In-situ Growth of MAX Phase Coatings on Ecological Carbon and their Terahertz Shielding Properties Investigations

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Research Article

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Abstract

Electromagnetic interference (EMI) shielding materials have received great interests in recent years. The EMI shielding effectiveness (SE) of materials not only depends on their composition, but also is influenced by their microstructures. Among various microstructure prototypes, porous structure has special advantage of low density and high electromagnetic wave reflections ability. Herein, a MAX@CW composite ($\text{Ti}_2\text{AlC@CW}$, $\text{V}_2\text{AlC@CW}$, $\text{Cr}_2\text{AlC@CW}$) with porous structure is fabricated through a molten salt method by using carbonized wood (CW) as template. The MAX@CW forms conductive network constructions and rich interface that can further improve the EMI shielding effectiveness. The average EMI shielding effectiveness of the three kinds of MAX@CW with the thickness of 1 mm are higher than 45 dB in the frequency range of 0.6 ~ 1.6 THz. Among them, $\text{V}_2\text{AlC@CW}$ show the best EMI shielding effectiveness with the average value of 55 dB.

1. Introduction

Owing to the rapid development of terahertz (THz) technology, especially the designation of terahertz band as the next generation (6G) communication band, THz shielding materials are urgently demanded for avoiding malfunction in electronic devices stemming from signal crosstalk and protecting people from electromagnetic pollution. Moreover, it is preferable to develop lightweight and environment-friendly THz shielding materials^[1–4]. In general, the effectiveness of THz shielding materials is highly related to their microstructure^[5, 6]. For instance, structures with specific interface contacts (e.g. core-shell structure, sandwich-like structure and porous foam structure) could induce interfacial polarization to dissipate electromagnetic waves, and thus improve electromagnetic shielding effectiveness^[7–11]. Among them, materials with porous structures show the merits of large specific surface area, lightweight and high strength to weight ratio, making them attract great attentions.

As one kind of the porous materials, the carbonized wood (CW) obtained through high-temperature carbonization of natural wood, has been widely studied due to their characteristics of light weight, multistage pore structure and anisotropy^[12–16]. The natural 3D porous conductive network makes it as a promising candidate for high-effectiveness electromagnetic interference (EMI) shielding materials^[17–20]. However, the single shielding mechanism of CW limits its applicable potential in EMI shielding fields. Employing the natural skeleton shape of CW as a template, integrated with other types of conductive materials, to obtain functional composite structural materials is treated as a feasible tactic to improve the EMI shielding effectiveness(SE) of CW^[21].

Based on above considerations, we employ CW as the template to design a wood-based conductive composite with three-dimensional porous structure as a THz shielding material. MAX phases are a family of layered ternary transition metal carbides/nitrides, which combines the good attributes of ceramics and metals, such as superior oxidation and corrosion resistance, eminent electrical/thermal conductivity, and high dielectric loss. With these virtue, MAX phases are proposed to be ideal candidates as EMI shielding

materials for harsh environment applications^[22–24]. Herein, a MAX@CW composite ($\text{Ti}_2\text{AlC@CW}$, $\text{V}_2\text{AlC@CW}$, $\text{Cr}_2\text{AlC@CW}$) with porous structure is fabricated through in-situ growth MAX phase coating on the CW in a molten salt bath. The MAX@CW retains the characteristics of porous structure and anisotropy from carbonized wood template. Meanwhile, the carbonized wood template guides the directional assembly of the MAX phase by making it filling into the porous structure of the CW, showing a multi-interfaces. The MAX@CW with the specific structure is supposed to manifold the electromagnetic dissipation paths of electromagnetic wave within the porous network structure, which greatly increased transmission loss and improved its EMI SE. As a result, the MAX@CW should much enhanced SE than the CW and show great potential as a high-effectiveness EMI shielding material.

2. Experimental Procedures

2.1 The synthesis of CW

Firstly, the natural linden is cut into pieces and put them into an alumina crucible. And then the high-temperature carbonization is carried out at 1000 °C for 6 h in argon atmosphere. After that, the carbonized wood slices are carefully polished with 1000 mesh sand-tray to obtain ones with thickness of 1 mm. Subsequently, the residual carbon is removed by ultrasonic washing with deionized water and ethanol for many times. The final CW samples can be obtained after drying in an ordinary oven.

2.2 Synthesis of MAX@CW

The MAX@CW (The MAX phases in use include Ti_2AlC , V_2AlC , Cr_2AlC) are prepared by molten salt method. The CW is used both as template and carbon source. The M-site metal powder (i.e. Ti, V and Cr) and A-site metal powder (Al) with both of their particle size of $\sim 1\ \mu\text{m}$ are used as the raw materials to synthesize the target MAX@CW. In addition, the analytical grade NaCl/KCl are selected for the molten salt bath, purchased from Shanghai Aladdin Industrial Co., Ltd.

