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Co²⁺/Co³⁺ Ratio Dependence of Electromagnetic Wave Absorption in Hierarchical NiCo₂O₄-CoNiO₂ Hybrids

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Abstract Amorphous hierarchical NiCo₂O₄-CoNiO₂ hybrids have been successfully fabricated via a facile one-pot hydrothermal route, followed by morphologic conversion into urchin-like structured NiCo₂O₄-CoNiO₂ nanorods and irregular-shaped hierarchical NiCo₂O₄-CoNiO₂ polyhedral nanocrystals through air-annealing treatment at 450 °C and 650 °C, respectively. The phase structure, morphology and chemical composition have been characterized in detail. Calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids show improved microwave absorption

properties, which is ascribed to the synergistic effect of dielectric CoNiO_2 and NiCo_2O_4 phase. In particular, the calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at $450\text{ }^\circ\text{C}$ exhibit significant enhancement in complex permittivity with respect to the others due to its remarkable dipole polarization and interfacial polarization. The maximum reflection loss (RL) of the calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at $450\text{ }^\circ\text{C}$ reaches -42.13 dB at 11.84 GHz with a matching thickness of 1.55 mm , and a relatively broad absorption bandwidth ($\text{RL} \leq -10\text{ dB}$) in $13.12\text{-}17.04\text{ GHz}$ range. Very interestingly, the electromagnetic (EM) wave absorption performance of the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids shows dependence on the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio. The calcined $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at $450\text{ }^\circ\text{C}$ of the most defect concentration possess the best EM wave absorption ability among all the samples. The results suggest that the proper interactions between the building blocks in hybrids can guide us to design and fabricate highly efficient EM wave absorption materials.

Keywords: Hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids; Microwave-absorbing materials; Interaction; Dielectric loss; Impedance matching characteristic

1. Introduction

Microwave absorbing materials (MAMs) working at a frequency of $2\text{-}18\text{ GHz}$ have attracted increasing attentions due to their prospective potential applications in industry, civil, commercial, and military technologies. Various absorbers with matching complex permittivity and permeability, including ferrites, magnetic metallic fillers, nanosized particles, carbon nanomaterials, conductive fibers, frequency

selective surface, and even meta-materials, have been developed to design MAMs during the last decades [1-25]. MAMs can absorb electromagnetic (EM) waves effectively and convert energy into thermal energy or dissipate the EM waves by interference. The effectiveness of a MAM is mainly dependent on its EM characteristics, *i.e.*, complex permittivity and permeability, so the key point in obtaining thin-layer broad-band MAMs is the control of the EM properties of such MAMs.

As one of the most important magnetic nanomaterials, soft magnet ferrite (MFe_2O_4) has large saturation magnetization, obvious Snoek's limit, great coercivity, excellent chemical stability, and corrosion resistance, which results in high complex permeability values at wide frequency ranges [25, 26]. Recently, in order to effectively improve the microwave absorption of graphene (GP)-filled composites, attention has been directed toward adding magnetic ferrite materials such as CoFe_2O_4 , MnFe_2O_4 or NiFe_2O_4 particles to GP-filled composites to improve their complex permeability [3, 27, 28]. For example, a minimum reflection loss (RL) of -18.5 dB was obtained at 12.9 GHz for the CoFe_2O_4 hollow sphere/GP composites with a thickness of 2.00 mm, and the effective absorption frequency of -10 dB ranged from 11.3 to 15.0 GHz [27]. The minimum RL of reduced graphene oxide (RGO)/ MnFe_2O_4 /PVDF composites could reach -29.0 dB at 9.2 GHz, and the bandwidth of frequency < -10 dB was from 8.00 to 12.88 GHz [3]. NiFe_2O_4 nanorod-graphene composites were synthesized by a facile one-step hydrothermal process in the presence of an ionic liquid and the result indicated that the RL below

-10 dB ranged from 13.6 to 18 GHz with a thickness of 2.00 mm [28]. These experimental results show that the enhanced microwave absorption of GP/ferrite particle-filled composites are mainly due to the increased magnetic loss and the unique microstructure as a result of the presence of magnetic particles. Hence, excellent EM wave absorption properties of the composites can be realized by reasonably incorporating magnetic ferrite particles with different EM properties, particle sizes, and morphologies.

Although the complex permeability can be tailored by adding magnetic ferrite particles to improve the microwave absorption of the composites, it is still a challenge to design and fabricate composites to satisfy the demand of ideal MAMs. For example, the complex permeability is increased as the magnetic ferrite (MFe_2O_4) particles are incorporated into the composites, but the values of the complex permeability is still lower compared with the complex permittivity, which results in such MAMs exhibiting no visible enhancement of RL. On the other hand, some negative values of μ'' of the composites also appear in the measured frequency range [19, 29-32], and few studies can give a detailed discussion on the mechanism of such a unique phenomenon. If the absolute values of μ'' of some reported composites are small in the measured frequency range (≤ 0.1), the negative μ'' may result from a problem with the calibration procedures of the microwave test setup. Therefore, we cannot use the complex permeability, *i.e.*, the negative value of μ'' of the composites, to calculate the magnetic loss and RL of such MAMs.

One feasible approach to overcome these drawbacks is the design and synthesis of novel hierarchical spinel nanocrystals with reasonable composition, morphology, microstructure, and architecture on the nanoscale, but there has been few report about the EM and microwave-absorbing properties of novel hierarchical magnetic spinel nanocrystals [25, 26]. In particular, hierarchical structures, which assembled by nanoscale primary building blocks (*e.g.*, nanoparticles, nanorods, and nanosheets) with porous characteristic, have drawn special interest [33]. It is anticipated that such hierarchical structures not only inherit the advantages from the single components but also arise novel properties due to the synergistic interactions between the nano building blocks [34, 35].

To date, spinel ferrites with various compositions have been already synthesized and used as MAMs [25, 28]. However, as an important spinel structure, nickel cobalt oxide (*i.e.*, NiCo_2O_4) was mainly used in electrochemistry field [33, 34], and to the best of our knowledge, there has been few report about the microwave absorbing property of NiCo_2O_4 so far [36]. Furthermore, little attention has been paid to nickel cobalt oxides with compositions other than NiCo_2O_4 (*i.e.*, CoNiO_2) for the applications as supercapacitor electrodes or MAMs. In order to achieve a novel absorption property, many efforts have been devoted to combine two or more than two kinds of functional materials to adjust the EM parameters for achieving a desired RL. Inspired by this thought, in this work, we reported the facile synthesis of novel hierarchical NiCo_2O_4 - CoNiO_2 hybrids through an one-step hydrothermal route without complex process, and used these hybrid nanostructures for microwave

absorption. The crystalline structure, morphology, and microwave absorption of these materials were investigated in detail. Our experimental method provides a facile and reliable route for the preparation of novel hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids, which could have important applications in modern science and technology due to its good mechanical and chemical stability. It could also be a general approach for the large-scale of novel hierarchical spinel hybrids of a wide range of materials.

2. Experimental section

2.1. Materials and sample preparation

D-glucose monohydrate purchased from National Reagent Corp. (Shanghai, China) was used as a carbon source to guide the synthesis of core-shell solid sphere precursor [37-39]. Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and urea ($\text{CO}(\text{NH}_2)_2$) were obtained from Tianjin Kemiou Chemical Reagent Corp. (Tianjin, China).

The hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids were prepared by the following one-pot process similar to our previous reports [37-39]. Briefly, D-glucose, metal source and urea were co-dissolved in 50 ml distilled water. The molar ratio of D-glucose (0.01 mol), dissolved metal (0.02 mol, molar ratio of $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2=1: 1$), and urea (0.02 mol) was controlled to a value of 1: 2: 2. After stirring for 0.5 h, the derived solution was transferred into a 100 ml capacity Teflon-lined stainless-steel autoclave followed by hydrothermal treatment at 180 °C for 20 h. The obtained products were washed and filtered off several times using distilled water and absolute

ethanol successively, and finally dried at 80 °C under vacuum overnight. After synthesis, the products were calcined at 450 °C or 650 °C in air for 3 h with a heating rate of 2 °C min⁻¹ to obtain hierarchical NiCo₂O₄-CoNiO₂ hybrids.

2.2. Characterization

X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 equipment with Cu $K\alpha$ radiation operated at 40 kV and 40 mA. The particle size and morphology were visualized by using a FEI Quanta 600 FEG scanning electronic microscope (SEM) and a FEI Tecnai G² F20 S-TWIN transmission electron microscope (TEM), and an energy-dispersive X-ray spectroscopy (EDS) attachment was used to obtain the surface element composition of synthesized samples. TEM samples were treated by sonicating in absolute ethanol for several minutes and then a few drops of the resulting suspension were deposited onto a holey-carbon film supported in a copper grid, which was dried naturally. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on the adsorption data. Raman spectra were obtained on a Nicolet Almega spectrometer. Thermogravimetric analysis (TGA) was carried out with a temperature ramp of 10 °C/min. The chemical states were investigated by X-ray photoelectron spectroscopy (XPS, ESCA PHI 5400) using a monochromatic Mg $K\alpha$ X-ray source (1253.6 eV). Curve fitting was carried out using Shirley function for background correction. An asymmetric Gaussian-Lorentzian line-shape was used to fit the asymmetric photoelectron bands while a Gaussian-Lorentzian line-shape was used to fit the symmetric bands. Photoelectron

bands were peak-fitted using a non-linear least-squares optimization routine with software provided by the instrument manufacturer. The magnetic properties of the products were studied by vibrating sample magnetometer (VSM, Lake shore 7, 304).

2.3. Electromagnetic measurements

The microwave absorption properties of hierarchical NiCo₂O₄-CoNiO₂ hybrids were investigated through a network analyzer (Agilent Technologies E8363B) in the frequency range of 2-18 GHz. The composites for microwave absorption measurement were fabricated by mixing paraffin wax with 50 wt.% sample powder and pressed into toroid shape ($\phi_{\text{out}} = 7.00$ mm, $\phi_{\text{in}} = 3.04$ mm). The complex permittivity and permeability were computed from the experimental scattering parameters through the standard Nicholson-Rossand Weir theoretical calculations.

3. Results and discussion

Fig. 1

The phase structures of synthesized NiCo₂O₄-CoNiO₂ hybrids were measured by XRD, as displayed in Fig. 1. For calcined NiCo₂O₄-CoNiO₂ hybrids, the positions and relative intensities of all the diffraction peaks are in consistent with the standard XRD patterns for cubic spinel structure of bulk NiCo₂O₄ (JCPDS No. 20-0781) and cubic face-center structure of CoNiO₂ (JCPDS No. 10-0188). The broadening diffraction peaks of the calcined sample at 450 °C are due to the small size effect of hierarchical NiCo₂O₄-CoNiO₂ nanocrystals. After annealing treatment at 650 °C, the XRD pattern of the sample shows obvious enhancement of characteristic peaks for hierarchical

NiCo₂O₄-CoNiO₂ hybrids, indicating the agglomeration of hierarchical NiCo₂O₄-CoNiO₂ nanocrystals. Particularly, the absence of characteristic peaks assigned to crystalline NiCo₂O₄-CoNiO₂ hybrids in uncalcined sample implies the amorphous nature of these components.

Fig. 2

The morphologies and microstructures of hierarchical NiCo₂O₄-CoNiO₂ hybrids were further characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a-b, 2e-f, 2i-j display the SEM images of uncalcined and calcined NiCo₂O₄-CoNiO₂ hybrids at 450 °C and 650 °C, respectively. As shown in Fig. 2a, the uncalcined NiCo₂O₄-CoNiO₂ hybrid shows a uniform microspheres structure with average diameter of ~ 1-2 μm. The high-magnification image of the microspheres shown in Fig. 2b indicates that the uncalcined NiCo₂O₄-CoNiO₂ hybrids are entirely wrapped by an amorphous NiCo₂O₄-CoNiO₂ hybrid layer, and the adjacent spheres are connected by the wrinkled amorphous layer. The TEM images (Fig. 2c-d) provide further insight into the detailed structure, showing that the amorphous layer thickness of the microspheres is approximately 300 nm. The amorphous hierarchical NiCo₂O₄-CoNiO₂ hybrid layer adhered to the microspheres can be observed in the magnified image (Fig. 2d).

After calcination at 450 °C, the amorphous hierarchical NiCo₂O₄-CoNiO₂ hybrid layer was transformed to highly crystalline urchin-like structure with average diameter of ~ 1-2 μm (Fig. 2e). The thin and wrinkled hierarchical NiCo₂O₄-CoNiO₂ hybrid layer

(Fig. 2f) appears and is almost bright under SEM observation, indicating that the structure has sharp and striking morphology which is beneficial for secondary electron images. The representative TEM images of the crystalline $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids are shown in Fig. 2g-h. An urchin-like structured $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrid is obtained. The uniform microsphere is constructed by a large number of small nanorods radially-grown from the center, and the typical diameter and length of these nanorods are $\sim 10\text{--}20$ nm and $\sim 200\text{--}300$ nm, respectively. Fig. 2h is the HR-TEM image of the nanorod from Fig. 2g. The clear lattice fringes with a d -spacing of 0.24 nm, 0.45 nm and 0.28 nm can be well indexed to the (111) plane of cubic CoNiO_2 as well as the (111) and (220) planes of cubic NiCo_2O_4 , respectively. These results further confirm that urchin-like spheres are composed of hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids.

For calcined $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at 650°C , irregular-shaped hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids with a size of $1\text{--}2\ \mu\text{m}$ are clearly observed (Fig. 2i-j). Moreover, the hybrids are composed of $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ polyhedral nanocrystals. The magnified SEM image shows that $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ nanocrystals have well-defined polyhedral shape with sharp edges and smooth surface (Fig. 2j, insert). For a better visualization of the polyhedral shape, Fig. 2k-l gives the TEM images of hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids. The $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ nanocrystals are aggregated with average size of $\sim 10\text{--}30$ nm to form a nearly hollow sphere (Fig. 2k). The lattice distance of $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ polyhedral nanocrystals in hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids is measured to be 0.23 nm and 0.47 nm (Fig. 2l), which can

be indexed to the (111) planes of cubic CoNiO_2 and NiCo_2O_4 . These results reveal that the synthetic method developed in this work could prepare high-quality hierarchical NiCo_2O_4 - CoNiO_2 hybrids composed of well-defined small nanorods and polyhedral nanocrystals. It could be noticed that the hierarchical NiCo_2O_4 - CoNiO_2 hybrids composed of well-defined small nanorods have isotropic crystal symmetry like isotropic antennas, which may play an important role in the attenuation of the microwave.

