Recent progress in microwave absorption of nanomaterials: composition modulation, structural design, and their practical applications

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Abstract: The increasing electromagnetic (EM) radiation arise from the vast usage of EM techniques in civilian and military fields has spawned extensive concerns on scientific research with respect to EM wave absorbers. Nanomaterials, as a new type of nano-absorbing agent, have been investigated in detail over the recent years. This review article aims at elaborating the influence of component regulation and structural design on microwave absorption (MA) performance. Combined with the experimental efforts towards the development of nano-absorbers, the relevant absorption mechanisms are also discussed. In addition, from a prospective point, only focus on the exploration of absorbent itself is not enough, but also need matrix material to support. Based on this circumstance, the study summarises various kinds of polymer-based nanocomposites used as excellent absorbers for practical MA applications.

1 Introduction

Electromagnetic (EM) pollution has been assigned as a novel kind of pollution in current society due to the massive usage of electronic equipment and communication technologies in commercial, civil, and military fields [1–3]. The excessive EM waves not only generate electromagnetic interference between various electronic instruments and communication facilities, but also are very harmful to human health [4, 5]. In order to reduce EM radiation hazard, an effective way is to make use of the absorbing material. High-performance microwave absorbing material is extensively in demand to eliminate incident EM waves and convert EM energy into thermal energy through dielectric loss or magnetic loss resulting from efficient complementarities between the relative permittivity and permeability [6, 7]. An ‘ideal’ EM wave absorber should exhibit tiny thickness, light weight, wide absorption frequency range, and strong EM wave absorption characteristics simultaneously [8–10].

At present, the species of wave absorbing material is varied. Qin and Brossseau [11] have summarised the microwave absorption (MA) of polymer composites filled with carbonaceous particles. Watts et al. [12] have reviewed the EM wave absorption of metamaterials. Moreover, the EM applications of hexagonal ferrites, magnetic metallic particles, nanomaterials, conductive fibres, and metamaterials have been summarised by Kong et al. [13]. In addition, Yin et al. [14] have reviewed the EM properties of Si–C–N-based ceramics and composites. Recently, Pawar et al. [15] have concluded the development of high-frequency millimetre wave absorbers derived from polymeric nanocomposites. Furthermore, Quan et al. [16] have systematically investigated the dielectric polarisation and related polarisation relaxation in EM wave absorption of dielectric materials. By comparison, it is found that each material has its own advantages and disadvantages. To solve the shortcomings of traditional absorbing materials, such as large density, narrow absorption band, and single-frequency absorption, the development of new type of absorbing materials has become the main current research direction [17]. Nowadays, as a new type of modern wave absorbing materials, the nanomaterials have obtained extensive attention because of their low density, distinct size effect, and special nanostructure [18]. In this regard, an in-depth and systematical research of nano-absorbers has become quite necessary.
2 Component effect

Intensive research demonstrate that the composition has significant effect on the EM wave absorption performance of nanomaterials. Depending on the different components, nanomaterials can be divided into conductive, dielectric, and magnetic types. The corresponding absorption mechanism is conductance loss, dielectric loss, and magnetic loss, respectively. For nanoconductive materials applied in wave absorption area, considerable research has been devoted to various carbon materials, such as carbon black [31], carbon nanotubes [32], carbon fibres [33], graphene [34] and so on. Besides, in recent studies, many researchers have introduced conductive polymers [like polypyrrole [35], poly(aniline [36], polythiophene [37], poly(3,4-ethylenedioxythiophene) [38] etc.] into nanomaterials. However, single conductive materials are not suitable for MA study due to good electrical conductivity makes the EM wave arise total reflection. Thus, to obtain efficient microwave absorbers, much effort has been devoted to conjugate the conductive materials with the dielectric or magnetic nanomaterials.

