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An Easy Method of Synthesis $\text{Co}_x\text{O}_y@\text{C}$ Composite with Enhanced Microwave Absorption Performance

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Abstract: Design of interface-controllable magnetic composite towards the wideband microwave absorber is greatly significance, however, it still remains challenging. Herein, we designed a spherical-like hybrids, using the Co_3O_4 and amorphous carbon as the core and shell, respectively. Then, the existed Co_3O_4 core could be totally reduced by the carbon shell, thus in Co_xO_y core (composed by Co and Co_3O_4). Of particular note, the ratios of Co and Co_3O_4 can be linearly tuned, suggesting the controlled interfaces, which greatly influences the interface loss behavior and electromagnetic absorption performance. The results revealed that the minimum reflection loss value (RL_{\min}) of -39.4 dB could be achieved for the optimal $\text{Co}_x\text{O}_y@\text{C}$ sample under a thin thickness of 1.4 mm. More importantly, the frequency region with $RL < -10$ dB was estimated to be 4.3 GHz, ranging from 13.7 to 18.0 GHz. The superior wideband microwave absorption performance was primarily attributed to the multiple interfacial polarization and matched impedance matching ability.

Keywords: controllable interfaces; magnetic $\text{Co}_x\text{O}_y@\text{C}$ composite; width band EM absorption; interfacial polarization; tunable content

1. Introduction

With the rapid development of electronic devices, e.g., radar communications, wireless and local area network, etc., the electromagnetic (EM) pollutions are becoming serious, especially for regarding as “health killer” and for simultaneously disturbing normal operation of other precious devices [1–3]. In case to reduce electromagnetic pollution, more attempts have been paid on exploration of functional materials with the strong dielectric or magnetic loss ability, so that the EM waves can be converted into heats by these materials [4,5]. Commonly, the efficiency of conversion from EM to heats is termed as reflection loss (RL) value. As an ideal EM material, it is commonly requested to a width band absorption (frequency region with $RL < -10$ dB, noted that -10 dB is regarded as the commercial standard with a conversion efficiency of 90%) [6,7]. Meanwhile, a thin thickness is quite vital to reduce the weight of absorption layer [8]. Nowadays, it is widely believed that EM performance is primarily influenced by both component and nanostructure; thus the strategy of component/nanostructure has been a general way to develop EM absorber [9]. As a desirable candidate, magnetic hybrids have been widely investigated, because of their dual magnetic and dielectric loss ability [10,11]. E.g., Jia et al. employed an in situ growth route to prepare Fe/ZnFe₂O₄ hybrids, and the frequency region (f_s) was up to 6.2 GHz under a matched thickness of 1.5 mm [12]. Zhao and coworker utilized a facile polyol reduction approach to prepare Co/CoO composite, and reported that f_s value was 4.2 GHz under a thickness of 1.7 mm [13]. Li et al. combined magnetic FeCo with SiO₂ and polypyrrole; the measured

f_s was ~ 6.8 GHz with a thickness of 2.5 mm [14]. For these desirable f_s values, the synergistic effect between magnetic and dielectric loss played a key role on the EM attenuation ability. Besides, the improved complex permeability value (μ_r) was also benefited to the impedance matching behavior [15]. In this case, more EM waves could enter into the interior of EM absorption layer for the subsequent attenuation. For this purpose, magnetic components are always decorated with a series of high dielectric material, to realize improvement of impedance matching behavior. These EM absorbers, such as included Fe/graphene, FeCo/graphene, Fe₃O₄/Mexnes, and so on, showed the distinct enhancement performance as compared to the single components [16,17].

Expecting for components, absorber with various morphologies also would make a great influence on the performance. E.g., Xu et al., taking graphene hybrid as a case, observed that loading same component with different nanostructure (nanoparticle/nanosheet), the dielectric loss ability was changed [18]. They explained that the changed dielectric loss ability was caused by interfacial polarization effect, which was highly associated with nanostructure. On the basis of this finding, Cao et al. designed a multiple-interface hybrid (namely, Co₃O₄@rGO/SiO₂) and achieved a f_s value of 4.2 GHz (covering the entire X band) [19]. Similarly, Zhang et al. reported a Fe₃Si/SiC@SiO₂ absorber and got a f_s value of 5.4 GHz ($d \sim 2.4$ mm) [20]. All these desirable results confirmed the contribution of interfacial polarization.

Inspired by these results, we prepared a core-shell structured EM absorber, using Co/Co₃O₄ as the cores. The magnetic loss behavior can be easily tuned by adjusting the content of Co. Initial, Co₃O₄ nanospheres are made by a hydrothermal route and then used as the source of magnetic Co. Afterward, the as-obtained Co₃O₄ was coated by amorphous carbon to induce carbon reduction. The temperature for carbon reduction played a key role on the final content of Co. The developed Co/Co₃O₄@C presented excellent wideband EM absorption performance.

