Facile preparation of in situ coated Ti$_3$C$_2$Tx/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites and their electromagnetic performance

Youbing Li,$^{a,b}$ Xiaobing Zhou,$^{a,b}$ Jing Wang,$^a$ Qihuang Deng,$^b$ Mian Li,$^b$ Shiyu Du,$^b$ Young-Hwan Han,$^c$ Jaehyung Lee$^c$$^*$ and Qing Huang$^b$$^*$

A novel family of Ti$_3$C$_2$Tx/ferrite composites with high reflection loss was developed using a facile in situ co-precipitation method. The as-synthesized Ti$_3$C$_2$Tx/ferrite composite with a 5 wt% Ti$_3$C$_2$Tx MXenes loading exhibited high reflection loss (~42.5 dB) at 13.5 GHz. The effective absorption bandwidth of the 5 wt% Ti$_3$C$_2$Tx/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composite reached ~3 GHz (12–15 GHz) in the K-band. The incorporation of Ti$_3$C$_2$Tx MXenes improved the electromagnetic impedance of the Ti$_3$C$_2$Tx/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composite resulting from the enhanced electrical conductivity. The potential electromagnetic wave absorption mechanisms were revealed, which may contain magnetic loss, dielectric loss, conductivity loss, multiple reflections, and scattering. The technique is facile, fast, scalable, and favorable for the commercialization of this composite. This study provides a potential way to develop EM wave absorbing materials for a large family of MXenes/ferrite composites.

1. Introduction

Electromagnetic (EM) radiation pollution is attracting increasing attention because it affects human health and the operation of electronic devices. High-performance electromagnetic interference (EMI) absorbing and shielding materials have attracted growing interest as a way to solve these problems.$^1$–$^3$ Three typical mechanisms are involved in the design of promising EMI absorbing and shielding materials suggested by Shahzad et al.$^4$ The first is to interact with the EM fields by charge carries, which require materials with high electrical conductivity. The secondary mechanism is absorbing EM radiation by the materials electric and/or magnetic dipoles interacting with radiation. The third mechanism is accounting for multiple internal reflections that arise from scattering centers and interfaces or defect sites within the shielding material, resulting in scattering and the absorption of EM waves. Therefore, a hybrid material that combines high electrical conductivity, magnetic loss, and multiple reflections was reported to be a promising candidate for EMI absorbing and shielding.$^5$ Furthermore, the effective absorption of composites was usually defined as reflection loss (RL) $<-10$ dB, which corresponds to more than 90% EM wave energy absorbed. The corresponding frequency range (RL $<-10$ dB) is denoted as the effective absorption bandwidth. The reflection loss (RL) values of the composites can be calculated using the transmission line theory:$$\text{RL (dB)} = 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|$$ (1)
$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left( \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right)$$ (2)
where $Z_{in}$ is the input impedance of the absorbing materials at the input interface, $\mu_r$ and $\varepsilon_r$ are the complex magnetic permeability and the complex permittivity respectively, $f$ is the frequency, $d$ is the thickness of the absorber, and $c$ is the light velocity in a vacuum. Therefore, from eqn (1) and (2), RL is decided by $Z_{in}$ which is determined by the $\mu_r$ and $\varepsilon_r$ of the materials. Thus the impedance matching is very important for hybrid EM absorbers.

Ni–Zn ferrites have been considered promising candidates as EM absorbers owing to their appropriate permeability and permittivity.$^5$–$^9$ On the other hand, Ni–Zn ferrites attenuate the EM wave mainly through magnetic loss and lead to the impedance matching is out of balance.$^9$ Furthermore, the high resistivity and narrow absorption bandwidth have limited their applications as EMI absorbers.$^{10}$ To solve these problems, high electrical conducting one-dimensional (1D) carbon nanotubes (CNTs) and two-dimensional (2D) graphene were...
introduced to ferrites. In our previous work, CNTs were coated in situ with Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ by a combined precipitation-hydrothermal method. The results showed that when the CNT content was 5 wt%, the reflection ratios were less than ~10 dB within the frequency range, 2–9 GHz, and the reflection ratios reached a minimum ~32.5 dB at 3.9 GHz. Shen et al. developed a novel polyetherimide (PEI)/grapheme@Fe$_3$O$_4$ (G@Fe$_3$O$_4$) composite foams, and when the G@Fe$_3$O$_4$ loading was 10 wt%, the PEI/G@Fe$_3$O$_4$ foam exhibited a high EMI shielding effectiveness of ~14.5 dB (g$^{-1}$ cm$^{-3}$) at 8–12 GHz. They suggested that most of the applied microwave was absorbed rather than reflected, resulting from the improved impedance matching, electromagnetic wave attenuation, and multiple reflections.

