Flexible, stretchable and magnetic Fe₃O₄@Ti₃C₂T_x/elastomer with supramolecular interfacial crosslinking for enhancing mechanical and electromagnetic interference shielding performance

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ABSTRACT Electromagnetic interference (EMI) and radiation of electronic devices are ubiquitous, which are potentially hazardous to the normal operation of electronic equipment and human health. MXenes are extremely attractive in the preparation of EMI shielding materials due to their excellent metallic conductivity and tunable surface chemistry. Herein, by virtue of the designed nanostructure and regulation of interface interactions, we fabricated flexible Fe₃O₄@Ti₃C₂T_x MXene/3,4-dihydroxyphenylacetic acid (DOPAC)-epoxidized natural rubber (ENR) elastomers (FMDE) with 3D segregated interconnected structures. The elaborately designed metal-ligand coordination crosslinking between Fe₃O₄ nanoparticles and DOPAC ligand molecules provides strong interfacial interactions, resulting in significantly reinforced mechanical properties. Compared with Ti₃C₂T_x/ENR elastomers, the maximum tensile strength and toughness of FMDE are elevated by ~306% and 475%, respectively. Moreover, the 3D segregated conductive network constructed by Fe₃O₄@Ti₃C₂T_x nanoflakes resulted from volume exclusion effect of ENR latex and the introduction of magnetic Fe₃O₄ nanoparticles with enhanced electromagnetic wave absorption greatly improved the EMI shielding performance of FMDE, exhibiting an excellent EMI shielding effectiveness of up to 58 dB in the X band (8.2–12.4 GHz) and stable EMI shielding capability during repeated deformations. This work provides a promising strategy for the design and manufacture of novel flexible EMI shielding materials.

Keywords: Ti₃C₂T_x, epoxidized natural rubber, Fe₃O₄, metal-ligand coordination, electromagnetic interference shielding

INTRODUCTION

With rapid growth of intelligent electronic devices, electromagnetic interference (EMI) pollution has become an increasing detrimental impact on devices, human and the surrounding environment [1–3]. Metal-based materials are widely used for EMI shielding, while their easy-to-corrode nature, high density and low flexibility restrict their applications in emerging flexible wearable devices [4,5]. Over the past decades, researchers have focused on the carbon-based conductive fillers (carbon nanotubes [6,7], graphene [8,9], etc.) and soft polymer matrices (cellulose [10,11], elastomer [12,13], etc.) as alternative to metal/alloy for flexible EMI shielding materials. Recently, newly emerged two-dimensional (2D) transition metal carbide and nitride known as MXenes have been increasingly favored by researchers [14–16]. As the first synthesized and mostly studied MXene, Ti₃C₂T_x (T_x stands for the surface termination groups) has been widely applied in the field of EMI shielding due to their metallic conductivity and rich surface chemistry. For example, Shahzad *et al.* [17] prepared ultrathin Ti₃C₂T_x films with an EMI shielding performance of up to 92 dB, which is the highest value of similar thickness in currently produced synthetic materials. Sun *et al.* [18] prepared a Ti₃C₂T_x/polystyrene nanocomposite with conductive cellular structure by electrostatic self-assembly and compression molding. Its EMI shielding performance reached 62 dB at a low Ti₃C₂T_x loading (1.9 vol%). A PVA/Ti₃C₂T_x film with excellent EMI shielding performance and thermal conductivity was fabricated by Jin *et al.* [19] through a multi-layered casting method. The continuous

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Ti₃C₂T_x layers were conducive to the construction of heat conduction and electronic networks, and the multi-layer architecture rendered the film flame retardant potential.

Besides conductive materials, magnetic nanoparticles (NPs) could contribute to the EMI shielding performance through high magnetic loss absorption. Fe₃O₄ NPs has attracted extensive attention due to its low cost, high magnetic loss, environmental friendliness and natural abundance [20–22]. Recently, some reports have studied the combination of MXene and Fe₃O₄ NPs for high-performance EMI shielding [23,24]. For example, Wang *et al.* [25] used Ti₃C₂ as substrate and added polyaniline and Fe₃O₄ NPs to enhance interfacial polarization, improving the attenuation loss and microwave absorption performance. Although impressive results have been achieved, there are few reports about MXene/Fe₃O₄-based flexible EMI shielding nanocomposites, which require strong interfacial bonding between the components to ensure reliable mechanical properties. The appropriate nanostructure design and regulation of component interactions within soft polymer matrices are indispensable for satisfying more stringent requirements of flexible EMI shielding applications.