Fig. 3

The specific surface areas and porous nature of hierarchical NiCo_2O_4 - CoNiO_2 hybrids were determined by measuring nitrogen adsorption-desorption isotherms at 77 K (Fig. 3). The N_2 sorption isotherms of the uncalcined sample exhibit type *IV* isotherms with a distinct hysteresis loop in the P/P_0 range of 0-1.0, typical mesoporous materials. Moreover, the pore size shows a relatively uniform distribution at 2.40 nm, illustrating the superior mesoporous nanostructures. The specific surface area, mesopore volume, and average pore diameter are $154.84 \text{ m}^2 \text{ g}^{-1}$, $0.31 \text{ cm}^3 \text{ g}^{-1}$, 8.32 nm, respectively, indicating high surface area and porosity of the materials, which is much higher than those ($36.84 \text{ m}^2 \text{ g}^{-1}$, $0.20 \text{ cm}^3 \text{ g}^{-1}$, 3.30 nm and $23.47 \text{ m}^2 \text{ g}^{-1}$, $0.10 \text{ cm}^3 \text{ g}^{-1}$, 4.33 nm) of the calcined samples at 450 °C and 650 °C. Note that both highly porous structure and large surface area are beneficial to the performance of microwave absorbing materials. The incident microwaves entering the materials are reflected and scattered many times between the hierarchical structures and cannot escape from the limited space

until they are completely absorbed.

Fig. 4

Phase changes of spinel structures are promised to have a great impact on the EM parameters and microwave absorption of spinel absorbers. As shown in the Raman spectra (Fig. 4), the uncalcined hierarchical NiCo₂O₄-CoNiO₂ hybrids display two distinguishable peaks of carbon in the range of 1000-2000 cm⁻¹, one broad peak centered at ~ 1370 cm⁻¹ (D band), and one other relatively sharp peak at ~ 1578 cm⁻¹ (G band). According to the previous literatures [40, 41], D band is a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary, which is forbidden in perfect graphite and becomes active in the presence of disorder or finite-size crystals of graphite (nanographite crystals); G band corresponds to the E_{2g} mode due to stretching vibrations of sp² bond, which can be produced by all sp² sites and not only by graphitic carbon. It can be seen that the value of the intensity ratio of these two bands, I_D/I_G , is 0.80, much smaller than that (0.92) of pristine carbon materials [23], which is a hint that carbon components in these composites have relatively low graphitization degree, which is very consistent with the XRD result.

The Raman spectra of spinel oxides have been predicted and shown to be characterized by five peaks [42]. There are three dominant peaks labeled for spinel Co₃O₄ [43]. The high-frequency peak at 693 cm⁻¹ has been assigned to a vibration largely determined by the octahedral oxygen ions, *i.e.*, octahedral/Co³⁺ [43]. As the Co³⁺ is replaced by Ni²⁺, the peak weakens and shifts to lower frequency due to lower

concentration of the octahedral/ Co^{3+} moiety (see Fig. 4, the bands at 665 and 652 cm^{-1}). Also, Ni^{2+} substitution at octahedral sites would be expected to induce a significant amount of disorder in the lattice, particularly since the octahedral units share edges [42, 44-46]. This disorder would reduce symmetry and promote an even more dramatic reduction (as observed) of the high-frequency Raman band intensity since it arises from a highly symmetric mode. The two lower frequency Raman bands labeled in Fig. 4 are due to combined vibrations of tetrahedral and octahedral oxygen atoms [46, 47]. Their behavior is also as expected: they weaken and broaden with Ni^{2+} substitution as the concentration of tetrahedral/ Co^{2+} (491 and 462 cm^{-1}) is diluted and octahedral/ Ni^{2+} (526 and 501 cm^{-1}) forms. It can be inferred that the disorder in the lattice would induce the formation of excess dipole and dipole polarization, which is benefit for EM wave dissipation and thus results in the enhanced microwave absorption properties.

Fig. 5

From the thermogravimetric (TG) curve of uncalcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrid in Fig. 5, one can see two weight losses due to the removal of adsorbed water (about 150 °C) and combustion of carbon (starting at about 250 °C), and one weak weight increase region (transformation of CoNiO_2 to NiCo_2O_4) in the temperature range of ~ 600-800 °C, and the residual weight is about 29 wt.% at 600 °C. For calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids, the slight mass loss occurs over the whole temperature range (11 wt.% and 9 wt.% for the samples calcined at 450 °C and

650 °C, respectively), which may be accounted for the transformation of CoNiO_2 to NiCo_2O_4 . According to the mass loss, we can draw a conclusion that the weight percentage of hierarchical NiCo_2O_4 - CoNiO_2 hybrids in the uncalcined sample is ~ 29 wt.%.

Fig. 6

The more detailed elemental composition and the oxidation state of the hierarchical NiCo_2O_4 - CoNiO_2 hybrids were further characterized by XPS measurements and the corresponding results are presented in Fig. 6. By using a Gaussian fitting method, the O1s emission spectra of the calcined samples (Fig. 6a) are best fitted with three oxygen contributions, denoted as O1 (526.5 eV), O2 (528.9 eV), and O3 (530.4 eV), associating with the typical of metal-oxygen bonds [48], the oxygen in hydroxyl groups [49], and the high number of defect sites with low oxygen coordination in the material with small particle size [50], respectively. The C1s spectra of all the samples are shown in Fig. 6b to elucidate its surface composition. The peaks centered at 282 eV and 285.9 eV can be attributed to interfacial carbon atoms bonded to hierarchical NiCo_2O_4 - CoNiO_2 hybrids or carbon deposited on the surface of hierarchical NiCo_2O_4 - CoNiO_2 hybrids and C-O groups [51, 52], respectively. The above result suggests that hierarchical NiCo_2O_4 - CoNiO_2 hybrids have a small distribution of C-O functional groups in the samples [53]. The Co2p spectra shown in Fig. 6c consist of one spin-orbit doublets characteristic of Co^{2+} and Co^{3+} and two shakeup satellites (identified as “Sat.”). Similarly, the Ni2p spectra given in Fig. 6d are composed of one

