



Modulation of electromagnetic wave absorption by carbon shell thickness in carbon encapsulated magnetite nanospindles—poly(vinylidene fluoride) composites

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ABSTRACT

A series of Fe₃O₄/C core-shell nanospindles with different shell thickness have been synthesized by a wet chemical method and subsequent high-temperature carbonization. The thickness of carbon shell can be well adjusted from 9 to 32 nm by changing the addition amounts of resorcinol and formaldehyde precursors during the coating process. Structure and morphology characterizations reveal that the carbon shell is amorphous structure and uniformly encapsulates on porous Fe₃O₄ nanospindles. For the first time, a flexible Fe₃O₄/C/poly(vinylidene fluoride) (PVDF) composite absorber was prepared by embedding the core-shell Fe₃O₄/C nanospindles in PVDF matrix. The electromagnetic properties of the composite show strong dependence on the carbon-shell thickness. The impedance matching for electromagnetic absorption is improved by the synergy effect between Fe₃O₄ nanospindles and encapsulated carbon shell. The Fe₃O₄/C/PVDF composite with thick carbon shell exhibits strong electromagnetic wave absorbing ability with thin absorber thickness. The minimum reflection loss for the absorber with thickness of 2.1 mm can reach −38.8 dB.

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1. Introduction

In the past decades, electromagnetic (EM) technology has been widely employed in military and civil applications such as wireless telecommunication technology, local area network and high frequency devices, etc [1–3]. As it brings convenience to people's life, it also causes EM pollution that is harmful to human health. To solve this problem, a wide variety of materials such as carbon materials, polymers, magnetic metals, ferrites, and non-ferrite ceramics have been extensively investigated as EM wave absorbers. However, it is difficult for a single magnetic or dielectric absorber to fulfill the fast growing demands for high-performance EM absorbing materials with the characteristics of strong absorption, light weight, small thickness, wide frequency range response and

antioxidation [4,5]. Take the traditional absorber-magnetite (Fe₃O₄) for example, in spite of its superior magnetic properties; it often suffers from narrow absorbing frequency bandwidth, high-frequency degradation of permeability, high density and low thermal stability, which hinder its practical applications in absorbing EM wave. Therefore, the synthesis of composite absorbers with the concept of combining both magnetic loss and dielectric loss has attracted considerable attention to improve the EM wave absorption performance.

To date, several strategies have been developed to synthesize Fe₃O₄-based composites that have good EM wave absorption abilities in gigahertz frequency range owing to the synergy effect between multiple components, such as Fe₃O₄-conductive polymer composites [6,7], Fe₃O₄-carbon composites [8,9] and Fe₃O₄-oxide composites [10,11]. Among these composites, Fe₃O₄-C absorber is particularly interesting and plenty of carbon materials including graphite [12], graphene [13], carbon tubes [14,15] and carbon fibers [16] are usually used as the main carbon components. Such Fe₃O₄-C composites have exhibited better EM absorption abilities

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than single Fe_3O_4 and carbon due to the synergetic and complementary behaviors between the magnetic loss and the dielectric loss. Besides, relative to other dielectric additives, the composites with carbon components possess exceptional advantages of light weight, high chemical and thermal stabilities [17]. So far, Xu et al. have fabricated Fe_3O_4 hollow spheres/reduced graphene oxide composites by solvothermal method. This composite absorber exhibited a maximum absorption of -24 dB with a thin absorber thickness [18]. Zhang et al. obtained good EM absorption abilities in Fe_3O_4 /carbon nanofiber absorber in low frequency range [9]. Zhao et al. prepared Fe_3O_4 decorated multi-walled carbon nanotube hybrids using poly(*N*-vinyl-2-pyrrolidone) as dispersant, demonstrating strong EM wave absorption and potential applications [19]. Yet it's worth mentioning that the Fe_3O_4 particles are often distributed in the carbon matrix irregularly and randomly. Thus, inhomogeneity, aggregation and oxidation of the Fe_3O_4 particles may occur and cause negative effects on their performances.

