_x through a hydrothermal process. Additionally, TiO₂ nanoparticles were obtained *in situ*. Due to these hierarchical structures, the MoS₂/TiO₂/Ti₃C₂T_x composites showed greatly enhanced microwave absorbing performance. The MoS₂/TiO₂/Ti₃C₂T_x composites exhibit a maximum reflection loss value of −33.5 dB at 10.24 GHz and the effective absorption bandwidth covers 3.1 GHz (13.9–17 GHz) at the thickness of 1.0 mm, implying the features of wide frequency and light weight. This work in the hierarchical structure of MoS₂/TiO₂/Ti₃C₂T_x composites opens a promising door to the exploration of constructing extraordinary electromagnetic wave absorbents.

Keywords: MoS₂/TiO₂/Ti₃C₂T_x hierarchical hybrids; microwave absorbing properties; dielectric loss

[†] Heng Du and Qipeng Zhang contributed equally to this work.

* Corresponding author.

E-mail: fanbingbing@zzu.edu.cn

1 Introduction

Electronic products are developing toward the direction of high power and high frequency, but there is a major problem for these electronic products that they come with leakage and mutual interference of microwaves [1]. In order to resolve this problem, more and more electromagnetic wave absorbing devices are added into the design of electronic products to ensure routine operation [2]. For practical microwave absorbing device applications, the new-generation electromagnetic wave absorbers are expected to possess strong absorption capability and light weight [3]. In recent years, 2D nanomaterials such as graphene, graphene oxides (GOs) [4], MoS₂ [5,6], and MXenes [7,8], have proven to be potential candidates for ideal microwave absorbers.

MXenes, an emerging group of layered materials, were synthesized by etching MAX phases by Naguib *et al.* [9] in 2011. They have a general formula of $M_{n+1}X_nT_x$, where M represents an early transition metal (e.g., Ti, Mo, and Nb); X usually is C and/or N; $n = 1, 2$, or 3 ; and T_x denotes the surface termination ($=O$, $-OH$, and/or $-F$). The distinguishing characteristics of MXenes, including special accordion-like morphology, outstanding electrical conductivity, and rich functional groups surface, have captured enormous attention in many applications, especially for microwave absorption (MA) [10,11].

Since 2016, Ti₃C₂T_x MXene has been developed as a potential microwave absorber candidate due to its positive dielectric loss ability [12]. Different etching time [13], HF concentration [14], etching temperature [15], and the ratio of Ti₃C₂T_x and paraffin [16] were all found to have a great influence on the microstructure, crystal morphology, and MA properties of Ti₃C₂T_x. The maximum reflection loss (*RL*) of Ti₃C₂T_x is -27.5 dB at 17.1 GHz with the thickness of 4 mm [14]. Therefore, pure Ti₃C₂T_x MXene alone is always limited to meet the requirement for practical application. Hence, incorporation of a second phase is very important. Semiconductors such as ZnO [17], SiC [18], MoS₂ [19], and TiO₂ [20] are usually introduced into Ti₃C₂T_x to enhance microwave absorbing abilities due to their moderate dielectric constant, effective heterojunction formation, and better impedance matching. Recently, a sandwich-like structure of the MoS₂/TiO₂/Ti₃C₂T_x as nanocomposite was shown to possess thinner microwave absorption thickness when compared to the pure Ti₃C₂T_x

[19]. However, the maximum *RL* was just -16.0 dB, which is not satisfactory in practical applications.

The electromagnetic wave absorption properties of a material are closely related to the microstructure [21]. Recent research in hierarchically structured materials opens a possible door into the exploration of constructing extraordinary electromagnetic wave absorbents [22]. In this work, we have successfully prepared MoS₂/TiO₂/Ti₃C₂T_x hierarchical composites by one-pot hydrothermal method and focused on the relationship between structures and electromagnetic wave absorbing properties. Supported by comprehensive characterizations, MoS₂ nanosheets were proved to be anchored vertically on the surface and interlayer of Ti₃C₂T_x through a hydrothermal process and *in situ* generated TiO₂ nanoparticles were obtained simultaneously. Due to these hierarchical structures, the MoS₂/TiO₂/Ti₃C₂T_x composites showed greatly enhanced microwave absorbing performance.