2.1 Dielectric nanomaterials

A dielectric material is an electrical insulator that can be polarised by an applied electric field. Quan et al. [16] even say that the dielectric materials are eternal jewels in the view of MA research due to their strong dissipation ability, low density, and high stability. The loss mechanism of such materials is mainly dielectric polarisation, including electronic polarisation, dipole polarisation, ionic polarisation, and interfacial polarisation. As is well known, the MA properties are assessed with the complexity permittivity and permeability values: the real part $\varepsilon'$ and $\mu'$ represent the storage capacity of electrical and magnetic energy, while the imaginary part $\varepsilon''$ and $\mu''$ are related to the dissipation (or loss) of electrical and magnetic energy [9]. Furthermore, their ratios, the dielectric and magnetic dissipation factors $tg\delta_{\varepsilon}=\varepsilon''/\varepsilon'$ and $tg\delta_{\mu}=\mu''/\mu'$ will provide a measure of how much power is lost in a material versus how much is stored [39]. With respect to dielectric nanomaterials, it is necessary to focus on the parameters of $\varepsilon'$ and $\varepsilon''$. On the basis of the Debye theory [40], $\varepsilon'$ and $\varepsilon''$ can be described as

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + (2\pi f\tau)^2}$$

(1)

where $f$, $\varepsilon_0$, $\varepsilon_{\infty}$, and $\tau$ are frequency, static permittivity, relative dielectric permittivity at the high-frequency limit, and polarisation relaxation time, respectively.

According to (1) and (2), the relationship between $\varepsilon'$ and $\varepsilon''$ can be described as

$$\left(\varepsilon' - \frac{\varepsilon_{\infty} + \varepsilon_0}{2}\right) + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon_0 - \varepsilon_{\infty}}{2}\right)^2$$

(3)

Thus, the plot of $\varepsilon'$ versus $\varepsilon''$ would be a single semicircle, generally denoted as the Cole–Cole semicircle [10]. Each semicircle corresponds to one Debye dipolar relaxation process. Debye dielectric polarisation take great part in the mechanism of EM wave absorption. The parameters of $\varepsilon'$ and $\varepsilon''$ have a close relationship with microwave absorbing properties of dielectric nanomaterials.

Until now, the dielectric nanomaterials are mainly focus on metal oxides/sulphides, ceramics, and carbon-based nanocomposites. For example, Xia et al. [41] have synthesised a novel microwave absorbing material called hydrogenated TiO$_2$ nanocrystals. It is proved that the hydrogenation would promote the growth of rutile–anatase interior–exterior structure which is beneficial to generate innovative collective-movement-of-interfacial dipole (CMID) and collective interfacial polarisation amplified microwave absorption (CIPAMA) mechanism. Except for anatase/rutile interface, another interfacial junction is caused by crystalline/disorder interfacial area of hydrogenated TiO$_2$ nanocrystals, as shown in Fig. 1a. Other metal oxides such as MoO$_3$ nanorods [44], MnO$_2$ microspindles [45], and ZnO nanocables [46] have also been studied widely. Compared to metal oxides, the metal sulphides usually possess higher conductivity which is conducive to enhanced MA performance. Ning et al. [42] have prepared few-layered MoS$_2$ nanosheets via the top-down exfoliation method from bulk MoS$_2$ and verified that its MA property can be comparable to those reported in carbon-related nanomaterials. The enhanced MA performance of MoS$_2$ nanosheets is attributed to the defect dipole polarisation arising from Mo and S vacancies and its higher specific surface area (Figs. 1b–e). Moreover, the CuS nanoflakes [47] and CdS nanoparticles (NPs) [48] have also exhibited satisfactory absorbing performance. In recent years, our group are mainly concentrated on MA property of transition metal oxides/sulphides like ZnO nanorods [49], 3D α-MnO$_2$ clusters [50], Co$_3$O$_4$ NPs [51], Ni$_3$S$_2$ microspheres [52], Cu$_2$S microspheres [53], Cu$_x$S hexagonal nanoplatelets [54], Bi$_2$S$_3$ nanorods [55], hierarchical Cu$_2$S/ZnS nanocomposites [56], 3D MoS$_2$ hierarchical nanospheres [57], PbS dendrite [58], and so on. Furthermore, to obtain good thermostable EM wave absorbers, ceramic nanomaterials have raised extensive concerns. Among them, SiC [59, 60] is an important candidate in EM wave absorbing application because it is a wide band gap semiconductor. In addition, Yang et al. [61] have studied the MA properties of ultrathin BaTiO$_3$ nanowires and BaTiO$_3$ nanotorus. It is found that the MA capability of the ultrathin BaTiO$_3$ nanowires is better than that of BaTiO$_3$ nanotorus. On the other hand, as a traditional EM wave absorber, the carbon materials exist in various forms. In order to acquire preferable dielectric microwave absorbers, many researchers have combined carbon materials with multifarious nanomaterials. There have been references on the MA capacity of multivalved carbon nanotubes decorated with Fe$_3$O$_4$ particles [62, 63]. Besides, as shown in Fig. 1f, Yan et al. [43] have arrayed SiC nanowires on the surface of carbon fibres and coated with conductive polymer polypyrrole (PPy) by a simple chemical polymerisation method. The results have indicated that the SiCnw-C/PPy nanocomposites exhibit superior EM absorption abilities. Recently, with the development of graphene, the reduced graphene oxide (RGO)-based nanocomposites have been utilised in MA field extensively, such as RGO/ZnO nanocrystals [64], RGO/CuS nanocomposites [65], graphene@Fe$_3$O$_4@$SiO$_2@$NiO
nanosheet [66], RGO/MoS₂ nanocomposites [67, 68], FeO₄/ graphene capsules [69], and so on. In order to further increase the dielectric loss, the common practice is to introduce conductive materials into nanomaterials because the conductivity is proportional to the imaginary permittivity, just as [70]