spin-orbit doublets characteristic of Ni²⁺ and Ni³⁺ and two shakeup satellites. These results show that the surface of the samples has a composition containing Co²⁺, Co³⁺, and Ni²⁺ species. Therefore, the formula of NiCo₂O₄-CoNiO₂ can be generally expressed as follows: Co³⁺[Co³⁺Ni²⁺]O₄-Co²⁺Ni²⁺O₂ (the cations within the square bracket are in octahedral sites and the outside ones occupy the tetrahedral sites) [54]. In addition, the quantitative analysis of the samples based on the XPS (see Table 2) reveals that the Ni/Co atomic ratios are 0.24, 0.69 and 0.63 for the stoichiometric spinel materials (the theoretical values are 0.5 and 1.0 for NiCo₂O₄ and CoNiO₂, respectively), indicating large enrichment in Co species (rich Co₃O₄ phase) on the surface of the uncalcined sample rather than co-existence of hierarchical NiCo₂O₄-CoNiO₂ hybrids in the calcined samples. Actually, energy-dispersive X-ray (EDX) spectrum of the calcined sample at 450 °C is presented in Fig. S1. The spectrum shows that the atomic ratio of Ni/Co is ~ 1 in hierarchical NiCo₂O₄-CoNiO₂ hybrid, which is a little higher compared with the XPS result. Furthermore, from Table 2, the Co²⁺/Co³⁺ ratio of the calcined samples at 450 °C is 1.76, which suggests that the CoNiO₂/NiCo₂O₄ molar ratio is close to 3.52 in the hierarchical NiCo₂O₄-CoNiO₂ hybrids. Similarly, the Co²⁺/Co³⁺ ratio of the calcined sample at 650 °C is close to 1.20. However, the Co²⁺/Co³⁺ ratio of the uncalcined sample is 0.59, which is very consistent with the result of pure Co₃O₄ according to the Ref. [55]. Herein, XPS analysis highlights the different cation distributions on the surface of various hierarchical NiCo₂O₄-CoNiO₂ hybrids. It can be observed that after calcination at 450 °C the proportion of Co²⁺ of the uncalcined sample significantly

increases, as the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio changed from 0.59 to 1.76. Most of the Co^{3+} was reduced by carbon during the heating process ($\text{Co}^{3+} \rightarrow \text{Co}^{2+}$). However, when the sample was further calcined at 650 °C the amount of Co^{2+} decrease due to its oxidation in air at high temperature ($\text{Co}^{2+}/\text{Co}^{3+}$ ratio= 1.20). Compared with uncalcined sample, the excess of Co^{2+} in the calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids will definitely induce the disorder in the lattice, which leads to the formation of a high concentration of oxygen vacancies [55]. This surface non-stoichiometry property are benefit to increase the dipole polarization and interfacial polarization of the materials, which is benefit for the increase of microwave absorption abilities.

Fig. 7

The magnetic properties of the samples were investigated and discussed. Fig. 7 shows the saturation magnetization vs applied coercivity field (M_s vs. H_c) curves of the samples acquired at representative temperature of 300 K (insert: enlarged view at low fields). The presence of the NiCo_2O_4 spinel phase in the samples gives rise to clear hysteresis loops, owing to its ferromagnetic (FiM) nature. The experimental magnetization has been found to not saturate, even at the maximum applied field (20 kOe), as expected from the contribution of the antiferromagnetic (AFM) phases and magnetic surface disorder effects often observed at reduced dimensions [56, 57]. It can be observed that the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrid calcined at 450 °C shows apparent hysteresis loop, the H_c and M_s is 211 Oe and 2.40 emu g^{-1} , respectively. The calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrid at 650 °C and

uncalcined one also show the weak hysteresis loops with the parameters of 332 and 830 Oe for H_c , and 0.57 and 0.75 emu g⁻¹ for M_s , respectively.

Importantly, the coercivity exhibits a monotonic behaviour, reaching value in excess of $H_c = 830$ Oe for the uncalcined sample (see Fig. 7). Due to the morphology and composition of these materials, H_c is likely to have two main contributions apart from magnetocrystalline anisotropy: shape anisotropy and AFM-FiM exchange coupling. As the material transforms from nanorods to polyhedral nanocrystals, its shape anisotropy may increase significantly, leading to an increase in coercivity. Moreover, when FiM materials are exchange coupled to AFMs, and the latter has a low anisotropy (like in the case of amorphous NiCo₂O₄-CoNiO₂ hybrid), the FiM has to drag the spins of the AFM during the reversal, which costs extra energy, resulting an increased H_c . Since this an interface effect, the amount of AFM material and the degree of coupling determine the coercivity enhancement. Moreover, FiM materials are known to have magnetic disorder at the surface, which depends on the shape, that also contributes to H_c at low temperatures. Cabo et al. reported that the NiO/NiCo₂O₄/Co₃O₄ composites rich in NiCo₂O₄ exhibit M_s in the range of $M_s = 2-3.5$ emu g⁻¹ and moderate coercivities $H_c = 5-300$ Oe [58].

Fig. 8

Since the microwave absorption properties of a material is determined by their complex permeability ($\mu_r = \mu' - j\mu''$) and permittivity ($\epsilon_r = \epsilon' - j\epsilon''$), the frequency dependence of complex permeability and permittivity for the hierarchical

NiCo₂O₄-CoNiO₂ hybrids are measured using a network analyzer and shown in Fig. 8 and Fig. 9. In the whole measurement, the samples were dispersed in a flexible paraffin wax with a concentration of 50 wt.%. For the calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids at 450 °C and 650 °C, the real part of complex permittivity (ϵ') decreases from about 18.7 and 6.2 to 14.7 and 4.7, respectively, with the increase of frequency from 2 to 18 GHz, whereas the real part of complex permittivity for the uncalcined sample is almost constant over the whole frequency range with an unobvious undulation ($\epsilon' \approx 3.3$). It has to point out that a frequency dispersion behavior in the range of 2-18 GHz exists in our case, that is, their complex permittivity will gradually decrease with the increasing frequency. However, it is very interesting that ϵ'' values in calcined sample at 450 °C shows a distinguishable frequency-dependence behavior. For example, ϵ'' values first decrease gradually in the range of 2-10 GHz and then present significant fluctuations with maximum of 4.3, 5.2 and 5.8 at 10.96 GHz, 14.32 GHz and 16.56 GHz, respectively, with the increasing frequency. For the other two samples, ϵ'' values decrease slightly from 1.45 to 1.30 and 0.75 to 0.31, respectively. The superior complex permittivity for the calcined sample at 450 °C is attributed to its higher concentration of oxygen vacancies caused by the excess of Co²⁺, which could destroy the balance of the charge distribution and induce dipole polarization and interfacial polarization as well as associated relaxation at the interfaces between NiCo₂O₄ and CoNiO₂ phase. Through the cooperation of different polarization models and relaxation process, a large amount of charges can accumulated at the interfaces, especially when the oxygen vacancies possess enough

concentration, charge redistribution happens and the density of the electron clouds in the conjugated area can be easily changed, resulting in the enhanced dielectric loss of the hierarchical NiCo₂O₄-CoNiO₂ hybrids.

Fig. 9

Fig. 9 shows the μ' and μ'' of all the samples in the frequency range of 2-18 GHz. The calcined sample at 450 °C decreases from 1.01 to 0.72 over the whole frequency range with slight fluctuation. While the μ'' values first decrease from 1.22 to 0.01 at 2-10 GHz and then keep almost constant with the increasing frequency. It can be seen that complex permeability of the calcined sample at 450 °C displays the same trend as that of the other two samples. The calcined sample at 450 °C exhibits lower μ' values at relatively low frequencies, particularly in the range of 2-10 GHz, whereas higher μ'' values are distinguished over 2-10 GHz. In comparison with the uncalcined and calcined samples at 650 °C, the enhancement of μ'' for the calcined sample at 450 °C is mainly due to its ferromagnetic resonance bands located at 2-6 GHz [11]. These ferromagnetic resonances are believed to related to the natural resonances of these materials.