Herein, Ti₃C₂T_x nanoflakes and Fe₃O₄ NPs were incorporated into modified epoxidized natural rubber (DENR) *via* a self-assembly method to obtain a conductive and flexible elastomer based on supramolecular metal-ligand coordination/non-covalent crosslinking and 3D hierarchically interconnected conductive network. Deposition of Fe₃O₄ NPs on the delaminated Ti₃C₂T_x nanoflakes provides iron center ions for interface design. The modification of ENR with 3,4-dihydroxyphenylacetic acid (DOPAC) produces a wealth of ligand molecules, facilitating the construction of supramolecular metal-ligand coordination bonding between the matrix and Fe₃O₄@Ti₃C₂T_x filler. The strong interfacial adhesion between the components greatly improves the mechanical performance of the composite. Our previous studies have confirmed that rubber latex as the isolation phase is essential for the construction of conductive segregated structure [26,27]. Owing to the excluded volume effect, the conductive filler homogeneously dispersed on the surface of rubber latex tended to be selectively squeezed toward the interstitial space of latex microspheres and densely connected to form a continuous conductive network. This kind of structure reveals great potential for desirable electrical conductivity and EMI shielding performance at lower filler contents. Furthermore, the introduction of Fe₃O₄ NPs facilitates the magnetic loss of incident electromagnetic waves in the composite, which

further improves the EMI shielding performance. The elaborately 3D segregated conductive structure and supramolecular interactions endow the obtained Fe₃O₄@Ti₃C₂T_x/DENR elastomer (FMDE) with excellent EMI shielding performance and outstanding mechanical properties. This easy-to-fabricate, flexible and scalable strategy could provide valuable guidance for the practical application of novel flexible EMI shielding materials.

EXPERIMENTAL SECTION

Preparation of Fe₃O₄@Ti₃C₂T_x nanocomposites

Ti₃C₂T_x aqueous dispersion was prepared according to our previous report [28]. The Fe₃O₄@Ti₃C₂T_x nanocomposites were fabricated by a chemical co-precipitation method. In a typical experiment, pre-degassed Ti₃C₂T_x dispersion (32 g, 0.3 wt%) was mixed with an aqueous solution containing 34.4 mg of FeCl₂·4H₂O and 71 mg of FeCl₃·6H₂O. After rapid stirring for 5 min, 2 mL of ammonia solution was added dropwise under nitrogen atmosphere, and the reaction was performed at 80°C for 2 h. After being centrifuged to near neutral pH, a certain amount of the obtained Fe₃O₄@Ti₃C₂T_x aqueous solution was dried and weighed to determine the concentration *via* vacuum-assisted filtration. The weight percentage of Fe₃O₄ in Fe₃O₄@Ti₃C₂T_x nanocomposites was calculated to be about 50%.

Modification of ENR latex

In a typical experiment, 0.363 g of DOPAC and 0.293 g of tetraethylammonium bromide as catalyst were sequentially added to 100 g of ENR latex (11.3 wt%) with vigorous stirring. After reacting at 100°C for 3 h, the catalyst was filtered off with absorbent cotton to obtain the product.

Preparation of Fe₃O₄@Ti₃C₂T_x/DENR nanocomposites

Benefiting from the desirable dispersibility of Fe₃O₄@Ti₃C₂T_x and DENR latex, 0.2 wt% Fe₃O₄@Ti₃C₂T_x dispersion was added dropwise to 1 wt% DENR latex under rapid stirring. After stirring at room temperature for 30 min, FMDE nanocomposites with 3D segregated network can be obtained after removing excess water through vacuum-assisted filtration. The FMDE nanocomposites with 5, 7.5, 10, 12.5 and 15 wt% of Ti₃C₂T_x were corresponding to FMDE-5, 7.5, 10, 12.5, 15, respectively. For comparison, Ti₃C₂T_x/ENR, Ti₃C₂T_x/DENR and Fe₃O₄@Ti₃C₂T_x/ENR samples with different Ti₃C₂T_x content were prepared by the same method. The samples

were all cut into rectangular strips with a length greater than 4 cm for mechanical performance testing, and at least four samples were tested in each group. The samples were all cut into discs of 12 mm in diameter for EMI shielding testing.