The in-situ preparation of MAX@CW is carried out on porous carbonized wood matrix within the salt bath. The steps are as follow: firstly, the raw material powders are mixed evenly, aiming to cover the CW completely; then, the MAX@CW is prepared from high-temperature sintering in argon atmosphere, where the sintering temperature for $\text{Ti}_2\text{AlC@CW}$ and $\text{V}_2\text{AlC@CW}$ are 1000 °C (holding for 6 h), and of $\text{Cr}_2\text{AlC@CW}$ is 900 °C; after that, the product is washed for many times with deionized water to remove the salt under the room temperature. The final MAX@CW is obtained after drying.

2.3 Characterization

The derived sample is analyzed by Bruker D8 Discovery X-ray diffractometer (XRD, irradiated by Cu K α ($\lambda = 1.5406\ \text{\AA}$), accelerated voltage 40 kV, filament current 40 mA, and the 2θ range of $10 \sim 70^\circ$ again with a step size of 0.02° . The structure and vibration characteristics of CW and MAX@CW are analyzed by confocal Raman microscope (Renishaw Invia Reflex) with the excitation wavelength of 532 nm. A scanning electron microscope (SEM, Quanta FEG 250, FEI) is performed to characterize the morphology

and microstructure of the CW and MAX@CW. The electrical conductivity of the material is measured by a four-probe detector (cresbox, Napson). The Terahertz time-domain spectroscopy (THz-TDS) test is carried out under the conditions of room temperature 22 °C and humidity of 5% (French i2S group company, model of TZCAM). The total spectral range is 0.2-3.0 THz (effective spectrum range: 0.3–1.65 THz); the repetition frequency is 1 kHz; and the size of the sample tested is 2×3 cm with thickness of 1 mm.

3. Results And Discussion

3.1 Materials Characterization

The composition of CW and MAX@CW is confirmed by XRD and Raman spectra. As shown in Fig. 1A, the CW has two wide diffraction peaks at about 23° and 44°, which means that the CW obtained is amorphous^[25]. For the MAX@CW samples, the peaks of CW disappear and the diffraction peaks of Ti₂AlC, V₂AlC and Cr₂AlC appear, indicating the formation of corresponding MAX phase coatings. The Raman spectra are more sensitive to the surface change of materials and thus are employed to detect the formation of CW and MAX@CW. As shown in Fig. 2B, the CW has two strong characteristic peaks near 1350 cm⁻¹ and 1600 cm⁻¹, which represent the D peak and G peak of carbon^[26]. For the Ti₂AlC@CW sample, the peaks at 260–270 and 360 cm⁻¹ correspond to the ω_2 , ω_3 and ω_4 vibration mode of Ti₂AlC is observed, indicating the formation of Ti₂AlC. For the V₂AlC@CW and Cr₂AlC@CW samples, the characteristic peaks of V₂AlC and Cr₂AlC were also detected, which confirms their composition^[27, 28].

The schematic of the fabrication process of MAX@CW composites is shown in Fig. 2A. The synthesis route consists of two steps. The first step is preparing CW with porous structure by carbonizing natural linden wood at high temperature. The following step is in-situ growing of MAX phase coatings on CW template by high-temperature molten salt reaction. The metallic elements existing as ionic form in the molten salt media can infiltrate into the pores of carbonized wood and react with carbon matrix to form MAX phase, which is driven by the pressure difference between inside and outside of the pores of carbonized wood (i.e. the capillary effect)^[29, 30].

The optical photo of the product is shown in Fig. 2B, we can see that the color of CW is black, while MAX@CW has metallic luster, indicating that MAX phase coating is successfully prepared on the carbonized wood substrate. As shown in Fig. 2C-F, the CW has a rich pore structure, this is because that linden is a kind of natural organic polymer compounds, mainly composed of cellulose, hemicellulose and lignin. These substances will further decomposed and evaporated during the process of high temperature carbonization, leaving honeycomb pore structures of different length-scales from nanometer to micron. The pore shapes of CW are mainly oval with large pores of 30 ~ 60 μm and small pores of 10 ~ 15 μm . In addition, as shown in Fig. 2E-F, the channels of CW are long and straight, which is favorable for the impregnation and infiltration of MAX phase coating. Since the microstructure of Ti₂AlC@CW, V₂AlC@CW and Cr₂AlC@CW is similar, we choose Ti₂AlC@CW as the representative to show their microstructure. As shown in Fig. 2G-J, owing to the atomic-level reaction in the molten salt, Ti₂AlC@CW inherits the natural

porous structure of CW, without morphological distortion and pore blockage. In addition, through Fig. 2G-H, we can see that the surface of MAX@CW samples is different from that of smooth carbonized wood substrate. The MAX@CW with this porous structure has a large number of surfaces and interfaces, which can increase the transmission path of incident electromagnetic waves and result in multiple scattering and increasing the attenuation of electromagnetic waves.