MXenes, developed by Naguib et al., are a new family of 2D transition metal carbides and/or nitrides obtained by etching the A layer of MAX phases, where M represents a transition metal, “A” are elements in the group 13–16, “X” represents carbon and/or nitrogen. The exposed transition-metal surfaces are terminated with a mixture groups (T$_x$), such as –OH, =O, and –F, after HF etching. More than 20 different MXenes have been synthesized. MXenes exhibit promising potential applications as Li-ion batteries and supercapacitors owing to their excellent chemical and physical properties. Recently, Han et al. developed 2D Ti$_3$C$_2$T$_x$ (where T$_x$ denotes the surface terminated groups) MXenes for novel EM absorbing applications. The fundamental EM loss mechanisms of Ti$_3$C$_2$T$_x$ before and after annealing were revealed. They suggested that the formation of a localized sandwich structure composed of Ti$_2$O$_2$ nanocrystals and amorphous carbon without sacrificing the original 2D layer structure improved the microwave absorbing capability. Moreover, Shahzad et al. first developed highly flexible MXene films and nacre-like MXene-sodium alginate (SA) composite films for EMI shielding. They reported that a 45 μm thick Ti$_3$C$_2$T$_x$ film exhibited an EMI shielding effectiveness of 92 dB (>50 dB for a 2.5 mm film), which is the highest among synthetic materials of comparable thickness produced to date. The excellent electrical conductivity of Ti$_3$C$_2$T$_x$ films (4600 S cm$^{-1}$) and multiple internal reflections from Ti$_3$C$_2$T$_x$ flakes in free-standing films were considered the reason for the high EMI shielding effectiveness. Furthermore, they suggested that the surface terminated groups (–OH, =O, and –F) play a role on the high EMI shielding effectiveness. The ability of each element to interact with input electromagnetic waves leads to polarization losses, which in turn improve the overall shielding.

Therefore, Ti$_3$C$_2$T$_x$ MXenes are promising candidates as EMI absorbing materials. Moreover, Ti$_3$C$_2$T$_x$ terminated with negative groups (–OH, and –F) can be potentially coated with metal positive ions (such as Ni$^{2+}$, Zn$^{2+}$, and Fe$^{2+}$). Herein, a novel Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composite, which potentially combines three EM wave absorbing mechanisms, was designed and synthesized. A facile chemical co-precipitation approach was developed to ensure that the Ti$_3$C$_2$T$_x$ flakes were coated in situ with Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrites, and without oxidation and sacrificing the original layer structure. The phase, microstructure, and electromagnetic properties of Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites were investigated systematically. To the best of the authors’ knowledge, this is the first effort to reveal the EM loss mechanisms of Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. The combination of Ti$_3$C$_2$T$_x$ MXenes may not only improve the impedance matching characteristics, but also combine the advantages of the individual components. The present work paves the way to develop a large family of MXenes/ferrites composites for EM wave absorbing.

2. Experimental section

2.1 Materials

Elemental powders of TiC (~200 mesh, 99% purity), Ti (~200 mesh, 99% purity), and Al (~300 mesh, 99% purity) were commercially obtained from Target Research Center of General Research Institute for Nonferrous Metals, Beijing, China. Nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O), ferric nitrate (Fe$_3$O$_4$·7H$_2$O), sodium hydroxide (NaOH), sodium lignosulfonate (SLS), and hydrofluoric acid (HF) were commercially obtained from Aladdin Chemical Reagent, China.