RESULTS AND DISCUSSION

Design and Fabrication of FMDE

In order to fabricate flexible MXene/ Fe_3O_4 -based EMI shielding materials, ENR was introduced as elastomer substrate to impart desirable mechanical properties. Fig. 1 schematically illustrates the key manufacturing process of FMDE nanocomposites with segregated conductive structure. $\text{Fe}_3\text{O}_4@/\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites were prepared by chemical co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions on delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (Fig. 1a). Iron ions tend to be adsorbed on $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes due to the strong

electrostatic attraction. After adding $\text{NH}_3\cdot\text{H}_2\text{O}$ solution, the obtained magnetic Fe_3O_4 NPs could uniformly deposit on the $\text{Ti}_3\text{C}_2\text{T}_x$ nano-template. Importantly, $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes with abundant hydrophilic functional groups served as dispersant to effectively prevent the accumulation of Fe_3O_4 NPs. Digital images of Fe_3O_4 NPs, $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@/\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. S1) nanocomposites dispersed in aqueous solution reveal their dispersion stability. It can be seen that Fe_3O_4 NPs completely precipitated after standing 3 h. Their dispersion stability significantly improved after deposition on $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The zeta potential of $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous solution (Fig. S2) increased from -35 to -22 mV after loading with Fe_3O_4 NPs due to the interaction of hydrophilic groups. In order to construct effective interfacial supramolecular cross-linking between the conductive fillers and elastomer matrix, DOPAC was employed to modify ENR latex (Fig. 1b). The grafting of DOPAC onto ENR is demonstrated in the

Figure 1 Schematic illustration of the synthesis of FMDE nanocomposite. (a) Schematic diagram of $\text{Fe}_3\text{O}_4@/\text{Ti}_3\text{C}_2\text{T}_x$ prepared by *in situ* deposition of Fe_3O_4 with $\text{Ti}_3\text{C}_2\text{T}_x$ as the template. (b) Surface modification of ENR latex with DOPAC. (c) Constructing FMDE nanocomposites with interconnected isolation structure *via* the self-assembly method.

Fourier transform infrared spectra (FTIR) (See Fig. S3 for details). Benefiting from the good water dispersibility, abundant surface oxygen-containing groups of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and modified DENR latex, self-assembly of the supramolecular crosslinking network between the matrix and fillers could be easily achieved by direct aqueous mixing (Fig. 1c). After excess water was removed by vacuum-assisted filtration, $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes were selectively squeezed between latex spheres to construct interconnected isolation structure due to the volume exclusion effect of ENR latex. The designed FMDE elastomers exhibit excellent flexibility, crimpiness and twistability.

Characterization of morphology, structure and supramolecular interactions

Fig. 2a shows the interfacial supramolecular metal-ligand coordination/non-covalent bond crosslinking and conductive segregated network structure, constructed by $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes and DOPAC-modified ENR latex. The chemical structures of metal coordination and non-covalent bond between $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites and DOPAC-modified ENR matrix interface are exhibited in Fig. 2b. C_3 and C_4 phenolic oxygen atoms of catechol form metal coordination bonds with the surface of Fe_3O_4 NPs. And oxygen-containing functional groups ($-\text{OH}$, $-\text{O}-$) on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ can also form non-covalent interactions such as hydrogen bonds

with DENR. The interfacial interactions lead to stable combination between the rubber matrix and conductive fillers. The obtained $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes and FMDE nanocomposites were characterized by transmission electron microscopy (TEM). Fe_3O_4 NPs with an average diameter of 10–30 nm (Fig. 2c) uniformly disperse on the $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes without significant magnetic aggregation, effectively expanding the specific surface area of magnetic particles. Fig. 2d reveals the ordered 3D segregated network structure of FMDE. The ENR latex microspheres are demulsified after removing excess water to form irregular shape (white part). $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes (black part) are located on the interstitial space of ENR, resulting in interconnected conductive channels. These results are consistent with the laser scanning confocal microscopy (LSCM) image (Fig. 2e). $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes were labelled with rhodamine 6G fluorescent dye, and the green fluorescent network of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes (non-fluorescent regions were unlabeled latex) could be clearly observed, indicating that FMDE nanocomposites with interconnected conductive network structure were successfully fabricated. Moreover, the 2D small angle X-ray scattering (SAXS) pattern (Fig. 2f) shows regular concentric circles, demonstrating that $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes evenly distribute in the DOPAC-modified matrix to construct an isotropic segregated network.