$$\varepsilon' = (\varepsilon_0 - \varepsilon_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2} + \frac{\sigma}{2\pi f \varepsilon_0}$$  

(4)

where \(\varepsilon_0\) and \(\varepsilon_\infty\) describe the dielectric constant in vacuum and the relative dielectric permittivity at high-frequency limit, respectively, \(\omega\) is the angular frequency, \(\tau\) the relaxation time, and \(f\) represents frequency. From this equation, a larger electrical conductivity leads to increased dielectric loss. On account of this, to further improve dielectric loss, a common method is to combine conductive polymer or metal with nanomaterials, such as PANI@MoO₃ [44], PPy@PANI [71], Fe₃O₄-PEDOT nanospheres [72], Al-doped SiC whiskers [70], and so on. Fig. 2 indicates that the reflection values of PPy@PANI composites are closely related with shell thickness. The coated conductive PANI shell will increase the complex permittivity and create interfacial polarisation to improve the MA performance.

2.2 Magnetic nanomaterials

In addition to dielectric loss, the magnetic loss existed in magnetic materials is another important wave absorption mechanism. On the basis of van der Zaan's research achievement [73], the magnetic dissipation mainly contains eddy current loss, hysteresis loss, residual loss, intragranular domain wall loss, and ferromagnetic resonance loss. In weak magnetic fields, hysteresis losses are negligible and domain wall losses typically occur at megahertz frequencies. The eddy current loss is related to the diameter of the NP (\(d\)) and electric conductivity (\(\sigma\)), which can be expressed by the equation as follows [74]:

$$\mu'' \approx 2\pi \mu_s (\mu''') \sigma d f / 13$$  

(5)

where \(\mu_s\) is the permeability of vacuum. According to the skin-effect criterion, if the magnetic loss only originates from the eddy current loss, the values of \(\mu''(\mu''')^{-3/2}\) would remain constant with changing \(f\). Except for the eddy current loss, the other mechanism for magnetic loss can be ascribed to the enhancement of anisotropic energy (\(H_a\)), which can be expressed in the following equation [75]

$$H_a = 4K |J|^3 \mu_s M_s$$  

(6)

where \(|J|\) is the anisotropic coefficient and \(M_s\) the saturation magnetisation.