2.2 Preparation and functionalization of Ti$_3$C$_2$T$_x$ MXenes

The Ti$_3$AlC$_2$ (purity of 98.5 wt%, containing a small amount of TiC and Al$_2$O$_3$ impurity phases, 300 mesh) was synthesized by the spark plasma sintering (SPS) of a mixture of Ti, Al, and C in a fixed mole ratio at 1400 °C for 20 min. After cooling to room temperature, the as-prepared Ti$_3$AlC$_2$ bulk samples were pulverized to powders and passed through a 300 mesh screen. The Ti$_3$C$_2$T$_x$ powders were synthesized using the procedure suggested by Naguib et al. A 1 g sample of Ti$_3$AlC$_2$ powder was added to a 10 ml of a HF solution (40 wt%) for 72 h at room temperature, the solution was stirred lightly every 12 h. The as-received solution was centrifuged, washed with deionized water and alcohol, and dried at room temperature for 48 h. To improve the dispersion behavior of the Ti$_3$C$_2$T$_x$ powders in water. The obtained Ti$_3$C$_2$T$_x$ powders were functionalized by a disperser of sodium lignin sulfonate (SLS). Typically, 0.1 g Ti$_3$C$_2$T$_x$ powders and 0.05 g SLS were added to 100 ml deionized water, followed by another ultrasonic dispersion process for 45 min. Finally, a modified 1 mg ml$^{-1}$ Ti$_3$C$_2$T$_x$ dispersion solution was obtained after removing the excessive SLS by filtration and washing.

2.3 Preparation of in situ coated Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites

The desired amount of the Ti$_3$C$_2$T$_x$ dispersion solution was added to a salt solution composed of Ni(NO$_3$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, and FeSO$_4$·7H$_2$O at a molar ratio of Ni : Zn : Fe = 0.5 : 0.5 : 2 according to the stoichiometric ratio of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, followed by magnetic stirring and ultrasonic dispersing for 60 min. According to the thermodynamic calculations reported in the literature, the pH needs to be controlled at 10.5 to fabricate the expected ferrite. The salt and Ti$_3$C$_2$T$_x$ of the mixed solution and 1 M NaOH solution were added dropwise at a flow rate of 2.5 ml min$^{-1}$ under continuous stirring with O$_2$ pumped into the reaction solution. After coprecipitation, a Ni, Zn, and Fe precursor slurry formed and
then continued to react at 80 °C for 4 h. The finally obtained precipitates were washed 5 times with deionized water and absolute ethanol, dried, ground, and passed through a 200 mesh sieve; the final Ti$_3$C$_2$Ti$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites were obtained. The schematic presents the facile co-precipitation processing of the Ti$_3$C$_2$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites (Fig. 1).

### 2.4 Characterization

X-ray diffraction (XRD, D8 Advance, Bruker AXS, Germany) was used to analyze the sample phase; the XRD data were collected using Cu Kα radiation at a step size of 0.02°/2θ with a collection time of 1 s per step. Fourier transform infrared (FTIR, Thermo, Nicolet6700, USA) spectroscopy was used to characterize the functional groups on the surface before and after the functionalization of Ti$_3$C$_2$T$_x$. The microstructure and chemical composition were observed by scanning electron microscopy (SEM, QUANTA 250 FEG, FEI, USA) equipped with an energy dispersive spectroscopy (EDS) system. Transmission electron microscopy (TEM Tecnai F20, FEI, USA) and high-resolution TEM (HRTEM) images were carried out at an acceleration voltage of 200 kV. The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method on an ASAP2020 instrument. The electromagnetic property was measured using a physical properties measurement system (PPMS, Quantum Design, USA) at the room temperature hysteresis loop.

The permittivity and permeability were measured using a microwave vector network analyser (8972ES, Agilent, USA) in the frequency range of 0.2–18 GHz. The specimens used for the permittivity and permeability measurements were fabricated by mixing different Ti$_3$C$_2$T$_x$ contents of the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites with 20 wt% paraffin. Typically, the composites and paraffin were dispersed in hexane after grinding to avoid aggregation. The mass ratio of paraffin to composite powders is 1 : 4. After the solvent was volatilized, the mixed powders were cold-pressed into the samples with a toroid (outside diameter is 7 mm, inside diameter is 3 mm, and thickness of 2 mm) under a pressure of 5 MPa. After that, the specimens were inserted into a copper holder and connected between the waveguide flanges of the instrument. The complex permittivity and permeability of the samples were calculated from S parameters ($S_{11}$ and $S_{21}$) which measured from vector network analyzer using the coaxial-line transmission method.