2 Experimental

2.1 Chemicals

Ti₃AlC₂ raw powders were obtained from the Institute of Metal Research, Chinese Academy of Sciences (minimum purity 99%, 200 mesh) and HF acid (40 wt%) was provided by Luoyang Chemical Reagent Factory. Na₂MoO₄·2H₂O (minimum purity 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. CH₄N₂S (minimum purity 99%) was commercially obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethanol was supplied by Tianjin Fuyu Fine Chemical Co., Ltd. Deionized water (18.25 MΩ·cm) was prepared by an ultra-pure water purifier (UPT-I-20L, ULUPURE).

2.2 Preparation of Ti₃C₂T_x

The Ti₃C₂T_x nanosheets were prepared by a typical etching process of MAX phase Ti₃AlC₂ [23]. 3.0 g Ti₃AlC₂ powder was added into 30 mL HF solution and stirred at room temperature for 12 h. Then, the Ti₃C₂T_x suspension was centrifuged and washed by ethanol and deionized water several times until the pH value was above 6. The obtained precipitates were then freeze dried.

2.3 Preparation of MoS₂/TiO₂/Ti₃C₂T_x composites

To synthesize MoS₂/TiO₂/Ti₃C₂T_x composites, 0.1 g

$\text{Ti}_3\text{C}_2\text{T}_x$ was dispersed in 70 mL deionized water. The solution was ultrasonicated for 5 min to form a uniform $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion. After that, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CH}_4\text{N}_2\text{S}$ were dissolved into the $\text{Ti}_3\text{C}_2\text{T}_x$ suspension followed by stirring. The above solution was then transferred into a 100 mL polyphenylene (PPL)-lined autoclave. The autoclave was kept at 200 °C for 12 h. After cooling naturally, the black precipitates were washed with deionized water and ethanol for many times. The samples were dried in a vacuum oven at 80 °C for 12 h. Based on the weight ratio of $\text{Ti}_3\text{C}_2\text{T}_x$ to MoS_2 , i.e., 2:1, 1:1, and 1:2, the obtained $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites were labeled as S1, S2, and S3, respectively. For comparison, pure MoS_2 and $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ powders were treated under the same procedure and condition. The schematic of the synthetic route and formation mechanism for the $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites is depicted in Fig. 1.

2.4 Characterization

The morphology and microstructure of MoS_2 , $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$, and $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites were identified by the field emission scanning electron microscope (FESEM, JEOL JSM-7001F) and transmission electron microscope (TEM, Jem-2100F). The crystal structure and phase composition were measured by X-ray diffractometer (XRD, Rigaku Ultima IV). The Raman spectroscopy (HORIBA LabRAM HR Evolution, $\lambda = 532$ nm) was applied to determine the surface characteristics of the composites. X-ray photoelectron

spectroscopy (XPS, ThermoFischer ESCALAB 250Xi) was employed to analyze the chemical states of the major elements on the sample surface.

2.5 Electromagnetic measurements

For electromagnetic parameter measurements, S1, S2, S3, and MoS_2 powders were homogeneously dispersed in the paraffin wax with 60 wt%. All the above mixtures were pressed into toroidal-shaped (outer diameter = 7.00 mm and inner diameter = 3.04 mm). The relative complex permittivities of samples were measured using a vector network analyzer (Agilent, N5244A) in the frequency range of 2.0–18.0 GHz with the coaxial-line method.

3 Results and discussion

The typical XRD patterns of MoS_2 , $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$, and $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites are shown in Fig. 2(a). The diffraction peak at 8.8° is considered to be a characteristic peak of $\text{Ti}_3\text{C}_2\text{T}_x$ [4]. Compared with the pure $\text{Ti}_3\text{C}_2\text{T}_x$, there are two main diffraction peaks in $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites at 25.3° and 54.3°, ascribed to anatase TiO_2 phase (JCPDS No. 21-1272) [4]. It also can be seen that, after coupling with MoS_2 , the relative peak intensity of TiO_2 is significantly weakened, while the diffraction peak intensity of $\text{Ti}_3\text{C}_2\text{T}_x$ is sharply enhanced, indicating that the formation of MoS_2 had inhibited the transformation process from $\text{Ti}_3\text{C}_2\text{T}_x$ to

Fig. 1 Fabrication process of $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites.

Fig. 2 (a) XRD patterns of Ti_3C_2 , MoS₂, and MoS₂/TiO₂/Ti₃C₂T_x composites; (b) magnification of XRD patterns of 5°–10° in (a). d represents the thickness of the sample.