It is well known that only dielectric loss for non-magnetic materials tends to form a weak EM impedance matching. The addition of magnetic materials helps to improve the magnetic permeability (\(\mu'\) and \(\mu''\)) which is beneficial to form impedance matching to achieve a low reflection [57, 76]. To date, the magnetic nanomaterials are in various types among wave absorption research, especially for many kinds of ferrites, including Fe₃O₄ [77, 78], MnFe₂O₄ [79, 80], CoFe₂O₄ [81, 82], Ni–Fe alloys [83] etc. For instance, Zhu et al. [84] have investigated the EM and microwave absorbing properties of nickel ferrite nanocrystals for the first time. By analysing the dynamic complex permittivity and permeability of the as-made nanocrystals in the frequency range of 2.0–18.0 GHz, it is found that the nanocrystals exhibit excellent microwave properties in the X-band (8.5–12.0 GHz) frequencies. However, the enhancement of MA performance by a single magnetic nanomaterial is limited. To change this, most current research has combined dielectric materials with magnetic materials, using dielectric–magnetic matching effect and the synergy between different materials to improve the wave absorption performance. For example, Liu et al. [85] fabricated multifunctional composite microspheres with spinel Fe₃O₄ cores and anatase TiO₂ shells (Fe₃O₄@TiO₂) by combining a solvothermal reaction and calcination process (Fig. 3). The MA properties of these microspheres with different core sizes and shell thicknesses are investigated systematically. The EM data demonstrate that Fe₃O₄@TiO₂ microspheres with thicker TiO₂ shells exhibit significantly enhanced MA properties compared to those with thinner TiO₂ shells, which may result from effective complementarities between dielectric loss and magnetic loss. Similarly, the elliptical Fe₃O₄/C core–shell nanorings (NRs) are synthesised via a one-pot hydrothermal route. It is found that the Fe₃O₄/C NRs reveal enhanced low-frequency MA performance due to improvements of permeability and impedance matching [86]. The synthetic process and absorbing mechanisms of Fe₃O₄/C core–shell NRs have been displayed in Figs. 3e and f. To further verify the dielectric–magnetic impedance matching effect, Liu et al. [87] present a facile continuous solvothermal/sol–gel/solvothermal/hydrothermal route for preparing a series of CoNi, CoNi@SiO₂ core–shell, CoNi@SiO₂@TiO₂ core–shell–shell, and CoNi@Air@TiO₂ yolk–shell microspheres. Combining magnetic CoNi cores for intrinsically contributing magnetic loss and SiO₂/TiO₂ shells for actively contributing dielectric polarisation loss can promote the impedance matching in terms of complex permittivity and permeability. In addition to magnetic–
dielectric synergistic effect, the magnetic hysteresis loss and eddy current loss are also important between microspheres. Fig. 4 shows the SEM, TEM images, and synthetic procedure of different samples.

3 Rational design on the nanostructure

To meet the demands of strengthening MA capability, just rely on the component effect to improve the absorbing performance is not enough, another effective way is to consider the nanomaterial itself. It is well known that except dielectric loss, magnetic loss, and impedance matching, MA performance of nanomaterials is very closely related to the special morphologies and nanostructures. From the material point of view, the nanomaterials have controllable morphology and structural diversification, so researchers can take advantage of the material itself to maximise the absorption of EM waves. Through the design and regulation of different morphology and structure, many researchers have found that the geometrical effect and structural effect could make incident EM waves generate multiple reflections, refraction, and scattering as much as possible to extend the transmission path. Furthermore, some particular structural features will tend to form more interface, attenuating the EM wave through the interface polarisation or interfacial impedance matching. Therefore, it is very valuable to investigate the relationship between the morphology/structure and EM wave absorption properties.

3.1 Morphological regulation

Up to now, many researchers have studied that some nanomaterials with special morphology (including flower-like [4, 88], nanoflake [47], nanochain [62, 89], hierarchical dendrite [90], and so on) often have excellent absorbing properties. As a matter of fact, the EM wave can be absorbed via the quarter-wavelength cancellation theory generated from the ‘geometrical effect’, which means that when the thickness of absorber satisfies the following equations

$$d = \frac{\lambda_m}{4} (l = 1, 3, 5\ldots)$$

In the above equation, $\lambda_m$ is the wavelength at certain frequency, $|\mu_r|$ and $|\varepsilon_r|$ are the moduli of $\mu_r$ and $\varepsilon_r$, respectively, and $\lambda$ is the wavelength in the free space. As displayed in Figs. 5a and c, the results indicate that the quarter-wavelength principle can account for the excellent MA performance of the yolk–shell Fe$_3$O$_4@$N-doped carbon nanochains. Furthermore, the maximum reflection loss (RL) values and effective absorption bands under different layer thicknesses are shown in Figs. 5b and d [91].