### 3. Results and discussion

Fig. 2a presents XRD patterns of the as-received Ti$_3$AlC$_2$ powders and after HF etching Ti$_3$C$_2$T$_x$ MXenes. The Ti$_3$AlC$_2$ typical XRD peak of (104) at 39° 2θ disappeared and was replaced with a low intensity broadened peak. This indicates that the Al atomic layers had been exfoliated successfully and the corresponding 2D Ti$_3$C$_2$T$_x$ MXenes had formed after HF etching. At the same time, new XRD peaks for Ti$_3$C$_2$F$_2$ were detected at 8.9° and 18.4° 2θ showing that F was inserted into the Ti$_3$C$_2$T$_x$ MXenes interlayer. Furthermore, a new peak at 27.4° 2θ was detected, which was assigned to Ti$_3$C$_2$(OH)$_2$. These results suggest that the Ti$_3$C$_2$T$_x$ surfaces were terminated with functional groups of –OH, and –F after HF etching. Fig. 1b and c exhibit SEM images of Ti$_3$AlC$_2$ and as-obtained Ti$_3$C$_2$T$_x$ MXenes after HF etching, respectively. Ti$_3$AlC$_2$ exhibited a typical layered structure, as shown in Fig. 2b. After HF etching, a similar accordions’ 2D layered structure was formed by extracting an Al atom from Ti$_3$AlC$_2$ (Fig. 2c). The terminated negative groups of –OH, and –F combined with the 2D layered structure provides potential channels for Ni, Zn, and Fe ion intercalation. Fig. 2d shows a TEM image of the Ti$_3$C$_2$T$_x$ MXenes sheets. The material showed a similar hexagonal symmetry and crystallinity to that of the parent Ti$_3$AlC$_2$ phase, as indicated by the fast Fourier transform (FFT) pattern shown in the inset image in Fig. 2d.

![Fig. 1 Schematic diagram of the co-precipitation processing of Ti$_3$C$_2$Ti$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites.](image)
solution and provided a nucleation channel for the *in situ* coated and intercalated NiZn ferrite.

The dispersion behavior of Ti₃CₓTₓ MXenes after modification by SLS was examined. Fig. 4 shows the zeta potential of Ti₃CₓTₓ MXenes after surface functionalization in the pH range of 4–11. The pH was tuned by diluted sodium hydroxide and nitric acid. Over the entire pH range, the zeta potential decreased with increasing pH (slight fluctuations were observed at pH = 9 and 11 for the measurement error). The zeta potential in the entire measured pH range was lower than −25 mV, which is the standard surface potential value of a stable dispersion colloidal solution. The zeta potential reached approximately −40 mV at the Ni²⁺, Zn²⁺, and Fe²⁺ co-precipitation pH of 10.5 ± 0.1. Therefore, after functionalization by SLS, a large number of negative charges were modified on the surface of Ti₃CₓTₓ MXenes. The aggregation of Ti₃CₓTₓ MXenes can be prevented by coulomb repulsion and steric-hindrance. On the other hand, the large number of negative charges would absorb Ni²⁺, Zn²⁺, and Fe²⁺, which is a benefit to the NiZn ferrite *in situ* coated Ti₃CₓTₓ MXenes surface and intercalated into the Ti₃CₓTₓ MXenes interlayer. Furthermore, the local dipole polarization may be induced between the surface functional groups and Ti₃Cₓ when subjected to an alternating EM field.

The chemical co-precipitation process is a facile scale approach to the synthesis of NiZn ferrite. After modification by SLS, Ti₃CₓTₓ were mixed with the salt solution of Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, and FeSO₄·7H₂O. Ti₃CₓTₓ/Ni₀.₅Zn₀.₅Fe₂O₄ composites with different Ti₃CₓTₓ contents were synthesized by a co-precipitation process at 80 °C for 4 h. Fig. 5 presents the XRD patterns of pure Ni₀.₅Zn₀.₅Fe₂O₄ and Ti₃CₓTₓ/Ni₀.₅Zn₀.₅Fe₂O₄ composites with different Ti₃CₓTₓ contents. All

---

**Fig. 2** (a) XRD patterns of Ti₃AlC₂ and Ti₃CₓTₓ MXenes. SEM images of Ti₃AlC₂ (b) and Ti₃CₓTₓ (c). (d) HRTEM image of Ti₃CₓTₓ sheets, the inset shows the FFT of the white rectangle area.