TiO₂. The characteristic diffraction peaks at 14.3 and 28.9 assigned to the (002) and (004) planes of 2H-MoS₂ (JCPDS Card No. 37-1492) [24], respectively, while the peak of (002) plane of $\text{Ti}_3\text{C}_2\text{T}_x$ slightly shifts to 7.1°, demonstrating the d -spacing between $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was expanded, and implying the successful anchoring of MoS₂ on the $\text{Ti}_3\text{C}_2\text{T}_x$ layers. The small diffraction peak at 9.12° of S3 is also related to the (002) plane of MoS₂, which ascribed to the insertion of thiourea molecules between the interlayer of S–Mo–S [25]. The corresponding magnification of the range of 5°–10° is shown in Fig. 2(b). It shows that the d -spacing of (002) plane of $\text{Ti}_3\text{C}_2\text{T}_x$ decreases with increase in MoS₂ content.

Raman spectroscopy of $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ and MoS₂/TiO₂/Ti₃C₂T_x composites (S2) is shown in Fig. 3. The characteristic bands of $\text{Ti}_3\text{C}_2\text{T}_x$ at 261, 411, 606 cm^{−1} were observed [26]. In the spectrum of S2, the strong E_{2g}^1 mode at ~374 cm^{−1} corresponds to in-plane vibration and the A_{1g} mode at ~402 cm^{−1} is ascribed to the out-of-plane vibration. These are mainly due to the worse crystallinity of MoS₂ and due to the interaction between MoS₂ and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets [27], which indicates that MoS₂ formed in the S2 samples. Additionally, the Ti–O peak appeared in all the samples. Compared with $\text{Ti}_3\text{C}_2\text{T}_x$, the Ti–O peak of both $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ and MoS₂/TiO₂/Ti₃C₂T_x composites (S2) shifts to ~154 cm^{−1}, suggesting that more defects were generated during the hydrothermal process [28]. Furthermore, the strong D and G peaks of the composites are at 1382 and 1576 cm^{−1}, respectively. This illustrates that amorphous C was formed in the hydrothermal process [29].

Figures 4(a) and 4(b) demonstrate the morphologies of Ti_3AlC_2 and pristine $\text{Ti}_3\text{C}_2\text{T}_x$, which is consistent with the previous results [12]. The bare MoS₂ spheres are composed of MoS₂ nanosheets, as shown in Fig. 4(c),

Fig. 3 Raman spectroscopy of $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ and MoS₂/TiO₂/Ti₃C₂T_x composites (S2).

and the average sphere diameter is about 12 μm. Figures 4(d)–4(f) exhibit FESEM images of the S1, S2, and S3 composites. We observed that all the MoS₂/TiO₂/Ti₃C₂T_x samples shared the same lamellar structure, indicating that the structure of $\text{Ti}_3\text{C}_2\text{T}_x$ is not destroyed during the hydrothermal process. The MoS₂ nanosheets are grown on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanolayers, which could increase the specific surface area and expand the $\text{Ti}_3\text{C}_2\text{T}_x$ layer spacing. Moreover, as the MoS₂ content increased, the redundant MoS₂ nanosheets are grown as nanospheres, anchored on the edge, or entered into the $\text{Ti}_3\text{C}_2\text{T}_x$ inter-layers, as shown in Fig. 4(f).

TEM and HRTEM were further applied to investigate the MoS₂/TiO₂/Ti₃C₂T_x composites. As displayed in Fig. 5(a), the MoS₂/TiO₂/Ti₃C₂T_x composites are composed of Ti_3C_2 matrix and MoS₂ blanket with the average thickness ~80 nm. The interlayer spacing was considered to be ~0.61 nm, which matched the crystal planes of MoS₂(002), as shown in Fig. 5(b). These images

Fig. 4 FESEM images of (a) Ti_3AlC_2 , (b) $\text{Ti}_3\text{C}_2\text{T}_x$, (c) MoS_2 , and $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites: (d) S1, (e) S2, and (f) S3.

Fig. 5 (a) TEM and (b) HRTEM images of $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites (S2).

further supported the hypothesis of the heterojunction structure of $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites.