With the rapid development of advanced nanotechnology, composite absorbers with core-shell or yolk-shell structures have drawn increasing attention. On one hand, the special structure facilitates the synergy effect between magnetic core and dielectric shell. On the other hand, the outer shell can endow the inner Fe_3O_4 nanoparticles good dispersity, antioxidation, and mechanical properties. Therefore, the core-shell composites are expected to be excellent EM absorbers in practical applications. Additionally, the modulation of EM absorption performance of the core-shell composite absorbers can be achieved by changing the shell features. This modulation is meaningful in designing particular absorbers according to the application requirements. Recently, some groups have successfully prepared Fe_3O_4 /C core-shell composites. Nevertheless, most studies focused on their utilities in lithium-ion batteries, drug delivery and catalysts [20–22]. The EM absorption properties of the Fe_3O_4 /C core-shell composites were still not systematically investigated. A few studies relevant to Fe_3O_4 /C core-shell nanospheres have predicted that such composites based on Fe_3O_4 core and carbon shell may be a promising candidate for EM absorber. For example, Du et al. prepared Fe_3O_4 /C core-shell nanospheres with tunable shell thickness and obtained improved absorption abilities [23]. Zou et al. prepared Fe_3O_4 /C yolk-shell nanospheres by a silica-assisted strategy. Such nanospheres exhibited obvious complementarities between complex permittivity and permeability, and the minimum reflection loss of -18.1 dB was obtained [24]. It is known that one dimensional (1D) Fe_3O_4 nanostructures may have higher magnetic loss in gigahertz frequency due to the large shape anisotropy field. Thus by coating a layer of carbon shell, the 1D Fe_3O_4 /C core-shell composites would probably exhibit enhanced EM absorption properties. To our knowledge, only in Chen's work, Fe_3O_4 nanorods were coated by a very thin layer of carbon (3.5 nm) and used as absorber by mixing with paraffin [25]. Unfortunately, the effect of the carbon shell thickness on the electromagnetic properties has not been systematically investigated until now. The study on the modulation of electromagnetic properties by carbon shell thickness is helpful for designing particular absorbers and understanding the enhanced absorbing mechanisms. Additionally, in our previous studies [26–28], it is found that the matrix materials not only play important roles in enhancing absorbing properties but also endow the absorbers additional functions which facilitate their practical applications. Therefore, some polymers with specific properties can be used as new matrix materials instead of traditional paraffin.

In this study, we prepared 1D Fe_3O_4 /C core-shell nanospindles with different carbon shell thickness, and made an effort to study the variation of EM absorption performance with carbon shell thickness as well as the absorption mechanisms. The carbon shell prepared using resorcinol-formaldehyde as precursors possesses a

stable structure and exhibits high specific surface area, light weight and adjustable conductivity, which are favorable to the improvements of impedance matching, EM wave absorption and the stability of Fe_3O_4 core. Based on our previous investigations, polyvinylidene fluoride (PVDF) instead of conventional paraffin was used as disperse matrix because the synergy effect between absorber and dielectric polymer matrix could further enhance the EM absorption of the composites. Additionally, the exceptional advantages of PVDF, i.e. flexibility, low weight and high chemical corrosion resistance, can also benefit the practical applications of the Fe_3O_4 /C/PVDF composite absorber. It has been found that the Fe_3O_4 /C/PVDF composite with a very thin absorber thickness shows strong EM absorption in gigahertz frequency, and the EM absorption ability can be well adjusted by changing the carbon-shell thickness.

2. Experimental

2.1. Synthesis of hematite nanospindles

All the chemicals and reagents were A.R. grade and were used as received without further purification. In typical synthesis, $\alpha\text{-Fe}_2\text{O}_3$ nanospindles were prepared by solvothermal method based on previous works [29]. Briefly, 338 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.5 mg $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved into 62.5 mL deionized water under vigorous stirring. The above homogeneous solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 8 h. As the autoclave cooled to room temperature naturally, the resultant precipitates were separated by centrifugation, washed with distilled water and ethanol for three times, and dried in an oven at 50°C for 10 h.

2.2. Synthesis of the Fe_3O_4 /C core-shell nanospindles

The Fe_3O_4 /C core-shell nanospindles were fabricated by coating RF polymer on $\alpha\text{-Fe}_2\text{O}_3$ nanospindles and subsequent carbonization process. Typically, 40 mg of the as-prepared hematite nanospindles were dispersed in 56.3 mL of distilled water, followed by the addition of 0.2 mL of hexadecyl trimethyl ammonium bromide (CTAB) (0.01 M) for surface modification. The above mixture was treated by ultra-sonication for 1 h to form homogeneous suspension. Then, the suspension was magnetically stirred for another 10 min before the successive injection of required amounts of 2.8 mL of resorcinol (0.18 M), 78 μL of formaldehyde and 1.2 mL of ammonium hydroxide solution diluted 9 fold with distilled water. After magnetic stirring for 24 h, the as-obtained $\alpha\text{-Fe}_2\text{O}_3$ /RF composites were washed with deionized water and ethanol, and finally dried at 50°C .

To obtain Fe_3O_4 /C composites, the above $\alpha\text{-Fe}_2\text{O}_3$ /RF powders were heated under Ar atmosphere to 600°C with a heating rate of $5^\circ\text{C}/\text{min}$, then maintained at 600°C for 4 h. After carbonization, the color of samples changed from reddish brown to black.

In our experiments, the thickness of the carbon shell on Fe_3O_4 was tuned by changing the concentration of RF precursors with the molar ratio of resorcinol to formaldehyde fixed constantly. For simplicity, the $\alpha\text{-Fe}_2\text{O}_3$ /RF samples with different shell thickness were denoted as P1, P2, and P3 (from thin shell to thick one), while the corresponding Fe_3O_4 /C samples were marked as C1, C2 and C3. For P1, P2 and P3, the amounts of resorcinol were 2.8, 3.5 and 4.2 mL, respectively.

2.3. Characterization

The crystalline phases of the as-synthesized samples were analyzed by D/max2500pc X-ray diffractometer (Rigaku) with Cu

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