Fig. 10

Moreover, the frequency dependence of dissipation factors represented by the magnetic loss tangent ($\tan\delta_m = \mu''/\mu'$) and dielectric loss tangent ($\tan\delta_e = \epsilon''/\epsilon'$) for the three samples were displayed in Fig. 10. The values of $\tan\delta_e$ for the calcined sample at 450 °C are obviously improved in the frequency range of 13-18 GHz, which indicates

that the hierarchical NiCo₂O₄-CoNiO₂ hybrids may generate many defects at the interfaces, resulting in high ϵ'' and improved dielectric loss. In the middle- and high-frequency range (6-18 GHz), the values of $\tan\delta_e$ are obviously larger than those of $\tan\delta_m$, which indicates that dielectric loss plays a key role in the enhanced absorption properties of the hierarchical NiCo₂O₄-CoNiO₂ hybrids. Furthermore, the dielectric loss may also be caused by dipole polarization and interfacial polarization at microwave frequencies [2, 11]. Besides the above-mentioned defect mechanism, the hierarchical NiCo₂O₄-CoNiO₂ hybrids have numerous surface atoms with local breaking of symmetry due to the surface effect as the size decrease to nanoscale (the typical diameter and length of these nanorods are $\sim 10-20$ nm and $\sim 200-300$ nm, respectively), causing dipoles and dipole polarization. Furthermore, the well dispersed NiCo₂O₄-CoNiO₂ hybrid nanocrystals anchored uniformly on the surface of microspheres, and CoNiO₂ phase adhered to NiCo₂O₄ nanorods may introduce extra interfaces, leading to interfacial polarization and stronger associated relaxation occurring at both hierarchical NiCo₂O₄-CoNiO₂ hybrids-microsphere and CoNiO₂-NiCo₂O₄ interfaces. These polarization effects may also contribute an increase of dielectric loss.

In view of the novel nanostructure and remarkable complex permittivity properties of the hierarchical NiCo₂O₄-CoNiO₂ hybrids, the microwave absorption behaviors of the samples were investigated. The physical model for the interaction of microwave and absorber is briefly described below. When the microwave is incident on the absorber backed by a metal plate, the incident microwave is mostly consumed by the absorber

through EM wave loss mechanisms. The dominant loss of the incident microwave is absorption mechanism, in which the energy consumption is owing to the magnetic and dielectric loss. The magnetic loss is attributed to the natural resonance loss of the magnetic hierarchical NiCo₂O₄-CoNiO₂ hybrids. The dielectric loss is mainly due to the dipole polarization and interfacial polarization of the dielectric hierarchical NiCo₂O₄-CoNiO₂ hybrids.

Typically, the reflection loss (RL) value is used to evaluate the microwave absorption efficiency of absorbers, for example, the RL value of - 10 dB is comparable to 90 % of microwave absorption. The RL values of an absorber backed by a metal plate were calculated according to the transmit line theory, which is based on the measured complex permittivity and permeability at a given absorber thickness and frequency by the following equation [37-39]:

$$RL = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (1)$$

$$Z_{in} = Z_0 \left(\frac{\mu_r}{\varepsilon_r} \right)^{1/2} \tanh \left\{ j \left(\frac{2\pi f d}{c} \right) (\mu_r \varepsilon_r)^{1/2} \right\} \quad (2)$$

Where Z_{in} is the input impedance of absorber, Z_0 is the impedance of air, f is the frequency of electromagnetic wave, d is the thickness of a microwave absorber and c is the velocity of light in vacuum.

Fig. 11

Fig. 11 shows the variations of the RL values vs frequency for the three samples at

different thicknesses. The RL values for the uncalcined and calcined samples at 650 °C (Fig. 11a and 11c) cannot reach -20 dB (99% microwave absorption) within the thickness of 1.0-5.0 mm, indicating that both samples could hardly be used for the practical applications. It is clear that the absorption peaks for the calcined sample at 450 °C shift toward low frequency region as the absorber thickness increases from 1.0 to 5.0 mm. The RL values less than -10 dB and -20 dB are found in the relatively wide frequency bandwidth of 3.92 GHz and 1.36 GHz with the thickness of only 1.55 mm, moreover, an optimal RL value of -42.13 dB is achieved at 11.84 GHz. The results suggest that the calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids at 450 °C have effective absorbing characteristic in wide frequency bands, which is of great interest for the military radar.

Fig. 12

The absorber thickness is one of the critical parameters which determines the intensity and position of the maximum RL. To investigate the physical phenomenon, the quarter-wavelength matching model ($\lambda/4$) was adopted, in which the maximum RL can be achieved at a certain frequency if the absorber thickness satisfies by the following equation [59-63]:

$$t_m = n\lambda / 4 = nc / (4f_m \sqrt{|\mu_r| |\varepsilon_r|}) \quad (n = 1, 3, 5, \dots) \quad (3)$$

Where t_m is the thickness of absorber, λ is the wavelength of the electromagnetic wave, f_m is the peak frequency of the maximum RL, $|\mu_r|$ and $|\varepsilon_r|$ are respectively the modulus of the measured μ_r and ε_r at f_m , and c is the velocity of light in a vacuum.

According to the quarter-wavelength matching condition, when the absorber thickness satisfies eqn (3), the two emerging reflected electromagnetic waves from the air-absorber interface and absorber-metal interface are out of phase by 180° , leading to an extinction of them on the air-absorber interface.

Fig. 12 reveals the variations of RL curves vs frequency of the calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at 450°C . Based on the quarter-wavelength model, a simulation of the thickness (t_m) vs peak frequency (f_m) for the sample is displayed. The red symbols are the matching thickness vs the peak frequency, which were directly extracted from the RL curves above. Obviously, all the red symbols are exactly located around the $\lambda/4$ curve, which suggests that the relationship between matching thickness and peak frequency for the EM wave absorption of the calcined $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at 450°C obeys the quarter-wavelength matching condition.

Impedance matching characteristic ($|Z_{in}/Z_0| = |(\mu_r/\epsilon_r)^{1/2} \tanh\{j(2\pi fd/c)(\mu_r\epsilon_r)^{1/2}\}|$) is also an important parameter for EM wave absorption [11, 64, 65]. The impedance characteristic of the absorber should approach that of free space, resulting in zero reflection at the air-absorber interface. The frequency dependence of $Z = |Z_{in}/Z_0|$ for the calcined $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at 450°C is obtained as shown in Fig. 12, below, in which the relationship between peak frequency and Z at the matching thickness is indicated by the dashed lines. When the matching frequency is 11.84 GHz, the minimum RL can be obtained in Fig. 12 and the relevant Z is the most close to 1;

furthermore the matching thickness is 1.55 mm on the $\lambda/4$ curve. Such enhanced absorption property of the calcined NiCo₂O₄-CoNiO₂ hybrids at 450 °C is ascribed to the combined contribution from its impedance matching characteristic and quarter-wavelength interference performance.