Among the prior research, Lv et al. [4] have synthesised porous 3D flower-like CoCoO nanocomposites which assembled by numerous ultrathin flakes. The results indicate that they present outstanding EM wave absorption properties with an optimal RL value of ~50 dB. It is found that the porous 3D flower morphology with a larger layer spacing between the flakes could lead to multi-scattering which is relatively favourable for EM wave absorption. To further illustrate the effectiveness of flower-like morphology, Li and co-workers [88] establish dependency of the tunable MA properties on the 3D geometric morphologies of CoO NPs. It can be supposed from their findings that various morphologies of self-assembling CoO NP might become an effective path to achieve high-performance MA materials. Compared to the spherical CoO NP and the octahedral CoO NP, the nano-flower CoO NP have highly enhanced MA capability because of nano-flower CoO NP with larger specific surface area can provide more active atoms at the material surface and more absorption dispersion regions as well as an enhanced interface dielectric loss caused by interface polarisation. All these results suggest that controlling the size and morphology of CoO NP is an effective way for MA enhancement. Furthermore, Liu et al. [92] study the MA capability of a series of Co$_3$O$_4$Ni$_2$ hierarchical structures with different surface morphologies, including flower-, urchin-, ball-, and chain-like morphologies, as shown in Fig. 6a. Besides, they also discuss the magnetic MA properties of CoNi flower-like hierarchical microstructures with different sizes. It can be supposed from their findings that different surface morphologies of magnetic hierarchical structures might become an effective path to achieve high-performance MA for EM shielding and stealth camouflage applications. Subsequently, this group [9] investigate the size-
dominant magnetic MA properties of CoNi flower-like hierarchical microstructures with different sizes of 0.6, 1.3, and 2.5 μm. The results have indicated that the 2.5 μm CoNi microflowers achieve the maximum RL value, while, on the other hand, the 0.6 μm flowers achieved a broader absorption bandwidth. It is proved that the strong absorption ability of the CoNi microflowers results from their hierarchical morphologies. To be specific, their large exposed surfaces lead to strong interfacial magnetic dipole interaction. Then, for each CoNi single microflower, there is an assembly tendency of surface nanoflakes with different density distributions to scatter or absorb the propagated microwave, resulting in repeated absorption and exhaustion. Besides, the propagated microwave might be multiply scattered in the space woven by nanoflakes as well, and hence, energy attenuation via the network of numerous overlapping nanoflakes gets enhanced, which has further resulted in larger MA intensities. In addition, Liu et al. [47] have designed construction of CuS nanoflakes vertically aligned on graphenene@CuS [47]; the microwave dissipated mechanism for the as-prepared PC samples, (c) EM wave attenuated mechanism, (d) Model of slit-shaped pores, (e) Model of cage-like pores [93]. Reproduced with permission from Liu et al. [92] Copyright 2015 The Royal Society of Chemistry, from Liu et al. [47] Copyright 2016 American Chemical Society, and from Huang et al. [93] Copyright 2014 American Chemical Society.

which gives rise to the specular reflection of the microwave in the plane. The specular reflection leads to less energy loss due to a decrease in the propagation paths of the microwave in the PC. Meanwhile, the presence of uniform cage-like pores in the PC is equivalent to the occurrence of cavities for microwave, implying that an appropriate space allows for the reflection and multi-reflections of microwave in the cavities. The multiple reflections should bring about more energy to be dissipated inside because they make a longer microwave travel in the PC.

3.2 Structural design

Based on the relationship between structure and performance, it is known that the absorption properties of a material are closely related to the structures of absorption. It has been reported that material with novel nanostructures such as core–shell [96], yolk–shell [97, 98], foamed [99], hollow [100], porous [101] etc. exhibit noticeably enhanced microwave adsorption performance. These structures cannot only make incident microwave generate multiple reflections, refraction, and scattering to dissipate EM energy via prolonging transmission path, but also come out space charge polarisation and interfacial polarisation to accelerate the dielectric loss. On the other hand, as is known, when EM radiation is incident on a material, the incident microwave is divided into two parts: the reflected microwave and the absorbed microwave. Some peculiar nanostructures tend the phase of the reflected microwave and the absorbed microwave to be contrary. When the frequency of reflected microwave is the same as that of absorbed microwave, the interference phenomenon will be generated. If the two-wave interference occurs, the destructive amplitude phenomenon will happen after the wave path difference between them is an odd multiple of half wavelengths, just as [102]

\[
\Delta = 2d = (2n + 1)\frac{\lambda}{4}
\]

that is

\[
d = (2n + 1)\frac{\lambda}{8}
\]