**Fig. 3** FTIR spectra of Ti₃CₓTₓ MXenes with and without functionalization.

**Fig. 4** Zeta potential as a function of pH for the surface functionalization of Ti₃CₓTₓ MXenes.
the specimens showed a typical spinel phase and good crystallization. The characteristic XRD peaks at 18.05°, 30.02°, 35.29°, 43.01°, 53.28°, 56.80° and 62.27° 2θ correspond to the (111), (220), (311), (400), (422), (511) and (440) plane of Ni0.5Zn0.5Fe2O4 crystal, respectively. This is consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 8-234. The typical XRD peaks of Ti3C2T x MXenes at 8.9° and 18.4° 2θ were not detected, which may due to the low content of Ti3C2T x MXenes, and/or full coverage of Ni0.5Zn0.5Fe2O4 nanocrystals on the Ti3C2Tx surface. Moreover, no anatase or rutile phases were detected, which indicates that Ti3C2Tx MXenes was not oxidized due to the facile low temperature co-precipitation process. The mean grain sizes of the Ti3C2Tx/Ni0.5Zn0.5Fe2O4 composites with different Ti3C2Tx contents were calculated from the XRD patterns using Scherrer’s equation:}

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where \(D\) is the mean grain size, \(k\) is a constant (0.89), \(\lambda\) is the wavelength of X-rays and equal to 0.154056 nm, \(\beta\) is the half-peak width, and \(\theta\) is the diffraction angle. The mean grain sizes of pure Ni0.5Zn0.5Fe2O4 and Ti3C2Tx/Ni0.5Zn0.5Fe2O4 composites with different Ti3C2Tx contents were 14.8 nm, 13.5 nm (1 wt%), 12.4 nm (2 wt%), and 10.5 nm (5 wt%), respectively.

Interestingly, the mean grain size of the Ti3C2Tx/Ni0.5Zn0.5Fe2O4 composites decreased with increasing Ti3C2Tx content. This can be obtained from the NiZn ferrite formation mechanism of the Ti3C2Tx surfaces. There were three steps as follows:

(i) Initially, Ni2+, Zn2+, and Fe2+ were absorbed in situ by the large number of negative charges of the Ti3C2Tx surfaces. They were co-precipitated by adding a NaOH solution. Fe(OH)2 formed first because of the higher Fe2+ concentration than Ni2+ and Zn2+ (eqn (4)). At the same time, the gel of [Fe(OH)3]m formed after the oxidation of Fe(OH)2 with pumped O2 (eqn (5) and (6)).

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2
\]

\[
\text{Fe(OH)}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe(OH)}_3
\]

(ii) According to the Fajans rule, Ni2+ and Zn2+ should be absorbed on the surface of colloid cores ([Fe(OH)3]m) because the colloid cores preference absorbed those metal ions, which can form flawless materials with Fe. When Ni2+ and Zn2+ were adsorbed on the colloid cores surface, hydrolysis of the metal ions took place, and the hydroxyl resembling the metal ions were then obtained.

\[
[\text{Fe(OH)}_3]_m + \text{Ni}^{2+} + \text{Zn}^{2+} + \text{OH}^- \rightarrow [\text{Fe(OH)}_3]_m \cdot \text{Ni(Zn)OH}^+
\]

(iii) In the last stage, as the reaction proceeded, the intermediate was transformed gradually to NiZn ferrite with the release of a proton, which can be written as:

\[
[\text{Fe(OH)}_3]_m \cdot \text{Ni(Zn)OH}^+ \rightarrow \text{NiZnFe}_2\text{O}_4 + \text{H}_2\text{O} + \text{H}^+
\]
Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites increased with increasing Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. This indicates that finer grain Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites were obtained at higher Ti$_3$C$_2$T$_x$ MXenes contents. This is consistent with the grain size calculation from the XRD patterns. The incorporation of the nonmagnetic phase of Ti$_3$C$_2$T$_x$ MXenes impeded the serious aggregation of magnetic NiZn ferrite nanoparticles.