Fig. 13

Fig. 13 shows the minimum RL value for the calcined sample at 450 °C is measured to be -42.13 dB at 11.84 GHz. The Lowest RL of the calcined sample at 650 °C is -12.83 dB at 7.68 GHz. The uncalcined sample has the worst EM absorption with the minimum RL value being -4.59 dB at 6.80 GHz. The order of the EM absorption for the three samples is ranked as follows: sample-450 °C > sample-650 °C > uncalcined sample.

The EM absorption performance of the hierarchical NiCo₂O₄-CoNiO₂ hybrids shows dependence on the Co²⁺/Co³⁺ ratio. As shown in Fig. 13, the calcined CoNiO₂-NiCo₂O₄ hybrid at 450 °C with the highest Co²⁺/Co³⁺ ratio (1.76) endows the material with the best EM absorption performance. Because of plenty of oxygen defects are formed in the calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids at 450 °C, which could destroy the balance of the charge distribution and induce dipole polarization and associated relaxation. The dipole moment is induced, which is proportional to the defect concentration in the hierarchical NiCo₂O₄-CoNiO₂ hybrids. The increased defect density will lead to enhanced dipole moments. Under the altering EM field, the enhanced dipole polarization can magnify energy dissipation,

resulting in the increase of the EM wave absorption ability. On the other hand, the electrons confined at the $\text{CoNiO}_2/\text{NiCo}_2\text{O}_4$ interfaces can move freely along the interfacial planes. The assembled movements of collective interfacial dipoles at the interfaces could enhance the EM absorption ability. Moreover, the calcined hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at 450 °C have special geometrical morphology as described in Fig. 2g. Such isotropic antenna-like structures may be available for the EM wave to penetrate the hybrids and the energy will be induced into dissipative current by random distributed isotropic antennas, and then part of the current will be consumed in the discontinuous networks. Besides, the multi-interfaces between isotropic antenna frame, matrix, and air bubbles can benefit for the microwave absorption [66]. As a result, the calcined $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids at 450 °C of the most defect content possess the best EM wave absorption ability among the three samples. Table 3 lists the results obtained in the literature for the spinel or spinel/GP absorbers. Compared with the reported spinel or spinel/GP materials, although the effective absorption coverage is not distinguished, $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ absorber has a relatively stronger RL value and thinner thickness. Besides, due to the facile and reliable synthetic method of $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ absorber, the developed material has great potential to find practical application as an EM wave absorber.

4. Conclusions

In summary, we successfully fabricated the amorphous hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids by a facile one-pot hydrothermal route. These amorphous hierarchical

NiCo₂O₄-CoNiO₂ hybrids could be further converted into urchin-like structured NiCo₂O₄-CoNiO₂ nanorods and irregular-shaped hierarchical NiCo₂O₄-CoNiO₂ polyhedral nanocrystals through air-annealing treatment at 450 °C and 650 °C, respectively. Experimental data indicate that both calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids show the improved microwave absorption properties, which is ascribed to the synergistic effect of dielectric CoNiO₂ and NiCo₂O₄ phase. In particular, calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids at 450 °C exhibited significantly enhancement in complex permittivity with respect to other two samples due to its remarkable dipole polarization and interfacial polarization of the dielectric hierarchical NiCo₂O₄-CoNiO₂ hybrids. As a result, the calcined hierarchical NiCo₂O₄-CoNiO₂ hybrids at 450 °C exhibited a minimum RL value of -42.13 dB at 11.84 GHz with a matching thickness of 1.55 mm and a relatively broad bandwidth (RL ≤ -10 dB) in 13.12-17.04 GHz range. Very interestingly, the EM wave absorption performance of the hierarchical NiCo₂O₄-CoNiO₂ hybrids shows dependence on the Co²⁺/Co³⁺ ratio. The calcined NiCo₂O₄-CoNiO₂ hybrids at 450 °C of the most defect concentration possess the best EM wave absorption ability among the samples. Considering the facile approach and high stability of the hierarchical NiCo₂O₄-CoNiO₂ hybrids, the present research also open the opportunities to fabricate other functional hierarchical spinel hybrids for various industrial applications such as energy conversion, lithium ion batteries, catalysis and electromagnetic shielding materials.

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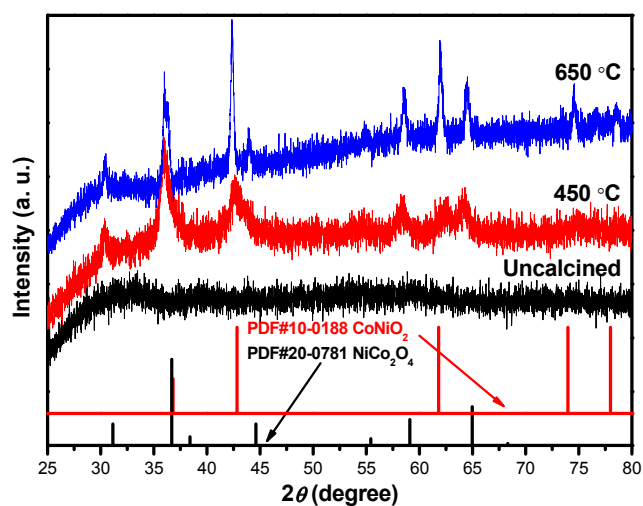


Fig. 1 XRD patterns of the hierarchical NiCo_2O_4 - CoNiO_2 hybrids.