X-ray photoelectron spectroscopy (XPS) analysis was

Figure 2 Chemical interactions and characterization of nanostructures. (a) Designed conductive segregated network coordinate with interfacial supramolecular interactions. (b) Metal coordination and hydrogen bonding interactions between the chemical structure of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and DENR latex. (c) TEM image of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (d) TEM images of the ordered 3D segregated network structure of FMDE. (e) LSCM image of the network structure in FMDE nanocomposite. (f) SAXS 2D patterns of FMDE.

Figure 3 (a) XPS survey spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposite. The inset magnifies the XPS spectra of Fe 2p. (b) Ti 2p XPS spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$. (c) XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and the inset magnifies (002) peak. (d) Laser confocal Raman spectrum of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x/\text{DNR}$, $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$, $\text{Fe}_3\text{O}_4/\text{DOPAC}$ and pure DOPAC. The characteristic signals at 500–700 cm^{-1} and 1200–1500 cm^{-1} confirm the iron-catechol coordination. 1D SAXS plot of (e) $\ln(I(q))-\ln(q)$ with the blue dashed line for visual observation and (f) $\ln(q^3I(q))-q^2$ with the straight line as the fitting slopes.

performed to study the chemical binding information of neat $\text{Ti}_3\text{C}_2\text{T}_x$ and the prepared $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$. The general XPS survey spectrum (Fig. 3a) shows the presence of F and O on both $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$, indicating possible surface termination and introduction of polarizing groups during the etch-exfoliating process [29]. The Fe 2p peaks could be noticed on the $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ spectrum and O 1s peak is significantly enhanced, demonstrating that Fe_3O_4 NPs are successfully deposited on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$. Deconvolution of Ti and C XPS peaks can further explore the changes in chemical structure during the reaction (Fig. 3b and Fig. S4). Compared with neat $\text{Ti}_3\text{C}_2\text{T}_x$ and the $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites, the intensity of Ti (IV)- TiO_2 peaks (458.2 and 464.1 eV) at Ti 2p core level and the C–O peaks (285.7 and 288.2 eV) at C 1s core level are significantly enhanced. These changes demonstrate that Ti atoms with chemically unstable state on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ are spontaneously transformed into more stable TiO_2 by reaction with H_2O and O_2 , and C atoms tend to form C–O bonds during the deposition process of Fe_3O_4 NPs [30,31]. The structural evolution from $\text{Ti}_3\text{C}_2\text{T}_x$ to $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ was reflected in their X-ray diffraction

(XRD) patterns (Fig. 3c). Additional characteristic diffraction peaks presenting Fe_3O_4 phase can be observed in the $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ curve, which can be assigned to (111), (200), (311), (400) and (511) according to JCPDS 19-629. And the intercalation of Fe_3O_4 NPs into $\text{Ti}_3\text{C}_2\text{T}_x$ expanded the layer spacing, which was demonstrated by the (002) peak of $\text{Ti}_3\text{C}_2\text{T}_x$ downshifting from 6.60° to 6.46° [32].

Laser confocal Raman microspectroscopy reveals the presence of supramolecular metal ligand coordination in the FMDE nanocomposite. The resonance Raman spectral characteristic of Fe^{3+} -catechol complexation was observed using a near-infrared (785 nm) laser (Fig. 3d). Clear similarities and differences exist in the spectra between the samples, especially the peaks at 500–700 cm^{-1} assigned to FMDE and $\text{Fe}_3\text{O}_4/\text{DOPAC}$, which correspond to the Raman vibrations originating from the chelation between iron ions and catechol [33,34]. The peaks at 581 and 625 cm^{-1} confirm the interaction between C₃ and C₄ phenolic oxygen atoms of catechol and iron ions, respectively [35]. It indicates that many metal coordinate bonds formed between the interface of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and DENR serve as supramolecular cross-linking points

to reinforce the interaction of nanocomposite components. It is worth noting that the carbon vibration region (712 cm^{-1}) corresponding to $\text{Ti}_3\text{C}_2\text{T}_x$ is restricted due to the small interlayer spacing in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ [36,37]. Once Fe_3O_4 NPs are introduced as an intercalator, the interlayer spacing becomes larger and the peak shifts to $\sim 720\text{ cm}^{-1}$ in the FMDE nanocomposite.