To obtain a novel microwave absorber, Qiang et al. [103] fabricate uniform yolk–shell Cu/C microspheres through a 'coating–etching' route. The results indicate that they exhibit excellent RL characteristics and possess ultra-wide response bandwidth. By analysing their EM parameters, it is revealed that the yolk-shell structure is favourable for the matching of characteristic impedance, and more importantly, desirable dielectric loss ability can be achieved at matched characteristic impedance. On the other hand, the multiple reflections between cores and shells are responsible for the improved dielectric loss. Furthermore, in order to elucidate the contribution of distinctive structure to the MA performance, Zhou et al. [100] investigate the EM wave absorption property of lightweight hollow carbon nanospheres (HCNs) with tunable sizes. It is found that compared to the counterpart solid carbon particle, HCNs all achieve substantially enhanced MA ability probably due to the good impedance matching, along with the multiple reflection and scattering originated from the hollow structure with the optimum sizes. In addition, hollow lightweight polydopamine@α-MnO₂ microspindles with tunable absorption frequency governed by their aspect ratio also confirm the existence of multi-scatter from the nanosheet of the external interface and the cavity of the internal interface which will intensively influence the MA properties [45]. Important as it is for the practical application, a high-performance MA material with a broadband MA ability is highly demanded. Meanwhile, the MA material enjoying the advantage of low density and thin thickness will be much favoured. Based on this, Zhang et al. [1] have fabricated an ultralight and highly compressible graphene foam (GF) and found that they possess broadband and tunable high-performance MA due to the individual 3D conductive network of the graphene sheets (Figs. 7a–d). The results indicate that the GF under 90% compressive strain achieves
the absorption bandwidth (RL ≤−10 dB) as broad as 60.5 GHz, ~70% wider than that of the best available MA material in open literatures. As shown in Fig. 7e, the intricate reticulated structures response to the broadband incident microwave as tremendous resistance-inductance-capacitance coupled circuits and time-varying EM fields-induced currents occur on cell walls and struts of the GF. Such long-range induced currents quickly attenuate in the resistive network and convert into thermal energy, leading to rapid decay of massive incident EM wave. Subsequently, this group [99] prepare series of GFs with various chemical compositions and physical structures. Through analyses, they conclude the MA performance of the GF foam is strongly correlated to the C/O ratio, sp2 carbon domain size, and graphene framework microstructure. The mechanism for the MA performance depends on the balance between interfacial matching and loss characteristic.

Except for GF, Zhao et al. [104] have studied the MA properties of ordered honeycomb-like SnO2 foams with different configurations. The results reveal that these unique ordered honeycomb SnO2 foams are favourable for the enhancement of EM wave absorption performance. The main reasons are as follows: first, the pore structures can tune the complex permittivity and improve impedance match between air and absorber, which allow more microwaves pass through absorbing materials; second, as shown in Fig. 7f, the ordered SnO2 foams bring about multiple reflections and scattering of the incident microwaves when the absorber is irradiated by EM wave, which results in the attenuation of EM energy. Moreover, the carbon nanowires (CNW) with hierarchically porous and polycrystalline structure have been fabricated by Pan et al. [101]. Results show that based on these unique structures, CNW demonstrates an extremely superior MA performance in X-band (8.2−12.0 GHz) due to the impedance match, strong conductive loss, and various dipoles polarization effects. As is well known, the porous and hollow structure with a lower density can be used as lightweight MA material. Fig. 7g displays the brochosomes−soccer ball-like microscale granules with nanoscale indentations of various materials, including metals, metal oxides, and conductive polymers. The scientists have systematically explored their structure−property relationships and found that the superior antireflection is attributed to the unique structural geometries of the brochosomes [105].