To confirm the surface properties of $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites, S2 samples were analyzed by XPS. The survey spectra (Fig. 6(a)) and the high resolution XPS of Ti 2p, C 1s, O 1s, Mo 3d, and S 2p (Figs. 6(b)–6(f)) are shown in Fig. 6. As shown in Fig. 6(a), we can see that the composites consist of Ti, C, O, Mo, and S elements. In the Ti 2p spectrum, the binding energies of the Ti–O $2p_{1/2}$ and $2p_{3/2}$ orbitals are 464.8 and 459.1 eV, and Ti–C $2p_{1/2}$ and $2p_{3/2}$ orbitals are 462.4 and 455.8 eV, respectively (Fig. 6(b)) [29]. In Fig. 6(c), the C 1s spectra can be separated into two peaks, related to C–C (284.7 eV) and C–O (285.9 eV), and the weak peak at 281.8 eV is assigned to Ti–C bond [30]. The O 1s profile was fitted by five symmetrical peaks. The fitting peak located at 530.3 eV attributes to TiO_2 . The peaks at 530.9, 531.7, 532.5, and 533.5 eV are assigned to C–Ti–O_x, C–Ti–(OH)_x, Al_2O_3 , and H_2O , respectively [31].

As for the Mo 3d spectra in Fig. 6(e), the obvious peaks located at 232.2, 229.0, and 226.1 eV are assigned to Mo $3d_{3/2}$, Mo $3d_{5/2}$, and S 2s, respectively, confirming that the Mo^{4+} ion exists in the nanocomposites [32]. There is an extremely small peak at 235.6 eV, which is corresponded to the $\text{Mo}^{(+6)} 3d_{3/2}$ orbit, probably caused by the incompletely reduced MoO_4^{2-} during the hydrothermal procedure [33]. The S spectra of the $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites can be divided into two peaks, and the peaks at 163.2 and 161.9 eV correspond to the S $2p_{3/2}$ and S $2p_{1/2}$, respectively.

Relative complex permittivity in the frequency range of 2–18 GHz was measured to clarify the electromagnetic wave absorbing properties of the MoS_2 and $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites at room temperature. The real part (ϵ') and the imaginary part (ϵ'') represent the storage and the loss capability of electromagnetic energy [29], respectively. As shown in Figs. 7(a) and 7(b), we can find that for the bare MoS_2 , the ϵ' value is approximately

7.5 and almost kept constant with frequency increasing, and meanwhile, the ε'' is within 0.2–2.3. After coupled with $\text{Ti}_3\text{C}_2\text{T}_x$, the complex permittivity is clearly enhanced; as the $\text{Ti}_3\text{C}_2\text{T}_x$ content increased, the real part reached to 13.8–34.5, and the imaginary part fluctuated in the range of 2.1–12.9.

Higher complex permittivity demonstrates that the composites can store and dissipate much more

electromagnetic energy, and the real part of complex permittivity is an expression of interfacial and relaxation polarization mechanism [11]. Based on the theory of free electric, the imaginary part (ε'') is related to the conductivity, which can be illustrated as the following equation [34]:

$$\varepsilon'' = \sigma(2\pi f \varepsilon_0)^{-1} \quad (1)$$

Fig. 6 (a) Survey spectra and (b–f) high resolution XPS of $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites (S2).

Fig. 7 Electromagnetic parameters of MoS_2 and $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ composites at 2–18 GHz: (a) ε' and (b) ε'' ; (c) dielectric loss tangent ($\tan \delta_\varepsilon$); and (d) attenuation constant (α).

where σ , f , and ε_0 represent the electrical conductivity, electromagnetic wave frequency, and permittivity of free space, respectively. For the MoS₂/TiO₂/Ti₃C₂T_x composites, as shown in Figs. 7(a) and 7(b), on the one hand, the increased content of Ti₃C₂T_x gives rise to enhanced conductivity, increased ε' , and increased ε'' of the MoS₂/TiO₂/Ti₃C₂T_x composites; on the other hand, the increased interface in the MoS₂/TiO₂/Ti₃C₂T_x composites due to the formation of MoS₂ and TiO₂ on Ti₃C₂T_x results in enhanced ε' , ε'' , and interfacial polarization. S1 possesses the highest ε' than those of others, which may be attributed to the higher conductivity of Ti₃C₂T_x than that of MoS₂.