Fractal theory has been used to characterize the surface structure, characteristics and irregularities of solid materials, and was widely used to analyze the distribution of fillers in composite materials [38]. Fractal dimension D , as an important parameter of fractal theory, quantifies the space filling ability of the substance. The logarithm of the raw data $I(q)-q$ of SAXS gives the following relationship: $\ln(I(q))^{-\alpha} \approx \ln(q)$, (1)

where α is related to the fractal dimension D . If $\alpha < 3$, the substance exhibits mass fractal, and the mass fractal dimension D_m is α . $D_m \approx 0$ implies a loose mass distribution, while D_m approaching 3 indicates that the material distribution is compact and concentrated [39]. Fig. 3e is obtained by logarithmically transforming the original SAXS data (Fig. S5). It can be divided into two parts according to different fitting slopes, which are related to the mass fractal of ENR matrix and conductive filler. The left side of the blue dashed lines is assigned to the ENR matrix, which exhibits similar slope (2.44 of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ and 2.49 of FMDE), indicating a mass fractal with randomly oriented polymer chains [40]. For comparison, the slope of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ on the right side is closer to 3, which is higher than that of FMDE (2.95 of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ and 2.52 of FMDE). It can be attributed to the weaker interaction between $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes and the surface of ENR, which leads to comparatively uneven mass distribution of the filler in the matrix.

In order to further explore the interaction between the matrix and filler, the thickness of two-phase interface layer was fitted and calculated. The theory of SAXS to calculate the interface layer thickness is based on the difference of electron density in the two-phase transition region. And the interface properties can be determined according to Porod law [41,42]. If the two-phase interface in the system is not clear, Porod law can be modified as Equation (2):

$$I(q) = kq^{-3}\exp(\sigma q^2), \quad (2)$$

where k is Porod constant and σ is related to interface layer thickness. The original SAXS data is converted into $\ln(q^3 I(q))-q^2$, and the existence of an interface layer in the system can be determined by fitting the slope of the curve in the high scattering region. The diversity can be in-

tuitively observed in the $\ln(q^3 I(q))-q^2$ curves (Fig. 3f), where the fitting slope of FMDE is 0.376 and that of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ is close to 0 (0.002). This result indicates that sharp phase interface between the components exists in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ composite and there is a transitional electron density conversion at the two-phase interface of FMDE. Furthermore, the interfacial layer thickness can be quantitatively calculated based on the $\ln(q^3 I(q))-q^2$ curve according to Equation (3).

$$E = \sqrt{2\pi\lambda}, \quad (3)$$

where E is the interfacial layer thickness and λ is the fitting slope of $\ln(q^3 I(q))-q^2$ curve in the high scattering area. The calculated interface layer thickness of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ is only 0.11 nm, while the increase in that of FMDE is 1300%, up to 1.54 nm, which can be attributed to the metal ligand coordination/non-covalent supramolecular interaction between the FMDE matrix and filler resulting in excellent interfacial compatibility. These significant improved interfacial interactions have a potentially critical impact on the mechanical properties of elastomers.

Effect of interfacial supramolecular bonding on mechanical properties of FMDE nanocomposites

Desirable mechanical properties are essential to the practical application of flexible EMI shielding materials. Fig. 4a exhibits the stress-strain curves of FMDE with various $\text{Ti}_3\text{C}_2\text{T}_x$ contents. The mechanical strength of DENR is significantly improved with the introduction of $\text{Fe}_3\text{O}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes. The tensile strength of FMDE-5 (10.08 MPa, $\text{Ti}_3\text{C}_2\text{T}_x$ content of 5 wt%) is markedly enhanced by $\sim 1280\%$ compared with neat DENR (0.73 MPa), and FMDE-10 reaches the highest 14.15 MPa. Meanwhile, FMDE (Fig. 4b) shows high toughness of $\sim 45 \pm 15\text{ MJ m}^{-3}$, revealing great flexibility and resistance to brittle fracture. Note that the decline in tensile strength and toughness of FMDE-12.5 and FMDE-15 may be caused by the increased loading of rigid $\text{Fe}_3\text{O}_4/\text{Ti}_3\text{C}_2\text{T}_x$ fillers. Fig. 4c, d compare the mechanical properties of FMDE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ with various filler contents. The tensile strength and toughness of FMDE are significantly superior to $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ at the same $\text{Ti}_3\text{C}_2\text{T}_x$ content (the detailed tensile stress, strain and toughness of FMDE, $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ and DENR are shown in Table S1). For example, $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ -10 exhibits a low tensile strength of 3.48 MPa and a toughness of 10.63 MJ m^{-3} , while the corresponding values of FMDE-10 (14.15 MPa and 61.14 MJ m^{-3}) are $\sim 307\%$ and $\sim 475\%$ higher, respectively. The stress-strain curves of FMDE-10, $\text{Fe}_3\text{O}_4/\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ -10, $\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ -10 and $\text{Ti}_3\text{C}_2\text{T}_x/$