SEM and TEM were carried out to further examine the microstructure of the as-synthesized Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. Fig. 7a shows a typical SEM image of the 5 wt% Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. Ti$_3$C$_2$T$_x$ MXenes were covered homogenously with spherical NiZn ferrite nanoparticles, and Ti$_3$C$_2$T$_x$ MXenes still retained the ordered layer structure. NiZn ferrite nanoparticles had a tendency to agglomerate because of the powerful magnetic dipole interactions and high surface energy. EDS was carried out to confirm the chemical composition of the composites. EDS analysis of the rectangle area marked in Fig. 7a revealed mainly Ti, C, O, Ni, Zn, and Fe (Fig. 7b). S and Na were not detected, showing that the SLS surfactant and NaOH precipitant can be removed by filtration and washing with water. Fig. 6c presents the HRTEM image of 5 wt% Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. The ferrite nanograins covered not only the surface of the Ti$_3$C$_2$T$_x$ MXenes sheets, but were also inserted into the Ti$_3$C$_2$T$_x$ MXenes interlayer. The mean grain size of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ was approximately 10 nm, which was very close to the value calculated from the XRD patterns. After detailed analysis of the lattice fringes, the lattice fringe spacing 0.25 nm (Fig. 7c) can be assigned to the (311) planes of the cubic spinel crystal Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. The corresponding selected area electron diffraction (SAED) pattern also indicates the good crystal structure of the cubic spinel phase. The lattice fringe spacing 0.48 nm (Fig. 7c) was a typical (0004) plane of the hexagonal structure of Ti$_3$C$_2$T$_x$ MXenes. Therefore, the morphology of the 5 wt% Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites further demonstrated that a large number of modified Ti$_3$C$_2$T$_x$ MXenes surface negative charges acted as nucleation centers and interacted with metal ions during coprecipitation, which was a benefit to the in situ coating by Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles. Furthermore, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles were attached firmly to the surface and were inserted into the interlayer of Ti$_3$C$_2$T$_x$ MXenes, and an ultrasonication processing was performed during TEM specimen preparation, which indicated an excellent electrostatic interaction between Ti$_3$C$_2$T$_x$ and ferrites.

The magnetic properties of the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites with various Ti$_3$C$_2$T$_x$ contents were examined in an applied magnetic field range from −30 to 30 kOe at room temperature. Fig. 8 shows the hysteresis loop of the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites with different Ti$_3$C$_2$T$_x$ contents. All of them exhibited typical soft ferrite properties because the coercive force and residual magnetization are nearly zero. Compared to the pure Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, the saturation magnetization ($M_s$) of the 5 wt% Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites decreased from 32.3 to 27.08 emu g$^{-1}$. The $M_s$ decreased slightly with decreasing Ti$_3$C$_2$T$_x$ contents. The decrease in $M_s$ might be due to the demagnetizing field produced by the incorporation of nonmagnetic Ti$_3$C$_2$T$_x$ and the decreasing grain size. Xia Li et al. observed similar trends for pure NiZn ferrite.
nanoparticles. Compared to the 19 nm NiZn nanoparticles, the saturation magnetization of 6 nm NiZn nanoparticles decreased from 38 to 32 emu g$^{-1}$. Kodama et al.\textsuperscript{23} attributed this to much more frozen spins on the surface that point to random positions, which reduced the saturation magnetization for finer particles.

To examine the EM wave absorption of the as-synthesized Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites, their relative complex permittivity and complex permeability were measured in the frequency range of 0.2–18 GHz. The complex permittivity and permeability are usually used to analyze the dielectric and magnetic properties of the microwave absorber materials. Generally, real part of the permittivity and permeability signify the storage capability of the dielectric and magnetic energy, respectively. While the imaginary part of the permittivity and permeability stand for the loss of dielectric and magnetic energy.\textsuperscript{9,14} Fig. 9a–d shows the permittivity and permeability of pure Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites with various Ti$_3$C$_2$T$_x$ contents, respectively. Both the real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the permittivity of the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites increased with increasing Ti$_3$C$_2$T$_x$ contents (Fig. 9a and b). A high electrical conductivity is benefit to a high complex permittivity according to free electron theory.\textsuperscript{37} Therefore, these increases are mainly due to the high electrical conductivity of Ti$_3$C$_2$T$_x$, which are already indicated by both the theoretical prediction and experimental results. Ti$_3$C$_2$T$_x$ shows the metallic-like electrical conductivity behavior, which was attributed to the high electron density of states near the Fermi level [$|\varepsilon(|)|$], as simulated from density functional theory.\textsuperscript{23} Shahzad et al.\textsuperscript{4} reported the electrical conductivity of Ti$_3$C$_2$T$_x$ films can reach 4600 S cm$^{-1}$. Therefore, the high aspect ratio of 2D Ti$_3$C$_2$T$_x$ flakes can form a conducting network easily within the NiZn ferrite and provide an electron carrier to improve the electrical conductivity of Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. In addition, the conductive network formed by 2D Ti$_3$C$_2$T$_x$ can be seen as a minicapacitor in the composite. The polarization effects improved the charge storage capacity and the real part of permittivity of the composite. An increase in the imaginary part of the permittivity can be attributed to the increasing ohmic loss in the composite. It is worthy to note that, according to the quarter-wavelength equation, the increases in complex permittivity at high frequency will benefit to decline the absorbing thickness.\textsuperscript{5}