2. Experimental

2.1. Preparation of Co₃O₄ Nanospheres

Co₃O₄ nanospheres were prepared by a hydrothermal and annealing process. Typically, 0.1 g PVP, Co(Ac)₂, and urea (~ 20 mg) were codissolved in a mixture solvent, containing EG (20 mL) and distilled water (20 mL) and maintain at pH = 13. The above solution was used for the hydrothermal reaction, which was heated at 140 °C for 6 h. Once cooled to room temperature, the precipitate was collected by centrifugation for two to three times with distilled water. Later, Co₃O₄ was obtained by directly heating the precipitate at 300 °C for 0.5 h. Argon gas (Ar) was used as the protective gas.

2.2. Synthesis of Co/Co₃O₄@C Hybrids

Typically, 0.1 g Co(OH)₂ nanosphere, 0.4 g phenolic resin, and 0.2 mL formaldehyde were added into solution (~ 60 mL distilled water) and stirred for 2 h. Then, the as-obtained precipitates were heated at 500, 600, and 700 °C under Ar atmosphere for 1 h with a slow ramping rate of 1 °C/min. The obtained products treated at 500, 600, and 700 °C were denoted as C-Co-500, C-Co-600, and C-Co-700, respectively.

2.3. Characterization

The composition and phase of samples were determined by an X-ray diffractometer (Bruker D8 ADVANCE X-ray diffractometer) in the range of 20–60°. Field emission scanning electron microscope (FESEM, JEOL JSM-6330F) and transmission electron microscope (TEM, JEOL 2100) were used to observe the morphologies of these specimens. The chemical valences of Co element were evaluated by an X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe systems). Raman spectrum (Jobin Yvon HR 800 confocal Raman system) was employed to detect the graphitization level of the amorphous carbon shell. The coercive force (H_c) and magnetization were recorded by a vibrating sample magnetometer (VSM, Lakeshore, model 7400 series) at room temperature. EM characteristics

were evaluated on basis of a coaxial-line theory. First, the composites used for the EM absorption measurement were prepared by mixing the $\text{Co}_x\text{O}_y@\text{C}$ with paraffin wax in 50 wt%. Afterwards, a cylindrical-shaped sample ($\Phi_{\text{in}} = 3.04 \text{ mm}$, $\Phi_{\text{out}} = 7.0 \text{ mm}$) was made by hot pressing the mixture into a mold. The electromagnetic parameters were tested by the two-port vector network analyzer (Agilent E5071C). Finally, the reflection loss value was calculated based on following equations [21–23]:

$$Z_{\text{in}} = Z_0(\mu_r/\epsilon_r)^{1/2} \tanh[j(2\pi f d(\mu_r \epsilon_r)^{1/2}/c)] \quad (1)$$

$$RL(\text{dB}) = 20 \log |(Z_{\text{in}} - Z_0)/(Z_{\text{in}} + Z_0)| \quad (2)$$

where Z_{in} is the input impedance of absorber, f relates to the frequency of electromagnetic wave, d represents the coating thickness of the absorber, while c is the light velocity. ϵ_r ($\epsilon_r = \epsilon' - j\epsilon''$) and μ_r ($\mu_r = \mu' - j\mu''$) are the complex permittivity and permeability of the absorption layer.

3. Results and Discussion

The formation process of $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ spherical-shaped hybrids are illustrated in Figure 1. First, the spherical-shaped $\text{Co}(\text{OH})_2$ samples are fabricated by a hydrothermal route. Second, $\text{Co}(\text{OH})_2$ is converted to Co_3O_4 via annealing products at $300 \text{ }^\circ\text{C}$ for 1 h (Figure S1). The diffraction peaks intensity of Co_3O_4 and $\text{Co}(\text{OH})_2$ are very strong, which are due to the good crystalline structure. $\text{Co}(\text{OH})_2@\text{phenolic resin (PS)}$: the precursor of amorphous carbon) is made by an in situ polymerization route. By heating the $\text{Co}(\text{OH})_2@\text{PS}$ at various temperatures (here is $500\text{--}700 \text{ }^\circ\text{C}$), $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ with various content of Co can be obtained. Figure S2 compares the EDS and FTIR spectra of $\text{Co}(\text{OH})_2@\text{PS}$ and C-Co-500 sample. The EDS spectra of $\text{Co}(\text{OH})_2@\text{PS}$ and $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ samples are provided in Figure S2a,b, where the C, Co, and O elements can be detected on both samples. Hence, it is hard to observe the changes of component. Subsequently, the FT-IR spectra have been added to compare the changes of chemical bonds (Figure S2c,d). Clearly, the wave number at around 575 cm^{-1} is assigned to the characteristic vibrating peak of $\text{Co}(\text{OH})_2$ and is consistent with the XRD result. After heating at $500 \text{ }^\circ\text{C}$, the C-OH peak disappeared and turned to two types of Co-O bonds, known as CoO_4 (550 cm^{-1}) and CoO_6 (670 cm^{-1}), suggesting the coexisted spinel phase of Co_3O_4 . Additionally, due to the carbonized reaction, the original C-H bond disappeared for the C-Co-500 sample.