Figure 4 (a, c) Stress-strain curves of FMDE, $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ nanocomposites, pure ENR and their comparison. (b, d) Mechanical properties of FMDE, $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ nanocomposites, pure ENR and their comparison. (e) Comparison of tensile stress of FMDE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ with previously reported results in the literature. The detailed data are listed in Table S2 in the Supplementary information. (f) LSCM image of the network structure in FMDE nanocomposite with a 100% stretched state. (g) Schematic representation of the stretch and fracture mechanism of FMDE nanocomposites. (h) Digital photograph of FMDE-10 lifting up a weight of 500 g. The inset images show the dimensions of the strip before and after stretching.

ENR-10 are shown in Fig. S6. The tensile stress of FMDE-10 is significantly higher than that of $\text{Fe}_3\text{O}_4@/\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ -10 (6.31 MPa) and $\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ -10 (6.92 MPa), indicating that the interfacial supramolecular metal-ligand coordination/hydrogen bonding interactions play a vital role in improving the mechanical properties of FMDE. Fig. 4e and Table S2 compare the mechanical properties of FMDE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ with some previously reported ENR-based composite elastomers. The tensile strength and strain of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ are comparable to that of most ENR-based composite elastomers, while FMDE exhibits much superior performance. The FMDE nanocomposite was stretched 100% under LSCM to observe the structural changes during the stretching

process (Fig. 4f). Original intertwined network was deformed under uniaxial tension, resulting in alignment (green part). The SEM images of the tensile fracture (Fig. S7) reveal obvious 3D concave-convex layered structure, and the extended 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are clearly visible. These results demonstrate that the enhanced mechanical properties of FMDE are derived from the supramolecular metal-ligand coordination/hydrogen bonding network, constructed by a large number of interface interactions between the elastomer matrix and 2D $\text{Fe}_3\text{O}_4@/\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes, significantly enhancing the load resistance of FMDE to failure and energy dissipation (Fig. 4g for tensile fracture schematic). To visually demonstrate the desirable mechanical properties of FMDE,

Figure 5 (a) Magnetic hysteresis loops of the $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ nanocomposites. The inset images show an enlarged view of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ (i) and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ (ii). (b) Digital photos visually exhibit the response behaviors of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ to permanent magnet.

it could easily lift up a weight of 500 g (Fig. 4h).

Magnetic properties of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ nanocomposites

Magnetic properties of the synthesized $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and FMDE nanocomposites were investigated at room temperature with a vibrating sample magnetometer, as shown in Fig. 5a. All hysteresis loops are S-shaped, with negligible remnant magnetization (M_r , ~ 0.9 – 1.1 emu g⁻¹ for $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and ~ 0.45 – 0.6 emu g⁻¹ for FMDE) and coercivity (H_c , ~ 18 Oe for $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and ~ 30 Oe for FMDE), indicating a superparamagnetic behavior. The saturation magnetization (M_s) of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ and FMDE are 10 and 4 emu g⁻¹, respectively, which are lower than the previously reported M_s of Fe_3O_4 NPs [43,44]. The reduced value might be ascribed to the presence of magnetically inactive $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes. Besides, $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes effectively prevented the aggregation of Fe_3O_4 NPs as a template (M_s depends on the content of magnetic NPs per unit volume). Digital images (Fig. 5b) visually exhibit that $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes and FMDE can be attracted by a magnet. The introduction of magnetic dipoles plays a vital role in design and fabrication of high-performance EMI shielding materials. In addition, Fe_3O_4 NPs with outstanding magnetic response performance and excellent photothermal conversion ability can endow the nanocomposites with magnetically driven response and high absorption of near infrared light [45,46]. Therefore, the flexible conductive and magnetic FMDE elastomers are expected to have potential applications in magnetic-response actuators,

automatic control and photothermal therapy.