Furthermore, both $\varepsilon'$ and $\varepsilon''$ of all specimens exhibits a certain degree of fluctuation in the frequency range of 0.2–18 GHz. The values of both $\varepsilon'$ and $\varepsilon''$ first decreased from 0.2–9 GHz and then increased from 9–18 GHz with some obvious resonances. It exhibits obvious frequency-dependent dielectric response. The phenomenon of the values of both $\varepsilon'$ and $\varepsilon''$ decreased from 0.2–9 GHz is a typical frequency dispersion behavior, which is common in most of carbon/magnetic composites.\textsuperscript{9,15} This may arise from the lag of the induced charges to follow the reversing external field at high frequencies and finally causes a reduction in the electronic oscillations.\textsuperscript{18} Furthermore, the permittivity of the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites showed typical nonlinear resonant characteristics at 9–18 GHz, which indicates the existence of polarization and relaxation behavior and implies better dielectric loss performance in the corresponding frequency range. Usually, the dielectric property of the material is determined by the electronic, ionic, space charge, Debye dipole and interfacial polarization. As we know, the electronic and ionic polarization is the main contribution in the THz and PHz frequency range. Therefore, the dielectric properties of the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites are mainly contributed to space charge, Debye dipole and interfacial polarization. Liu et al.\textsuperscript{5} observed the similar phenomenon in the co-doped Ni-Zn ferrite/graphene (CNZF/GN) composites. Because of the dielectric properties of Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites are similar with the CNZF/GN composites. According to the conclusion of Liu et al.,\textsuperscript{5} the Debye dipolar relaxation effect may be ascribed to the following reason: during the alternation EM wave radiation, the lags in induced charge caused by the ferrite–ferrite, ferrite–Ti$_3$C$_2$T$_x$, and Ti$_3$C$_2$T$_x$–Ti$_3$C$_2$T$_x$ interfaces that encounter the external applied field will lead to relaxation and transformation of EM energy into thermal energy. Furthermore, the lattice defects and functional groups produced from Ti$_3$C$_2$T$_x$ and
The microwave absorption of pure Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} can be calculated from the equation $t_m(n) = nC/2m$ (where $n$ is an integer). From this equation, the peak frequency is inversely proportional to the thickness of the absorber. To examine the influence of the Ti_{3}C_{2}T_{x} contents on the absorbing performance of the Ti_{3}C_{2}T_{x}/Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} composites, the RL of Ti_{3}C_{2}T_{x}/Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} composites with various Ti_{3}C_{2}T_{x} contents were calculated further at a constant thickness of 6.5 mm (Fig. 10f). The minimum reflection loss of the Ti_{3}C_{2}T_{x} content with 0 wt%, 1 wt%, 2 wt%, and 5 wt% was −15.7 dB at 13.5 GHz, −17.4 dB at 13.2 GHz, −18.9 dB at 13.7 GHz, and −42.5 dB at 13.5 GHz, respectively. Two absorption peaks were observed, which indicated that the thickness of the absorber is greater than a critical level of $n = 3$ (eqn (9)). As expected with the experimental design, both the minimum RL value and the effective absorption bandwidth were improved significantly with increasing Ti_{3}C_{2}T_{x} content. This may be due to the increase in permittivity, as shown in Fig. 9. The effective absorption bandwidth of the 5 wt% Ti_{3}C_{2}T_{x}/Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} composite reached ~3 GHz (12–15 GHz) in the K-band. It can be observed that, 5 wt% Ti_{3}C_{2}T_{x}/Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} composite exhibits superior microwave absorption properties in both the minimum RL value and the effective absorption bandwidth in compare with the other samples. The results indicate that the remarkable effect of Ti_{3}C_{2}T_{x} incorporation on EM wave absorption.