3.2 EMI shielding performance

The electromagnetic interference shielding effectiveness (EMI SE) of CW and three kinds of MAX@CW ($\text{Ti}_2\text{AlC@CW}$, $\text{Cr}_2\text{AlC@CW}$, $\text{V}_2\text{AlC@CW}$) are shown in Fig. 3. With the thickness of 1 mm, the average EMI SE in the frequency range of 0.6 ~ 1.6 THz of all the three kinds of MAX@CW is higher than 45 dB, which have been improved comparing to the CW (~ 42 dB). Among them, $\text{V}_2\text{AlC@CW}$ show the highest EMI shielding effectiveness with the average value of ~ 55 dB. Notably, as shown in Fig. 3B-3C, the dominant shielding mechanism of CW is EMW absorption with the average absorption coefficient of 79%, while that value of $\text{Ti}_2\text{AlC@CW}$, $\text{Cr}_2\text{AlC@CW}$, $\text{V}_2\text{AlC@CW}$ is 36%, 42%, and 23%. On the contrary, $\text{Ti}_2\text{AlC@CW}$, $\text{Cr}_2\text{AlC@CW}$, $\text{V}_2\text{AlC@CW}$ show high reflection coefficient of 64%, 58%, and 77%.

The shielding mechanism change is caused by to the structure evolution from CW to MAX@CW. For the CW, the highly porous structure allows electromagnetic waves to easily enter into the low reflection wood channel and be attenuated multi-reflection inner the structure^[18]. While when the MAX phase coating is fabricated on the CW channel, the pore size is reduced that decreased the ratio of incident electromagnetic waves. Another important reason is the impedance matching property is changed after the MAX phases coating fabrication. Owing to the porous structure and relatively low dielectric constant, CW has better impedance matching property with the free space than the MAX@CW, which allows more electromagnetic waves entering into the channel, and enhanced the ration of higher EMW absorption. In contrast, MAX phase with high dielectric constant greatly increased the impedance mismatching between the free space and MAX@CW, which result in more incident electromagnetic waves being reflected at the surface^[24, 31].

In order to further understand the EMI shielding mechanism of the MAX@CW, the electrical conductivities of the materials were measured. As shown in in Fig. 3D, $\text{V}_2\text{AlC@CW}$ shows the highest electrical conductivity among the three kinds of MAX@CW. As we know, the increased conductivity can result in higher impedance mismatch between the free space and MAX@CW interface, which can contribute to higher reflection loss and increase its EMI shielding effectiveness^[32]. In addition, when the electromagnetic wave enters the body of the material, the higher conductivity will lead to a larger eddy current and converts EMW energy into Joule heat, which can improve the electromagnetic wave absorption loss^[33]. Therefore, the MAX@CW show enhanced EMI shielding effectiveness than the CW, and $\text{V}_2\text{AlC@CW}$ shows the best shielding effectiveness.

4. Conclusions

In conclusion, MAX@CW composites were prepared on carbonized wood templates by the in-situ reaction in molten salt bath. The as-obtained MAX@CW composites inherit the specific microstructure of carbonized wood template, showing a three-dimensional interpenetrating pore structure and high available specific surface areas. The MAX@CW with porous structure forms continuous conductive network structure, which can increase the transmission paths for incident electromagnetic waves, achieving multiple reflections and increasing the attenuation of electromagnetic waves. Therefore, MAX@CW show excellent electromagnetic shielding performance in THz band. Within the frequency range of 0.6–1.6 THz, the total electromagnetic shielding effectiveness of the three kinds of MAX@CW are higher than 45 dB, and the V₂AlC@CW has the highest EMI SE that higher than 55 dB. The results indicate the large potential of developing functional materials by using natural biological structure as templates.

Declarations

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Figures

Figure 1

XRD patterns (A) and Raman spectra (B) of CW and MAX@CW

Figure 2

Schematic illustration of the fabrication process and macro- and microstructure of sample. (A) Schematic illustration of the fabrication process, (B) Optical photos of nature, CW and MAX@CW, (C-F) SEM image of bare CW, (G-J) SEM image of Ti₂AlC@CW.

Figure 3

The EMI SE and conductivity of CW and MAX@CW with thickness of 1 mm in perpendicular channel direction. (A) Total EMI SE of CW and MAX@CW, (B) Reflection of CW and MAX@CW, (C) Absorption of CW and MAX@CW, (D) Conductivity of CW and MAX@CW.