In addition, Fig. 7(c) shows the dependence of $\tan\delta_e$ ($\tan\delta_e = \varepsilon''/\varepsilon'$) on frequency of MoS₂ and MoS₂/TiO₂/Ti₃C₂T_x composites, and the $\tan\delta_e$ values of MoS₂/TiO₂/Ti₃C₂T_x composites exhibit a higher $\tan\delta_e$ values than that of pure MoS₂, suggesting a superior dielectric loss ability of the MoS₂/TiO₂/Ti₃C₂T_x composites. Due to the existence of the resonance phenomenon, the curve of S2 shows two distinct peaks.

According to the Debye's dipolar theory, the relationship between ε' and ε'' can be described as the following equation [35]:

$$(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2 = (\varepsilon_s - \varepsilon_\infty)^2 \quad (2)$$

where ε_s stands for the stationary frequency dielectric constant and ε_∞ represents the infinite frequency dielectric constant.

According to the theory of transmission line and the theory of electromagnetic wave propagation, the attenuation constant α can be expressed by the following equation [35]:

$$\alpha = \frac{\sqrt{2\pi f}}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}} \quad (3)$$

where c represents the speed of light in the vacuum. As shown in Fig. 7(d), it can be seen that most of the α values of S2 samples are greater than those of other samples, and most of the α values are above 100, indicating a good microwave attenuation ability, which can be attributed to the enhanced polarization relaxation and conductive loss.

As shown in Fig. 8, the Cole–Cole semicircles consist of several semicircles, which diverge from the ideal Cole–Cole semicircles, indicating the polarization loss mechanism in S2 samples. The introduction of TiO₂ not only could provide the dielectric loss, which derives

Fig. 8 Cole–Cole curves of MoS₂/TiO₂/Ti₃C₂T_x composites (S2).

by dipole polarization of dangling bonds around oxygen vacancies and the interfacial polarization between MoS₂–TiO₂, TiO₂–Ti₃C₂T_x, and MoS₂–Ti₃C₂T_x, but also could give rise to multiple semicircles in the Cole–Cole curve and improved dielectric loss. It is also well illustrated that the relaxation loss plays an important role in dielectric loss.

The electromagnetic wave absorption performance of the MoS₂ and MoS₂/TiO₂/Ti₃C₂T_x composites was investigated over 2–18 GHz and the RL s are calculated by the following equations [36]:

$$RL = 20 \log \left| \frac{(Z_{in} - Z_0)}{(Z_{in} + Z_0)} \right| \quad (4)$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left(j \frac{2\pi f d \sqrt{\mu_r \varepsilon_r}}{c} \right) \quad (5)$$

where c represents the velocity of light; Z_{in} and Z_0 are the input impedance of the composite and free space, respectively; and ε_r and μ_r are the complex relative permittivity and complex permeability, respectively. In general, the RL value exceeding -10 dB indicates 90% consumption of incident electromagnetic wave, implying an ideal electromagnetic wave absorber, and the corresponding frequency band is called the effective absorbing bandwidth (EAB)[11]. As shown in Fig. 9(a), the maximum RL (RL_{max}) of bare MoS₂ is -11.2 dB at 10.3 GHz with a thickness of 3.0 mm, suggesting its poor electromagnetic wave absorption properties. After coupling with Ti₃C₂T_x, the MoS₂/TiO₂/Ti₃C₂T_x composites exhibit an enhanced electromagnetic wave absorption characteristic, and the maximum RL values of S1, S2, and S3 are -29.2 , -33.5 , and -18.2 dB, respectively, as shown in Figs. 9(b)–9(d). Especially for S2, the effective absorption bandwidth (EAB) covers 3.1 GHz (13.9–17 GHz) at the thickness of 1.0 mm, implying the characteristic of wide frequency and light weight. In order to highlight the electromagnetic absorbing properties, some typical similar composites and their corresponding

Fig. 9 RL curves of (a) MoS₂ and MoS₂/TiO₂/Ti₃C₂T_x composites: (b) S1, (c) S2, and (d) S3 with different thicknesses.