EMI shielding efficiencies of $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2\text{T}_x/\text{DENR}$ nanocomposites

EMI shielding performance of the FMDE composites were investigated in the X-band (8.2–12.4 GHz), as shown in Fig. 6a. The EMI shielding effectiveness (EMI SE) of all samples exhibit weak frequency dependence in the measured frequency band. FMDE-5 has an EMI SE of ~ 23 dB, which reaches the requirements of most industrial applications. While FMDE-15 achieves superb EMI shielding performance of >50 dB and maximum 58 dB over the entire X-band. Fig. 6b compares the EMI shielding performances of FMDE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$. It can be seen that the EMI SE of FMDE elastomer is higher than that of $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ composite with the same $\text{Ti}_3\text{C}_2\text{T}_x$ content. For example, the EMI SE of FMDE-15 is $\sim 35\%$ better than $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ -15 (~ 43 dB). Thickness plays a crucial role in the EMI shielding performance. Fig. 6c investigates the EMI SE of FMDE-15 with various thicknesses. Average EMI-SE of less than 10 dB is achieved with the thickness of 0.102 mm. As the thickness ranges from 0.571 to 1.197 mm, the EMI SE increases rapidly from 29 to 58 dB, attributed to the increase in conductive filler and a more complete conductive segregated network.

Generally, reflection, absorption, and transmission can be observed when incident microwaves pass through the shielding material. In order to further explore the EMI shielding mechanism in FMDE, reflection (SE_R) and absorption (SE_A) effectiveness of FMDE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$

Figure 6 Characterization of EMI shielding effectiveness. (a) Plots of EMI SE versus frequency for FMDE with different Ti₃C₂T_x contents (thickness ~1.2 mm). (b) Comparison of EMI SE of FMDE and Ti₃C₂T_x/ENR with different Ti₃C₂T_x contents (thickness ~1.2 mm). (c) EMI SE in the X-band of FMDE-15 at various thicknesses. (d, e) Shielding by reflection, absorption, and total shielding of FMDE and Ti₃C₂T_x/ENR nanocomposites. (f) EMI SE of FMDE-10 elastomer under cyclic 140° bending and 30% stretching. The illustration shows the resistance change during the bending and stretching cycles. (g) Schematic representation of shielding mechanism for FMDE with 3D segregated network. (h) Comparison of EMI SE of FMDE (red stars) with currently reported results in the literature. The detailed data are listed in Table S3 in the Supplementary information.

were calculated based on the measured scattering parameters S_{11} and S_{21} , as shown in Fig. 6d, e. The histogram shows that the contribution from SE_A is far greater than SE_R in the overall shielding efficiency (SE_{Total}). For example, the SE_{Total} , SE_A and SE_R of FMDE-10 are 31.18, 25.72 and 5.46 dB, respectively. Whereas the corresponding values are 43.99, 38.18 and 5.81 dB for the

nanocomposite with 12.5 wt% of Ti₃C₂T_x, confirming that FMDE nanocomposites follow an absorption-dominant shielding mechanism. Incident electromagnetic wave energy is mainly absorbed and dissipated as heat through the hierarchical network instead of reflecting back, which reduce the secondary pollution of reflected waves. The conductivity measurement data (Fig. S8) shows that

FMDE presents lower conductivity than $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$, which could be attributed to the fact that the Fe_3O_4 NPs anchored on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ prevent the close contact of conductive nanoflakes. In contrast, FMDE exhibits significantly higher EMI SE. One of the possible reasons for the improved EMI SE is that the addition of magnetic Fe_3O_4 NPs balanced electromagnetic parameters, enhancing impedance matching and reducing reflections [47,48]. Besides, incident electromagnetic wave attenuation caused by dielectric loss and magnetic loss is another important factor (as shown in schematic illustration of Fig. 6g). For non-magnetic $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$, the electromagnetic wave absorption is mainly contributed by conductivity and dielectric loss caused by the polarization of abundant surface functional groups ($-\text{O}-$, $-\text{F}$) [49]. The uniform growth of Fe_3O_4 NPs on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes effectively avoids the magnetic aggregation and increases the coupling effect between neighboring Fe_3O_4 NPs to enhance magnetic loss ability [20]. Magnetic NPs and $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes form a large number of “micro-resistor-capacitor circuit” models owing to the difference in conductivity, which further magnifies the interface polarization and dielectric loss capabilities under an alternating electromagnetic field [50]. Multiple internal reflection is another important electromagnetic wave absorption mechanism. Based on the 3D conductive segregated network structure and intercalation of Fe_3O_4 between $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, the expanded layer spacing generates plentiful interfaces and surfaces to reflect incident electromagnetic waves within the elastomer. The increased propagation paths and extra electromagnetic energy dissipation improve the EMI shielding performance [51].