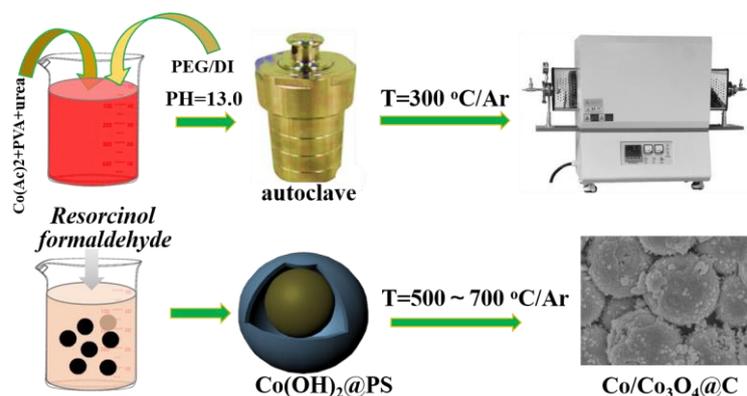


Figure 1. Schematic presentation for the preparation route of $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ composites.

Figure 2 shows the morphology evolution from initial $\text{Co}(\text{OH})_2$ to ultimate $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$. $\text{Co}(\text{OH})_2$ exhibits significant spherical-shaped structure with average size of $\sim 400 \text{ nm}$ (Figure 2a,b). The surface of $\text{Co}(\text{OH})_2$ is very smooth and dense. As for Co_3O_4 , it still maintains original spherical shape with the same size, according to Figure 2c,d. But Co_3O_4 exhibits a tiny rough surface attributing to the loss of phase conversion from $\text{Co}(\text{OH})_2$ to Co_3O_4 . Similarly, structure can be maintained for $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ (C-Co-700), expecting for the surface (Figure 2e,f) to be rough, which was attributed to the amorphous carbon shell.

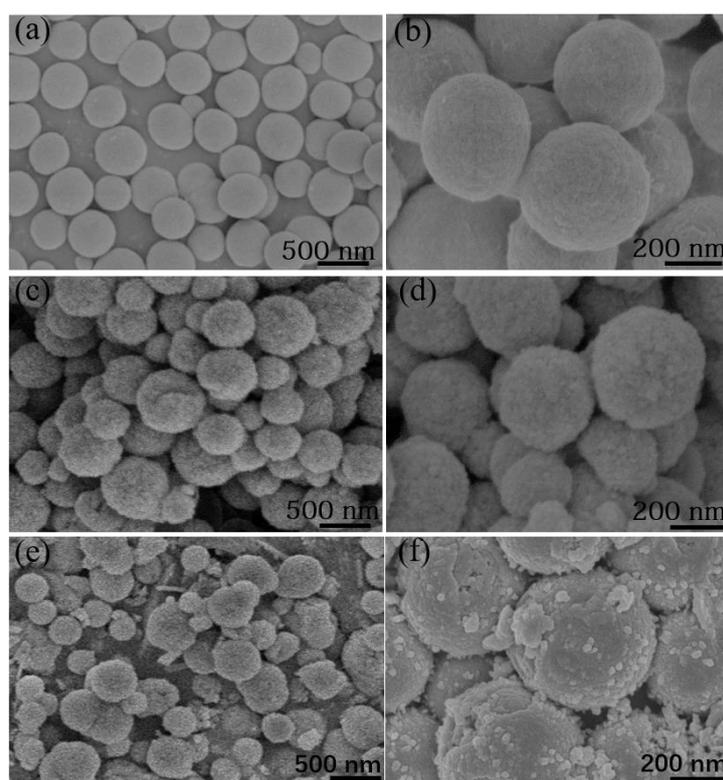


Figure 2. FESEM images of the products as received at different stages: (a,b) $\text{Co}(\text{OH})_2$, (c,d) Co_3O_4 , and (e,f) the representative $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ as treated at 700°C .

Figure 3 shows the HRTEM images of C-Co-700 sample. The lattice with the distance of 0.24 nm corresponds to the (111) crystal plane of the Co phase. The lattice with the distance of 0.21 nm can be ascribed to the (311) plane of Co_3O_4 . It shows one selected area of electron diffraction pattern, which is indexed to the (311), (440), and (400) planes of Co_3O_4 and (111) crystal plane of Co, respectively.