4 Practical application

To the best of our knowledge, the ultimate goal of basic research is for practical application. Either nanomaterials or ferrites, metallic magnetoelectric ceramics, and their hybrids are utilised as absorbers. From a point of practical view, only applying absorbers is not enough, it is necessary to employ matrix materials to satisfy various applications. To date, the commonly used matrix is mainly focus on different types of polymers in the form of coating, film, plate, textile, and so on. For instance, Yang et al. [105] have fabricated brochosome coatings (BCs) using various materials including metals, metal oxides, and conductive polymers via double-layer colloidal crystal templates in conjunction with site-specific electrochemical growth method. Their experimental results suggest the brochosomal structure is beneficial to obtain strong ultra-antireflective performance of wavelengths from 250 to 2000 nm, which can make the brochosomes serve as camouflage coating to protect leafhoppers or their eggs against potential predators in their natural habitats. In addition, Song et al. [106] propose a novel strategy to fabricate strong and thermostable polymeric graphene/silica textile composites for practical MA applications (Fig. 8). For achieving homogeneous configuration, a unique silica textile coupled with freeze−drying method is employed as the critical factor in the formation of the polymeric composites, allowing RGO to in situ form 3D conductive frameworks. Furthermore, this group [107] have developed a wearable MA cloth via in situ employing carbon materials into a non-woven matrix. In the design of wearable MA materials, the mechanical, functional, and manufacturing requirements should be simultaneously considered (Fig. 9a–g). As for practical service, various criteria including effective absorption intensity, broad absorption bandwidth, sufficient mechanical properties, and excellent stability are required. It is well known that the narrow operation bandwidth and discrete spectral absorption peaks can hinder its further development in many real-world applications to a great extent. Therefore, considerable efforts have been made to improve this situation. Like Zhou et al. [108] propose a comprehensive scheme for the efficient and flexible design of metasurface Salisbury screen (MSS) capable of absorbing the impinging EM wave in an ultra-wide frequency band from 6 to 30 GHz with an efficiency >85%. Moreover, as shown in Figs. 9a−d, Guo et al. [74] design controllable magnetic Ag@Ni core−shell NPs on skin collagen fibre (SCF) to form biologic SCF−derived composites. Their work has a significant potential for the development of novel, lightweight, low-cost, flexible, and highly efficient microwave absorption materials.

Besides, in recent years, our group devote to investigate the MA performance of polymer-based nanocomposites. In order to increase the practical application, our group select polypyrrole fluoride (PVDF) as polymer matrix due to its flexibility, film-forming ability, easy processing, and so on. On the other hand, PVDF itself is a typical dielectric material because of the existence of electrophilic fluoride in its molecular structure which can generate polarisation loss to dissipate wave energy. Also based on
our previous research, it is found that a synergic effect between nanomaterials and PVDF also exists to increase the wave absorption properties. Fig. 10 shows the PVDF-based nanocomposites with utilising various nanomaterials (including 3D MoS$_2$, RGO/MnFe$_2$O$_4$, Fe$_3$O$_4$@C, PbS, ZnO, CuS etc.) as filler. Combining with the component effect and structural effect, it is concluded that these nanocomposites possess enhanced MA performance.

5 Conclusions

This review introduces recent development of nanomaterials used as effective absorbers in EM wave absorption field. A large number of research results have concluded that nanomaterials are promising absorbing materials. The composition and structure of nanomaterials exert vital influence on wave absorption performance. According to the different components, nanomaterials can be classified into conductive, dielectric, and magnetic materials, corresponding to conductance loss, dielectric loss, and magnetic loss mechanism, respectively. Apart from component effect, it is known that the absorption properties of a material are very closely related to the morphology/structure of nano-absorbents. Through structure–performance relation, various morphologies (e.g. flower-like, nanoflake, nanochain, hierarchical dendrite) and structures (e.g. core–shell, yolk–shell, foamed, hollow, porous) have been utilised to improve MA performance via geometric effect and structural effect. In addition, from a point of practical view, it is very important to choose appropriate matrix to support absorbers. The commonly used matrix is mainly focus on different types of polymers in the form of coating, film, plate, textile, and so on.

In the past decades, despite the tremendous advances have been achieved in EM wave absorption research and applications, great effort is still required to enhance microwave attenuation in multi-frequency band and higher frequency region. Furthermore, for the nanomaterial itself, lightweight, strong absorption ability, tunable effective absorption frequency band, thermal stability, and durability seem to be meaningful and practical.

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