Table 1 Microwave absorption properties of similar materials

Material	Matrix	Loading (wt%)	<i>d</i> (mm)	<i>RL</i> _{max} (dB)	EAB (<i>RL</i> < 10 dB)	Ref.
Ti ₃ C ₂ T _x	Epoxy	50	1.4	−17	5.6	[12]
TiO ₂ /Ti ₃ C ₂ T _x	Wax	50	1.1	−40.07	3.6	[20]
C/TiO ₂ /α-Fe	Wax	70	3.5	−45.1	3.3	[37]
Co/TiO ₂ -C	Wax	45	3.0	−41.1	3.04	[38]
Ti ₃ C ₂ T _x /CNZF	Wax	—	3.6	−58.4	2.2	[39]
Ti ₃ C ₂ T _x /ZnO	Wax	75	4.0	−26.3	1.4	[17]
Ti ₃ C ₂ T _x /C spheres	Wax	50	4.8	−54.67	—	[29]
MoS ₂ /TiO ₂ /Ti ₃ C ₂ T _x	Wax	50	2.8	−16	2.6	[19]
MoS ₂ /TiO ₂ /Ti ₃ C ₂ T _x	Wax	60	1.0	−33.5	3.1	This work

EMW absorbing performances are presented in Table 1.

In general, the MoS₂/TiO₂/Ti₃C₂T_x composites (S2) exhibited excellent electromagnetic wave absorption performance, which originated from three aspects: enhanced interface polarization relaxation, scattering effects, and appropriate conductivity loss. The possible electromagnetic wave absorption mechanism of MoS₂/TiO₂/Ti₃C₂T_x composites is proposed in Fig. 10. Firstly, the conductive laminate Ti₃C₂T_x could enhance the conductance loss, and the unique laminated structure with MoS₂ as blanket could generate multiple reflections and scattering to attenuate electromagnetic waves. Secondly, a large number of TiO₂ nanoparticles could form many capacitor-like structures, which are benefit of dissipating the electromagnetic wave [40], and the introduction of TiO₂ could also enhance the interface

Fig. 10 Diagrammatic drawing of the electromagnetic wave absorption mechanism of the MoS₂/TiO₂/Ti₃C₂T_x composites.

polarization effects due to the interface between MoS₂-TiO₂, TiO₂-Ti₃C₂T_x, and MoS₂-Ti₃C₂T_x. Finally, the localized defects and the residual surface functional

groups can cause dipole polarization, which could enhance the dielectric loss.

4 Conclusions

MoS₂/TiO₂/Ti₃C₂T_x composites were successfully prepared by a simple hydrothermal method. All the MoS₂/TiO₂/Ti₃C₂T_x samples share the same lamellar structure, and the MoS₂ nanosheets are grown on the Ti₃C₂T_x nanolayers, which could increase the specific surface area and expand the Ti₃C₂T_x layer spacing. The MoS₂/TiO₂/Ti₃C₂T_x composites exhibit a maximum reflection loss value of −33.5 dB at 10.24 GHz and the effective absorption bandwidth (< 10 dB) covers 3.1 GHz (13.9–17 GHz) at the thickness of 1.0 mm, implying the features of strong absorption, wide frequency, and light weight. The superior electromagnetic wave absorbing performance originated from the enhanced polarization relaxation, scattering effects, and appropriate conductivity loss. This work in the hierarchical structure of MoS₂/TiO₂/Ti₃C₂T_x composites opens a promising door into the exploration of constructing extraordinary microwave absorbents.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. U2004177), Outstanding Youth Fund of Henan Province (No. 212300410081), and Natural Science Research Project of Henan Educational Committee (No. 20A43001).