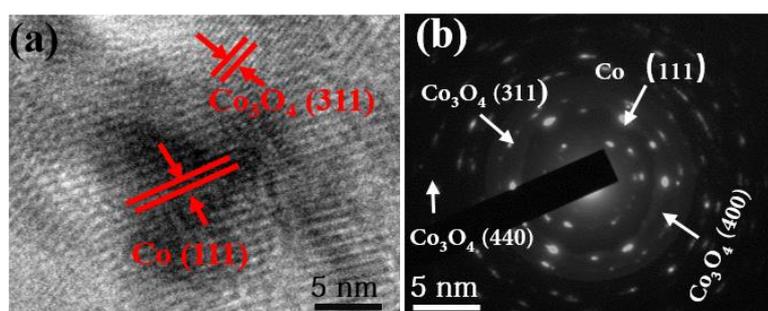


Figure 3. (a) HRTEM and (b) SAED image of C-Co-700 product.

The crystal structures for $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ are characterized by X-ray pattern (XRD). As shown in Figure 4a, the diffraction peaks at 36.2° and 42.7° are assigned to the (311) and (400) crystal planes of Co_3O_4 . Besides, other diffraction peaks at 44.2° and 51.1° can be ascribed to the (111) and (200) crystal planes of Co. Furthermore, the intensity of Co signals is gradually stronger as it increases for the product treated with a high temperature, revealing the increased content of Co. As for amorphous carbon shell, there is no obvious signal, because of amorphous state. To confirm existence of carbon, the Raman spectrums are employed here, as plotted in Figure 4b. Clearly, two noticeable peaks at 1360 and 1590 cm^{-1} , representing D and G band, respectively, are found for these $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ hybrids [24]. It is widely accepted that G band is generated by the graphitized carbon atom which adopts sp^2 hybridized form [25]. D band is induced by the crystal defects or disorders existing in

carbon materials [26]. Commonly, the ratio of D/G band is an indicator of the graphitization degree. In our case, the ratios are estimated to be 0.98, 0.91, and 0.88 for the C-Co-500, C-Co-600, and C-Co-700, respectively. The increased graphitization degree is ascribed to a high carbonization temperature, according to recent achievement [27]. The magnetization loops (M-H) curves were measured by a vibrating sample magnetometer (VSM) (Figure 4c,d). In general, the magnetization value has a vital correlation with permeability parameters, includes real part of permeability and magnetic loss value (μ'/μ''), as can be expressed by the following equations [28]:

$$\mu' = 1 + (M/H)\cos\sigma \quad (3)$$

$$\mu'' = (M/H)\sin\sigma \quad (4)$$

where M represents the magnetization, H means the external magnetic field, and σ refers to the phase lag angle of magnetization behind external magnetic field. From Equations (3) and (4), a high magnetization value is related to a bigger μ' and μ'' values, thus benefiting to the impedance matching and magnetic loss ability. In Figure 4c, the magnetization values are estimated to be 9.0, 33, and 75 emu/g for C-Co-500, C-Co-600, and C-Co-700 samples. The increased magnetization value confirms the enhancement of Co content [29]. The X-ray photoelectron spectrum (XPS) is also performed to analyze the valances of Co. The binding energy values of Co 2p_{3/2} are located at 782.1 and 778.2 eV, which can be corresponded to Co₃O₄ and Co, respectively (Figure 4e–g) [30]. The surface area ratio of S_{Co}/S_{Co₃O₄} are 0.23, 0.43, and 0.81 for C-Co-500, C-Co-600, and C-Co-700, respectively, representing the molar ratio.

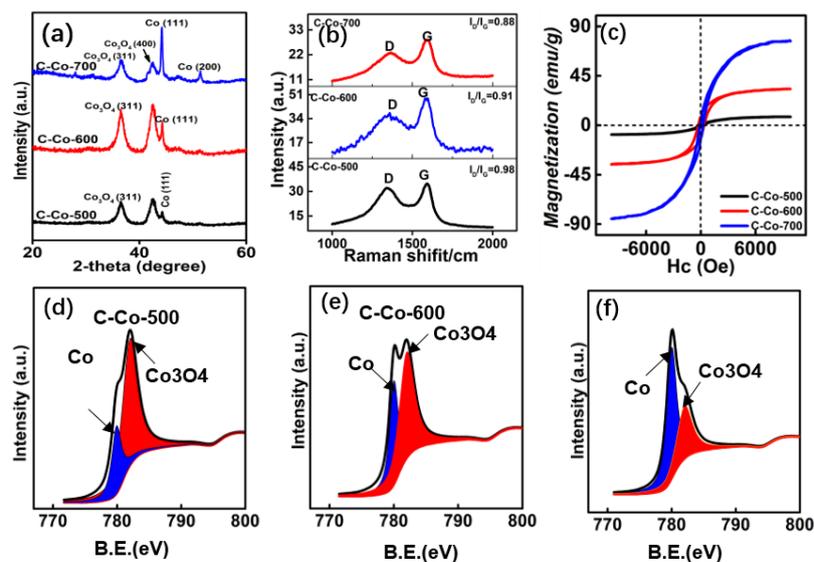


Figure 4. (a) XRD patterns, (b) Raman spectrum, (c,d) M-H curves of Co/Co₃O₄@C samples treated at various temperatures, and (e,f) XPS spectra for the Co 3/2 p.