The good microwave absorption performance of Ti_{3}C_{2}T_{x}/Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} composites may be explained as follows (Fig. 11):

(1) First, electromagnetic impedance matching plays a key role in the microwave absorption performance of composites. The microwave absorption of pure Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} can be attributed mainly to magnetic loss. The imaginary part of magnetization is very small at high frequency. Therefore, impedance matching is out of balance. The incorporation of high conductive Ti_{3}C_{2}T_{x} enhanced the conductivity and improved the impedance matching of the Ti_{3}C_{2}T_{x}/Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} composites. Therefore, the microwave absorption performance was also improved.

(2) Second, the dielectric loss and magnetic loss are important factors that contribute to EM wave absorption for the
The magnetic loss was attributed to the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. As suggested by Han et al.\textsuperscript{24} and Shahzad et al.\textsuperscript{4}, the dipolar polarization caused by the surface functional groups, localized defects, and dangling bonds of Ti$_3$C$_2$T$_x$ MXenes plays an important role in the dielectric loss. In addition, it is a heterogeneous system. Interfacial polarization, called Maxwell–Wagner polarization, will be generated at the interface of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Ti$_3$C$_2$T$_x$ MXenes due to the different conductivity and dielectric constants. The in situ co-precipitation method used made the nano Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ coat the Ti$_3$C$_2$T$_x$ MXenes surfaces and inserted interlayer, which can produce a much larger interface of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$–Ti$_3$C$_2$T$_x$, Ti$_3$C$_2$T$_x$–Ti$_3$C$_2$T$_x$, and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$–Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. This can cause strong interface polarization. Under an electromagnetic field, dipolar polarization and interface polarization can increase the energy dissipation, which gives the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites enhanced microwave absorption ability.

(3) Third, as demonstrated in the graphene/ferrite composites system, the conductivity loss cannot be ignored because of...
the similar excellent conductivity of Ti$_3$C$_2$T$_x$ MXenes with graphene. The conductivity network will be formed by the random 2D Ti$_3$C$_2$T$_x$ flakes in the Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composites. When the vertical component of an electromagnetic wave is inputted into the composites in an alternating EM field, the EM wave energy is transferred in the form of a micro current due to the good impedance matching. The NiZn ferrites act as an insulator. During micro current transmission, a large portion of the electrical energy would be dissipated due to the high resistance of NiZn ferrites. Moreover a small part is attenuated immediately because of the high conductivity of NiZn ferrites. The remaining waves pass through the MXene and ferrite, where the interaction with the MXenes and ferrite induces a microcurrent that contributes to conductivity losses, resulting in a decrease in the energy of the EM waves. The surviving EM waves will be entered as the next layer of Ti$_3$C$_2$T$_x$ and could be reflected and scattered repeatedly between these interfaces. The first and second layers of Ti$_3$C$_2$T$_x$ act as the reflecting surface and are enhanced to multiple internal reflections with each other. Furthermore, the NiZn ferrite coated with each Ti$_3$C$_2$T$_x$ surface will attenuate the EM waves by magnetic loss and multiple scattering. Therefore, it is difficult for the EM waves to escape from the composites until they are dissipated completely as heat.

4. Conclusion

A facile, fast, and scalable approach to synthesize a novel family Ti$_3$C$_2$T$_x$/ferrite composite with good electromagnetic wave absorption was developed using an in situ co-precipitation method. The potential electromagnetic wave absorption mechanisms were proposed. The incorporation of high conductivity Ti$_3$C$_2$T$_x$ MXenes improved the EM impedance of NiZn ferrite, and contributed to the dielectric loss and conductivity loss of the composites. In addition, the multiple reflections caused by the layer structure of Ti$_3$C$_2$T$_x$ MXenes further improved the EM wave absorption performance. The minimum RL value of $-42.5$ dB at $13.5$ GHz with a thickness of $6.5$ mm with the $5$ wt% Ti$_3$C$_2$T$_x$ was obtained. The effective absorption bandwidth of $5$ wt% Ti$_3$C$_2$T$_x$/Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composite reached $\sim 3$ GHz (12–15 GHz) in the K-band. Although the corresponding thickness of the minimum RL value was relative high, in future work, it is expected to decrease with increasing Ti$_3$C$_2$T$_x$ MXenes content. This study is expected to open the door for the potential applications of MXenes/ferrite family in the microwave absorbing field.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant No. 51502310), the Natural Science Foundation of Zhejiang Province (Grant No. LY15E020007), and the Natural Science Foundation of Ningbo city (Grant No. 2016A610248). This study was supported by the National Key Research and Development Program of China (No. 2016YFB0700901).

References