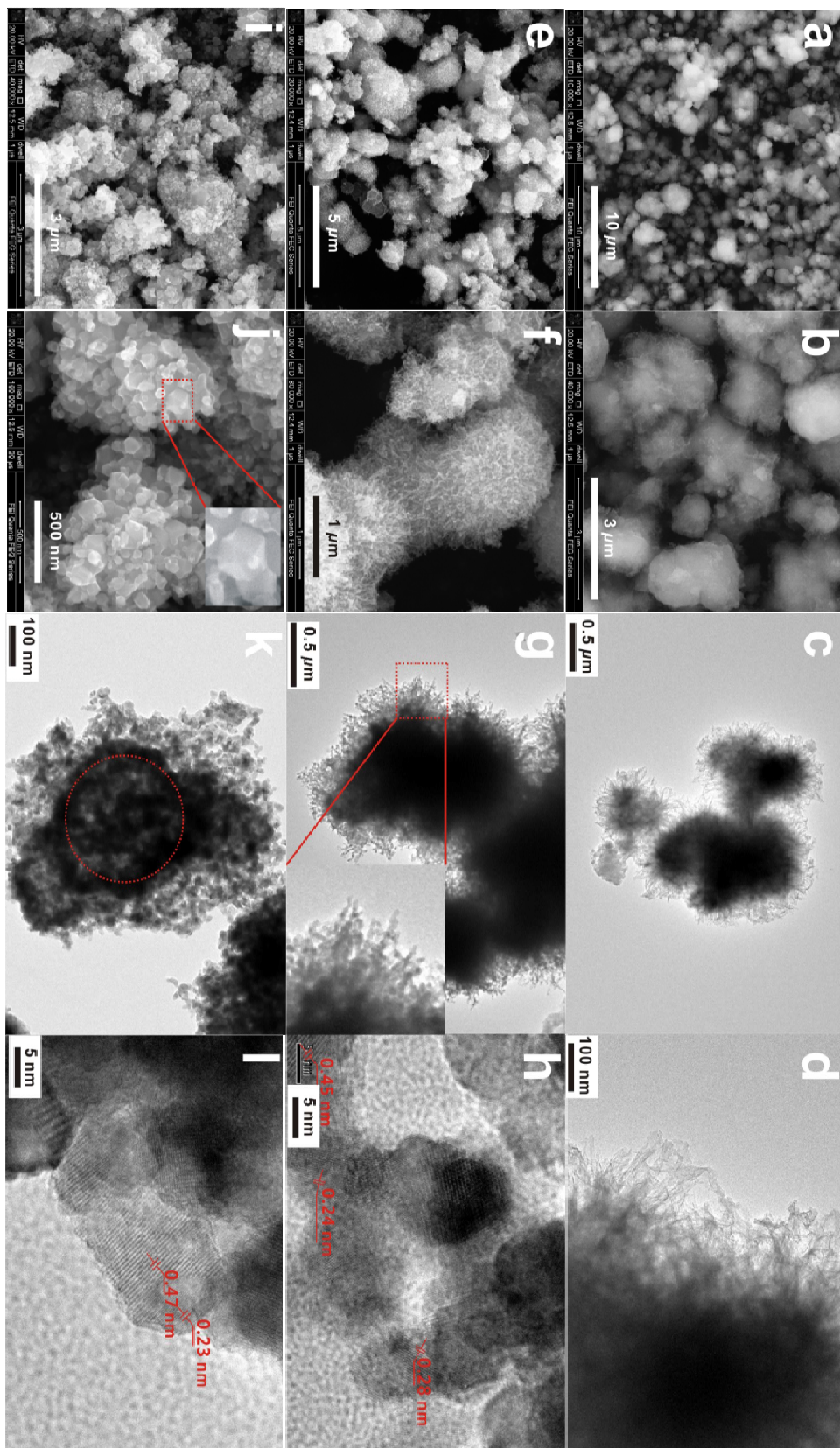


Fig. 2 SEM and FE-SEM images of (a-b) uncalcined sample, (e-f) calcined sample at 450 °C, and (i-j) calcined sample at 650 °C. insert of image (j) shows the enlarged image of a single $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ polyhedral nanocrystal. TEM and HR-TEM images of (c-d) uncalcined sample, (g-h) calcined sample at 450 °C, and (k-l) calcined sample at 650 °C. insert of image (g) shows enlarged image of $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ nanorods.

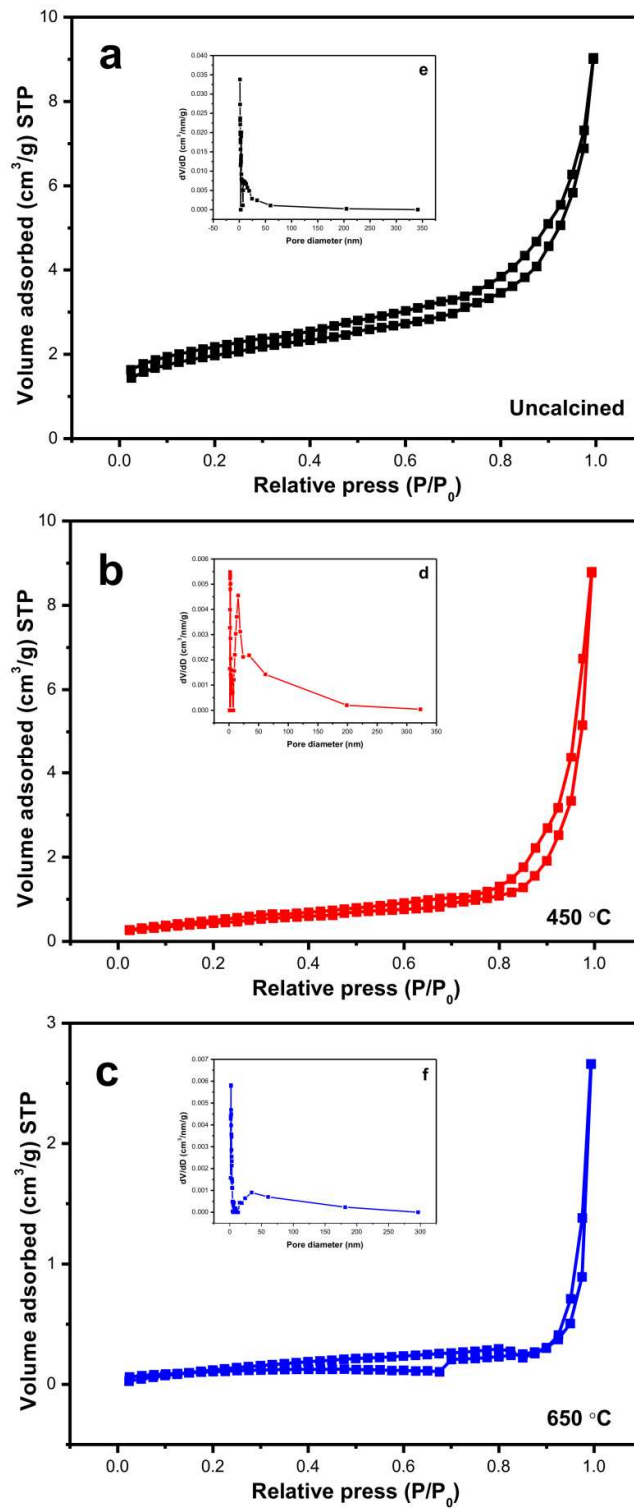


Fig. 3 N_2 adsorption-desorption isotherms and the pore-size distributions (inserts) of the hierarchical $NiCo_2O_4-CoNiO_2$ hybrids.

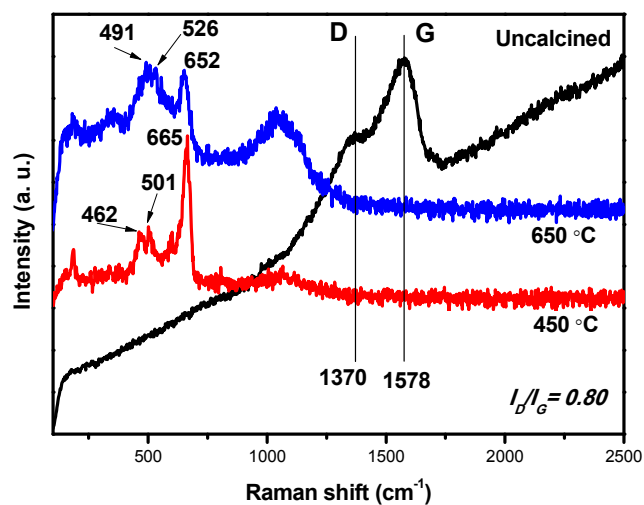


Fig. 4 Raman spectra of the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids.