References

- [1] Zhang F, Du H, Shang SY, *et al.* Constructing γ -MnO₂ hollow spheres with tunable microwave absorption properties. *Adv Powder Technol* 2020, **31**: 4642–4647.
- [2] Xue W, Yang G, Bi S, *et al.* Construction of caterpillar-like hierarchically structured Co/MnO/CNTs derived from MnO₂/ZIF-8@ZIF-67 for electromagnetic wave absorption. *Carbon* 2021, **173**: 521–527.
- [3] Tang M, Zhang JY, Bi S, *et al.* Ultrathin topological insulator absorber: Unique dielectric behavior of Bi₂Te₃ nanosheets based on conducting surface states. *ACS Appl Mater Interfaces* 2019, **11**: 33285–33291.
- [4] Qin F, Brosseau C. Comment on “The electromagnetic property of chemically reduced graphene oxide and its application as microwave absorbing material” [Appl. Phys. Lett. 98, 072906 (2011)]. *Appl Phys Lett* 2012, **100**: 046101.
- [5] Zhang XJ, Li S, Wang SW, *et al.* Self-supported construction of three-dimensional MoS₂ hierarchical nanospheres with tunable high-performance microwave absorption in broadband. *J Phys Chem C* 2016, **120**: 22019–22027.
- [6] Liu ZC, Pan F, Deng BW, *et al.* Self-assembled MoS₂/3D worm-like expanded graphite hybrids for high-efficiency microwave absorption. *Carbon* 2021, **174**: 59–69.
- [7] Yao YQ, Zhao J, Yang XH, *et al.* Recent advance in electromagnetic shielding of MXenes. *Chin Chem Lett* 2021, **32**: 620–634.
- [8] Deng BW, Xiang Z, Xiong J, *et al.* Sandwich-like Fe&TiO₂@C nanocomposites derived from MXene/Fe–MOFs hybrids for electromagnetic absorption. *Nano-Micro Lett* 2020, **12**: 1–16.
- [9] Naguib M, Kurtoglu M, Presser V, *et al.* Two-dimensional nanocrystals produced by exfoliation of Ti₃AlC₂. *Adv Mater* 2011, **23**: 4248–4253.
- [10] Jiang XT, Kuklin AV, Baev A, *et al.* Two-dimensional MXenes: From morphological to optical, electric, and magnetic properties and applications. *Phys Rep* 2020, **848**: 1–58.
- [11] Wang Z, Cheng Z, Fang CQ, *et al.* Recent advances in MXenes composites for electromagnetic interference shielding and microwave absorption. *Compos A: Appl Sci Manuf* 2020, **136**: 105956.
- [12] Qing YC, Zhou WC, Luo F, *et al.* Titanium carbide (MXene) nanosheets as promising microwave absorbers. *Ceram Int* 2016, **42**: 16412–16416.
- [13] Fan BB, Li N, Dai BZ, *et al.* Investigation of adjacent spacing dependent microwave absorption properties of lamellar structural Ti₃C₂T_x MXenes. *Adv Powder Technol* 2020, **31**: 808–815.
- [14] Cui GZ, Sun XD, Zhang GY, *et al.* Electromagnetic absorption performance of two-dimensional MXene Ti₃C₂T_x exfoliated by HCl+LiF etchant with diverse etching times. *Mater Lett* 2019, **252**: 8–10.
- [15] Cui GZ, Zheng X, Lv X, *et al.* Synthesis and microwave absorption of Ti₃C₂T_x MXene with diverse reactant concentration, reaction time, and reaction temperature. *Ceram Int* 2019, **45**: 23600–23610.
- [16] Zhang JY, Xue W, Chen XY. Ti₃C₂T_x MXenes as thin broadband absorbers. *Nanotechnology* 2020, **31**: 275301.
- [17] Qian Y, Wei HW, Dong JD, *et al.* Fabrication of urchin-like ZnO–MXene nanocomposites for high-performance electromagnetic absorption. *Ceram Int* 2017, **43**: 10757–10762.
- [18] Li XL, Yin XW, Xu HL, *et al.* Ultralight MXene-coated, interconnected SiCnws three-dimensional lamellar foams for efficient microwave absorption in the X-band. *ACS Appl Mater Interfaces* 2018, **10**: 34524–34533.
- [19] Wang HY, Ma HB. The electromagnetic and microwave absorbing properties of MoS₂ modified Ti₃C₂T_x nanocomposites. *J Mater Sci: Mater Electron* 2019, **30**: 15250–15256.
- [20] Fan BB, Shang SY, Dai BZ, *et al.* 2D-layered Ti₃C₂/TiO₂