Figure 5 plots the frequency dependence of two-dimensional reflection loss (RL) curves. Considering the transmission line theory, the reflection loss values are calculated using the measured data of relative permittivity and permeability at a given frequency region (2–18 GHz) and thickness layer (1–5 mm). Obviously, the absorption layer filled with Co₃O₄ exhibits the poor EM performance, due to the unqualified RL values (<−10 dB) [31]. But significant improvement can be found for these Co/Co₃O₄@C sample. In fact, a desirable EM absorber is requested to a broadband absorption for the thickness < 2.0 mm. To clarify it, the reflection loss curves at 1.0–2.0 mm are given in Figure 6. In such a thickness region, RL_{min} values of Co₃O₄ are all higher than −2.0 dB, thus cannot be used as absorber. For C-Co-500 product, the minimum RL_{min} value of −10.8 dB is achieved under a thickness of 1.8 mm. In other thickness, there is no frequency region with $RL < -10$ dB. As the content of Co is increased,

the absorption intensity becomes distinctly stronger. The minimum RL_{min} value can up to -39.4 dB for C-Co-600, while the thickness is only 1.4 mm (Figure 6c). Meanwhile, the qualified frequency region covers 4.3 GHz, ranging from 13.8 to 18.0 GHz. While for C-Co-700 (Figure 6d), the lowest RL_{min} value can be gained is -38.6 dB under a matched thickness of 1.6 mm. The corresponding f_s value is 4.9 GHz. For comparison, the EM performance of Co or C containing hybrids are listed in Table 1, demonstrating that the Co/Co₃O₄@C hybrids shows improvement of EM absorption ability [32–39].

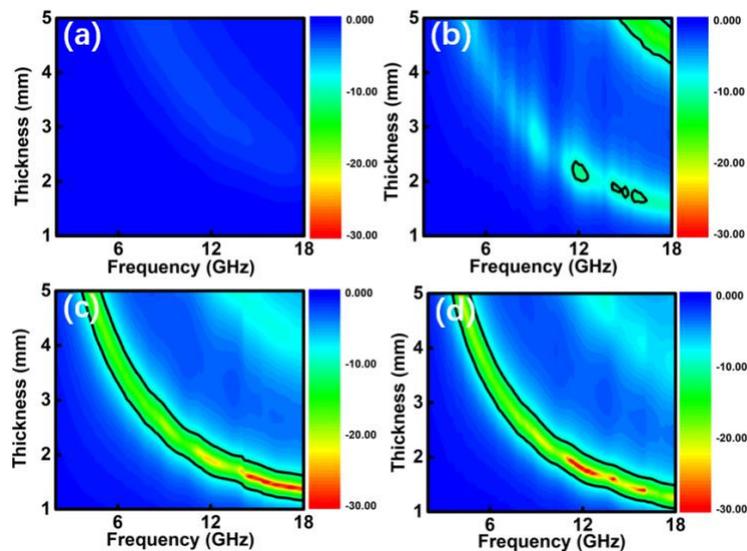


Figure 5. Color-mappings of reflection loss curves for the Co/Co₃O₄@C and Co₃O₄ samples: (a) Co₃O₄, (b) C-Co-500, (c) C-Co-600, and (d) C-Co-700.