Long-term performance reliability under complex deformations is a critical concern for flexible and wearable EMI shielding devices. Fig. 6f and Fig. S9 evaluate the EMI performance of FMDE with cyclic deformation. The EMI SE of FMDE-10 slightly decreases with stretching by 30% (from 35 to 30 dB). After 1000 simultaneous 140° bending and 30% stretching cycles, the conductivity of FMDE-10 exhibits a small resistance change of 10.5% and FMDE-10 still retains approximately 85.7% of EMI SE, exhibiting excellent EMI shielding reliability. It can be attributed to the improved supramolecular interfacial interactions constructed by metal-ligand coordination crosslinking between Fe_3O_4 NPs and DOPAC ligand molecules. The main part of EMI SE reduction is SE_A (Fig. S10), which may be the result of attenuation of the conductivity and reduction in thickness during stretching [52,53]. Fig. 6h and Table S3 summarize some of pre-

viously reported nanocomposites based on conductive carbon materials (graphene and carbon nanotubes) or $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. It can be seen that the FMDE elastomers exhibit excellent EMI shielding performance with low filler content and thickness.

CONCLUSIONS

Flexible and stretchable FMDE elastomer with 3D segregated conductive network structure was fabricated by self-assembly of $\text{Fe}_3\text{O}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes and DOPAC-modified ENR latex. The introduction of Fe_3O_4 NPs can not only effectively facilitate the magnetic attenuation and loss of incident electromagnetic waves, but also provide central ions for constructing metal-ligand coordination within FMDE. Grafting DOPAC onto the surface of ENR latex as ligand molecule constructs supramolecular metal-ligand coordination/non-covalent crosslinking with $\text{Fe}_3\text{O}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nanofillers, which significantly improves the interface interactions between the components and therefore enhances the mechanical properties of FMDE. An outstanding tensile strength of above 14.15 MPa was achieved for FMDE-10, which was 1838% and 306% higher than that of pure DENR and $\text{Ti}_3\text{C}_2\text{T}_x/\text{ENR}$ -10, respectively. Moreover, according to the excluded volume effect of rubber latex, $\text{Fe}_3\text{O}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes were selectively squeezed toward the interstitial space of ENR latex microspheres, resulting 3D segregated conductive network. The elaborately designed structure of FMDE and the addition of magnetic Fe_3O_4 NPs significantly improved the EMI shielding performance of FMDE. FMDE-15 achieved superb EMI shielding performance of >50 dB and maximum 58 dB over the entire X-band. In addition, the improved supramolecular interfacial crosslinking of FMDE led to outstanding EMI shielding stability against repeated deformation. This strategy provides a valuable guidance for the preparation and application of high-performance flexible EMI shielding materials.

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Author contributions Lu C and Zhou Z were responsible for the experimental concept and design; Song Q and Chen B carried out most of the experiments, characterization and data analyses. Song Q wrote the paper with support from Lu C and Zhou Z. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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界面超分子交联提高柔性、可拉伸和磁性 Fe_3O_4 @ $\text{Ti}_3\text{C}_2\text{T}_x$ /弹性体的机械和电磁屏蔽性能

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摘要 电磁干扰和辐射无处不在, 可能对电子设备的正常运行和人体健康造成危害。MXene具有出色的金属导电性和可调的表面化学, 在屏蔽材料的制备中极具吸引力。本文通过结构设计和界面调控, 制备了具有隔离网络结构的柔性 Fe_3O_4 @ $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/3,4-二羟基苯基乙酸(DOPAC)-环氧化天然橡胶(ENR)弹性体(FMDE)。 Fe_3O_4 与DOPAC配体分子之间的金属-配体配位交联提供了强大的界面相互作用, 从而显著增强复合材料的机械性能。与 $\text{Ti}_3\text{C}_2\text{T}_x$ /ENR弹性体相比, FMDE的最大拉伸强度和韧性分别提高了~306%和~475%。此外, 借助ENR胶乳的体积排斥效应构建的3D隔离导电网络, 以及引入的磁性 Fe_3O_4 纳米颗粒有效地改善了FMDE的电磁屏蔽性能, 且证实了FMDE在反复弯曲拉伸后仍具有稳定的电磁屏蔽能力。