- hybrids derived from Ti_3C_2 MXenes for enhanced electromagnetic wave absorption. *Ceram Int* 2020, **46**: 17085–17092.
- [21] Zhang WD, Zhang X, Wu HJ, *et al.* Impact of morphology and dielectric property on the microwave absorbing performance of MoS_2 -based materials. *J Alloys Compd* 2018, **751**: 34–42.
- [22] Cui YH, Yang K, Wang JQ, *et al.* Preparation of pleated RGO/MXene/ Fe_3O_4 microsphere and its absorption properties for electromagnetic wave. *Carbon* 2021, **172**: 1–14.
- [23] Shahzad F, Alhabeab M, Hatter CB, *et al.* Electromagnetic interference shielding with 2D transition metal carbides (MXenes). *Science* 2016, **353**: 1137–1140.
- [24] Ning MQ, Lu MM, Li JB, *et al.* Two-dimensional nanosheets of MoS_2 : A promising material with high dielectric properties and microwave absorption performance. *Nanoscale* 2015, **7**: 15734–15740.
- [25] Liu N, Guo YL, Yang XY, *et al.* Microwave-assisted reactant-protecting strategy toward efficient MoS_2 electrocatalysts in hydrogen evolution reaction. *ACS Appl Mater Interfaces* 2015, **7**: 23741–23749.
- [26] Li JH, Rui BL, Wei WX, *et al.* Nanosheets assembled layered MoS_2 /MXene as high performance anode materials for potassium ion batteries. *J Power Sources* 2020, **449**: 227481.
- [27] Zhang K, Ye MQ, Han AJ, *et al.* Preparation, characterization and microwave absorbing properties of MoS_2 and MoS_2 -reduced graphene oxide (RGO) composites. *J Solid State Chem* 2019, **277**: 68–76.
- [28] My Tran N, Thanh Hoai Ta Q, Noh JS. Unusual synthesis of safflower-shaped TiO_2 / Ti_3C_2 heterostructures initiated from two-dimensional Ti_3C_2 MXene. *Appl Surf Sci* 2021, **538**: 148023.
- [29] Dai BZ, Zhao B, Xie X, *et al.* Novel two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes/nano-carbon sphere hybrids for high-performance microwave absorption. *J Mater Chem C* 2018, **6**: 5690–5697.
- [30] Wang Y, Dou H, Wang J, *et al.* Three-dimensional porous MXene/layered double hydroxide composite for high performance supercapacitors. *J Power Sources* 2016, **327**: 221–228.
- [31] Zheng M, Guo RS, Liu ZC, *et al.* MoS_2 intercalated p- Ti_3C_2 anode materials with sandwich-like three dimensional conductive networks for lithium-ion batteries. *J Alloys Compd* 2018, **735**: 1262–1270.
- [32] Hu L, Sun YY, Gong SJ, *et al.* Experimental and theoretical investigation on MoS_2 /MXene heterostructure as an efficient electrocatalyst for hydrogen evolution in both acidic and alkaline media. *New J Chem* 2020, **44**: 7902–7911.
- [33] Mao ML, Mei L, Guo D, *et al.* High electrochemical performance based on the TiO_2 nanobelt@few-layered MoS_2 structure for lithium-ion batteries. *Nanoscale* 2014, **6**: 12350–12353.
- [34] Ferrari AC. Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Commun* 2007, **143**: 47–57.
- [35] Ding X, Huang Y, Li SP, *et al.* FeNi_3 nanoalloy decorated on 3D architecture composite of reduced graphene oxide/molybdenum disulfide giving excellent electromagnetic wave absorption properties. *J Alloys Compd* 2016, **689**: 208–217.
- [36] Liu QH, Cao Q, Bi H, *et al.* $\text{CoNi@SiO}_2\text{@TiO}_2$ and CoNi@Air@TiO_2 microspheres with strong wideband microwave absorption. *Adv Mater* 2016, **28**: 486–490.
- [37] Zhao GL, Lv H, Zhou Y, *et al.* Self-assembled sandwich-like MXene-derived nanocomposites for enhanced electromagnetic wave absorption. *ACS Appl Mater Interfaces* 2018, **10**: 42925–42932.
- [38] Liao Q, He M, Zhou YM, *et al.* Rational construction of $\text{Ti}_3\text{C}_2\text{T}_x$ /Co–MOF-derived laminated $\text{Co/TiO}_2\text{–C}$ hybrids for enhanced electromagnetic wave absorption. *Langmuir* 2018, **34**: 15854–15863.
- [39] Liu PJ, Yao ZJ, Ng VMH, *et al.* Novel multilayer-like structure of $\text{Ti}_3\text{C}_2\text{T}_x$ /CNZF composites for low-frequency electromagnetic absorption. *Mater Lett* 2019, **34**: 214–217.
- [40] Han M, Yin X, Wu H, *et al.* Ti_3C_2 MXenes with modified surface for high-performance electromagnetic absorption and shielding in the X-band. *ACS Appl Mater Interfaces* 2016, **8**: 21011–21019.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.