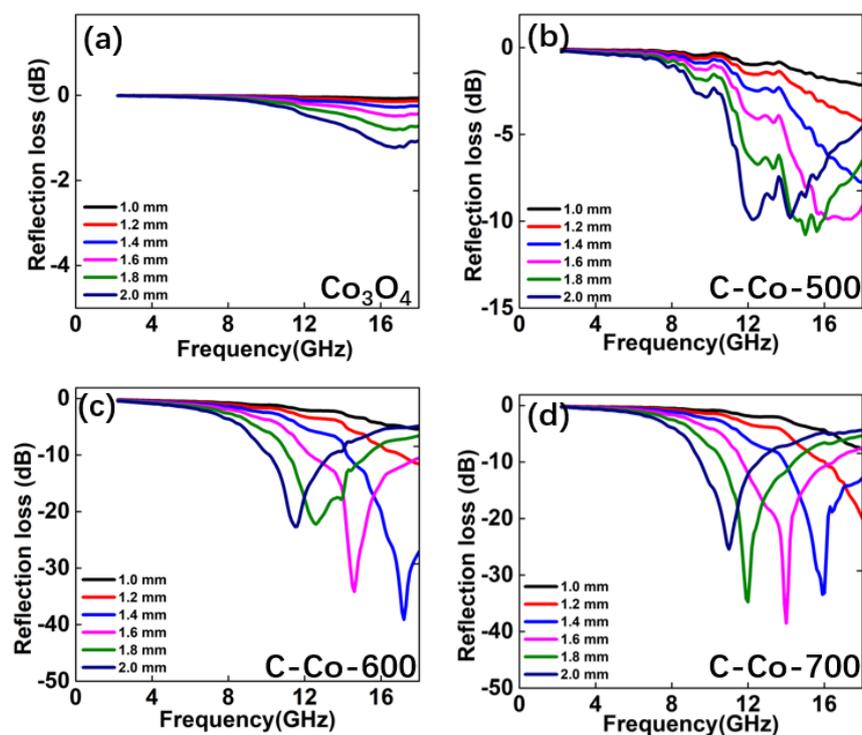


Figure 6. Frequency dependent of reflection loss curves for the Co/Co₃O₄@C and Co₃O₄ samples: (a) Co₃O₄, (b) C-Co-500, (c) C-Co-600, and (d) C-Co-700; noted that the thickness < 2.0 mm.

Table 1. Electromagnetic (EM) performances of Co- or C-based hybrids as reported by recent literatures.

Samples	RL _{min} (dB)	Effective Absorption Region (GHz)	Thickness (mm)	Ref.
Co@C	~−10	<3.0	1.5	[32]
Porous carbon	−23.8	~3.8	2.0	[33]
CoO@Co/ZnO/graphene	−51.5	4.7	2.6	[34]
CoNi@C	−24.03	4.32	2.5	[35]
Co/ZnO/C	−52.6	4.9	3.0	[36]
Co ₃ O ₄ /graphene	−31.88	3.4	2.0	[37]
Co ₃ O ₄ @PANI	−37.39	~4.2	4.0	[38]
Co/CoO	−50 dB	4.2	2.0	[39]
C-Co-600	−39.4 dB	4.3	1.4 mm	This work

It should be noted that EM absorption performance is always determined by the impedance matching and EM attenuation ability. The key factor for the impedance matching ability can be estimated by the ratio of complex permeability/permittivity (μ_r/ϵ_r) [40]. Figure 7 plots the curves of μ_r , ϵ_r , and their ratios of μ_r/ϵ_r . Due to the nonmagnetic characteristic, μ_r of Co₃O₄ is almost a constant of 1.0, according to Figure 7a. ϵ_r decreases from 4.6 to 4.2. As compared to Co₃O₄, μ_r of C-Co-500 is only a little higher than Co₃O₄, attributing to the low content of Co (Figure 7b). But significant enhancement can be found for ϵ_r ranging in 7.2~9.9. By further increasing the content of Co, both μ_r and ϵ_r increase, e.g., μ_r values are ~1.1 and 1.2 for C-Co-600 and C-Co-700, respectively (Figure 7c,d). Meanwhile, ϵ_r of C-Co-700 is highest and distributed in the region 15.9~12. The ratios of μ_r/ϵ_r values are then applied to estimate the impedance matching ability (Figure 7e). The ratio of Co₃O₄ is distinct larger than these Co/Co₃O₄@C samples, revealing the good impedance matching behavior. In this case, it can be deduced that the poor EM performance of Co₃O₄ is primarily due to the weakened attenuation ability. For these Co/Co₃O₄@C hybrids, the ratios of C-Co-600 is much closer to C-Co-700, and all are smaller than C-Co-500.

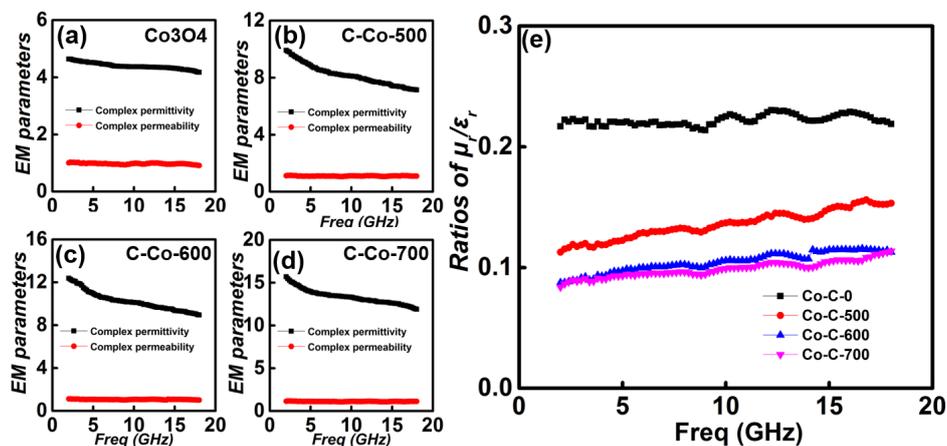


Figure 7. Frequency dependence of μ_r/ϵ_r curves for the Co/Co₃O₄@C and Co₃O₄ samples: (a) Co₃O₄, (b) C-Co-500, (c) C-Co-600, (d) C-Co-700, and (e) the ratios of μ_r/ϵ_r for the Co/Co₃O₄@C and Co₃O₄ sample.

Commonly, the mechanism for EM attenuation results from dielectric and magnetic loss. Figure 8a plots the ϵ'' - f curves for these products. It can be clearly seen that Co₃O₄ achieves the lowest ϵ'' value (~0.35), representing the worst dielectric loss ability. For Co/Co₃O₄@C samples, the ϵ'' slowly decreases first as the frequency increases. Then, multiple dielectric loss peaks are observed in high-frequency region ($f > 6.5$ GHz), revealing polarization relaxation behavior. In such a frequency region ($f > 6.5$ GHz), polarization forms primarily included are interfacial and dipole polarization, according to recent discussions on mechanism [41,42]. In general, either dipole or interfacial polarization relaxation

effect can be revealed by the Cole–Cole semicircle. In detail, the relative complex permittivity can be described by the following equations [43–46]:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j2\pi f\tau} = \varepsilon' - j\varepsilon'' \quad (5)$$

where ε_s , ε_∞ , and τ are static permittivity, relative dielectric permittivity at high-frequency limit, and polarization relaxation time, respectively, whereas, ε' and ε'' can be calculated based on the following equations.

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi f)^2\tau^2} \quad (6)$$

$$\varepsilon'' = \frac{2\pi f\tau(\varepsilon_s - \varepsilon_\infty)}{1 + (2\pi f)^2\tau^2} \quad (7)$$

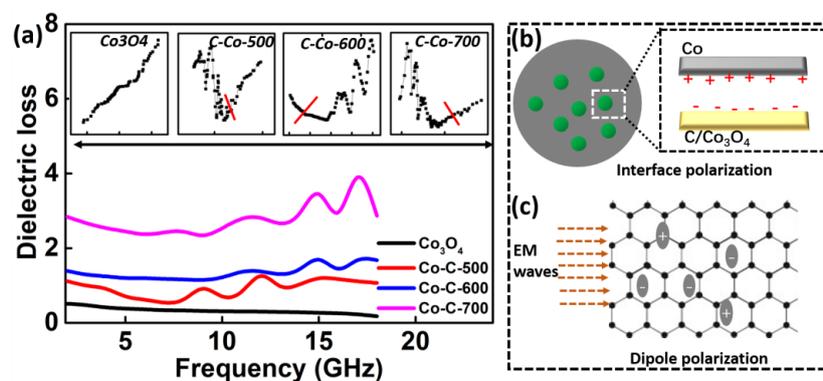


Figure 8. Frequency dependence of dielectric loss curves for the $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ and Co_3O_4 samples: the schematic illustration of proposed interface (b,c) dipole polarization mechanism; noted the inserted images in Figure 8 (a) represents the Cole–Cole curves.

Based on Equations (6) and (7), the ε' - ε'' can be expressed as above:

$$(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2 = (\varepsilon_s - \varepsilon_\infty)^2 \quad (8)$$

If the plot of ε' - ε'' is a semicircle, it represents one Debye polarization relaxation process which make a contribution for ε'' . Commonly, such a semicircle is termed as Cole–Cole semicircle. The inserted images in Figure 8a show the Cole–Cole curves of these products. It can be revealed that only $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ products exhibit Cole–Cole semicircles, indicating the polarization behavior. The proposed mechanisms for polarization are illustrated in Figure 8b,c. In our case, the developed $\text{Co}/\text{Co}_3\text{O}_4@\text{C}$ exhibits multiple interfaces, including $\text{Co}/\text{Co}_3\text{O}_4$, Co/C , and $\text{Co}_3\text{O}_4/\text{C}$. When an external EM field is provided, the electrons from the Co will be attracted by Co_3O_4 or groups of amorphous carbon, because of difference in electronegativity. Consequently, the interfacial relaxation process occurs, favoring the dielectric loss. In addition to interfacial polarization, dipole polarization may also attribute to the dielectric loss value.

Amorphous carbon shell always contains various forms of defects, such as crystal defects, presence of C-containing groups, e.g., $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{COH}$, etc. (Figure 8c). These defects can act as the dipole center and induce dipole polarization. Such a dipole process has a contribution for ε'' [47].

Magnetic loss ability is discussed in Figure 9. Because of the biggest content of Co, C-Co-700 has a largest μ'' value, equaling to 0.24. Meanwhile, μ'' versus frequency exhibits multiple peaks. As we know, μ'' mainly comes from hysteresis loss, domain wall resonance, natural resonance, exchange resonance, and eddy current effect [45]. The hysteresis loss arising from irreversible magnetization is negligible in a weakly applied field, and the domain wall resonance occurs only in multidomain

materials and usually in 1–100 MHz region, and thus, the contributions from hysteresis loss and domain wall resonance to magnetic loss can be excluded in our material system. If the magnetic loss originates from eddy current effect, the values of C_0 ($C_0 = \mu'' (\mu')^{-2} f^{-1} = 2\pi\mu_0\sigma d^2/3$) should be a constant when the frequency increases [48,49]. The C_0 values of all samples fluctuate at full frequency region (Figure 9b). Hence, we can deduce that the magnetic loss mainly results from natural resonance and exchange resonances.

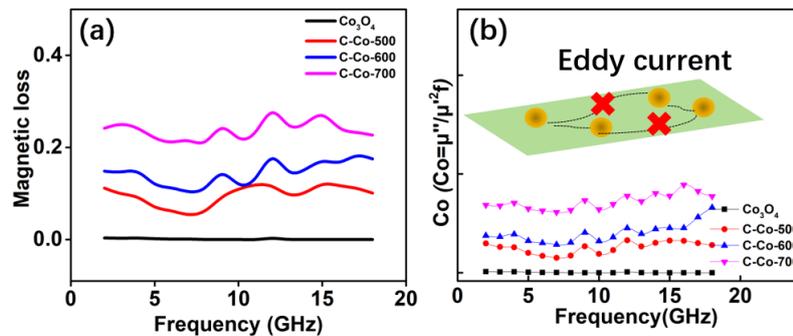


Figure 9. (a) Frequency dependence of magnetic loss curves for the Co/Co₃O₄@C and Co₃O₄ samples and (b) the Co-f curves of the four products.

The attenuation constant α represents the integral loss ability, including magnetic or dielectric loss, which can be calculated by following equation [50]:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu'' \varepsilon'' - \mu' \varepsilon') + \sqrt{(\mu'' \varepsilon'' - \mu' \varepsilon')^2 + (\mu' \varepsilon'' + \mu'' \varepsilon')^2}} \quad (9)$$

From Figures 8 and 9, we can find that C-Co-700 sample has the highest dielectric and magnetic losses, thus leading to a biggest attenuation constant α (Figure 10). The content of Co plays a key role on tuning the dielectric and magnetic loss ability. It also has proven that Co₃O₄ has a quite lower attenuation constant α . Overall, C-Co-600 achieves the best EM performance which attributes to the several factors. First, the Co/Co₃O₄ as the core has efficiently prevented the eddy current effect. Second, the suitable component of Co ensures the strong interfacial polarization, which is beneficial to dielectric loss. In addition, a suitable content of Co also maintains a moderately ε_r value, hence enabling to balance the impedance matching ability.

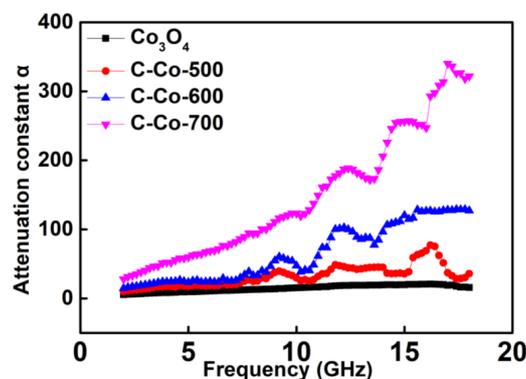


Figure 10. Wave-attenuation constant α for these products.

4. Conclusions

In this work, a Co/Co₃O₄@C product was developed by a facile hydrothermal and annealing method. First, the spherical-shaped Co₃O₄ with an average size of ~400 nm was prepared and then coated by carbon. The as-obtained Co₃O₄@C was heated at various temperatures, resulting in

Co/Co₃O₄@C hybrids. The content of Co was tunable by only controlling the temperatures. The EM performance were studied, based on the transmission line theory. The minimum reflection loss value (RL_{\min}) of -39.4 dB could be achieved for the Co/Co₃O₄@C sample. The corresponding thickness was only 1.4 mm. Furthermore, the frequency region with $RL < -10$ dB, was up to 4.3 GHz, covering 13.7~18.0 GHz. The excellent electromagnetic absorption mechanism was discussed in depth, which was attributed to the multi-interface-induced interface polarization. Meanwhile, the existed magnetic Co enabled balancing the impedance matching behavior.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-4991/10/5/902/s1>, Figure S1: XRD patterns of Co(OH)₂ and Co₃O₄, Figure S2: (a,b) EDS and (c,d) FR-IR spectral of Co(OH)₂@PS and C-Co-500.

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