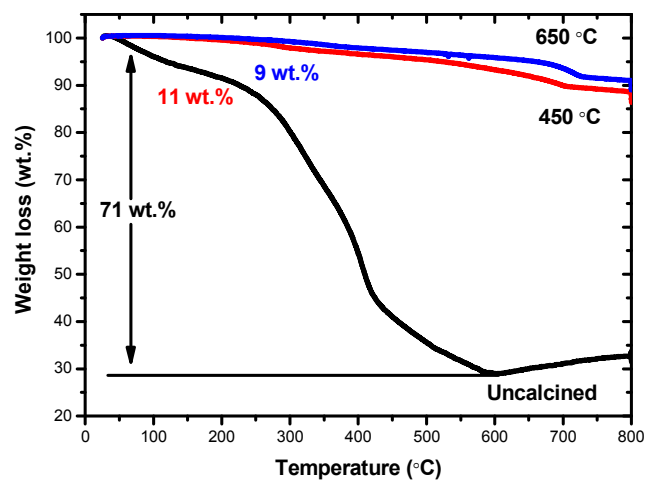


Fig. 5 TG curves of the hierarchical NiCo₂O₄-CoNiO₂ hybrids.

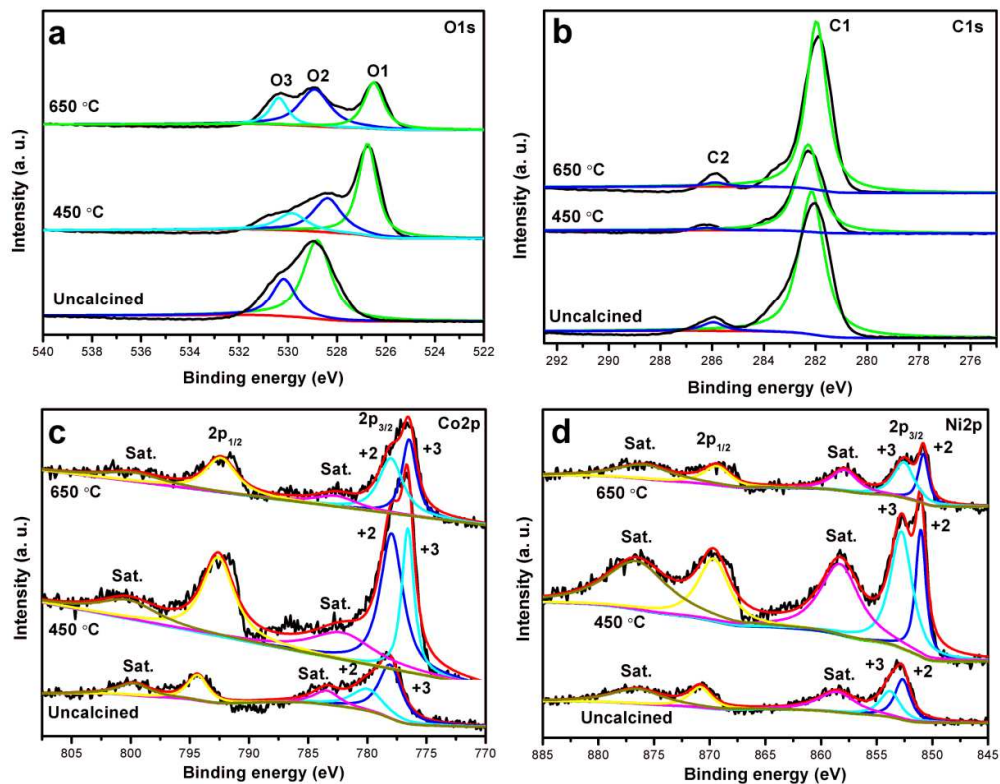


Fig. 6 (a) O1s, (b) C1s, (c) Co2p, and (d) Ni2p spectra of the hierarchical NiCo₂O₄-CoNiO₂ hybrids.

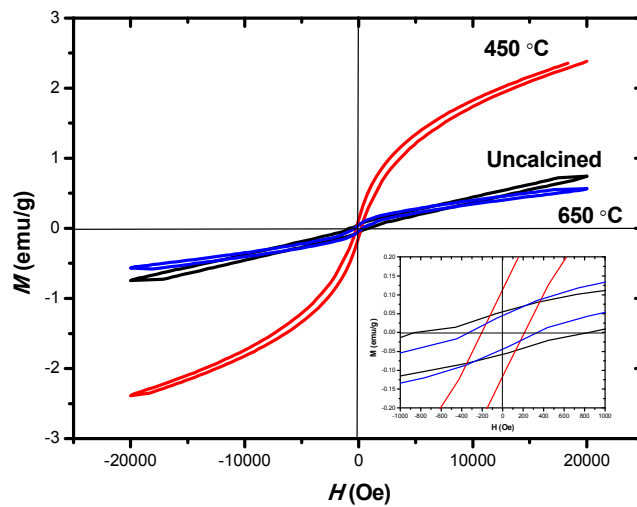


Fig. 7 Magnetic hysteresis loops of the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids.

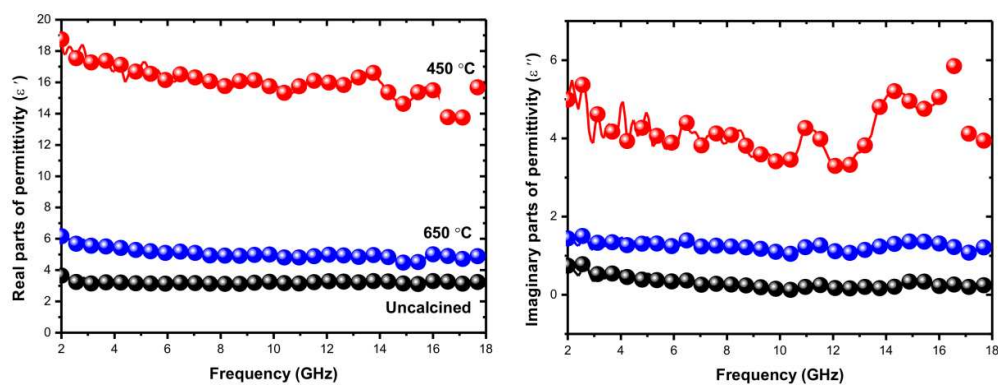


Fig. 8 The frequency dependence of complex permittivity for the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids.

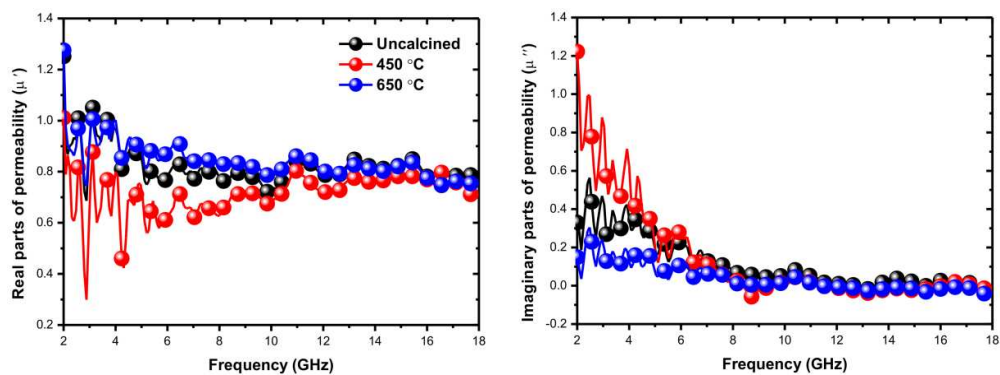


Fig. 9 The frequency dependence of complex permeability for the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids.

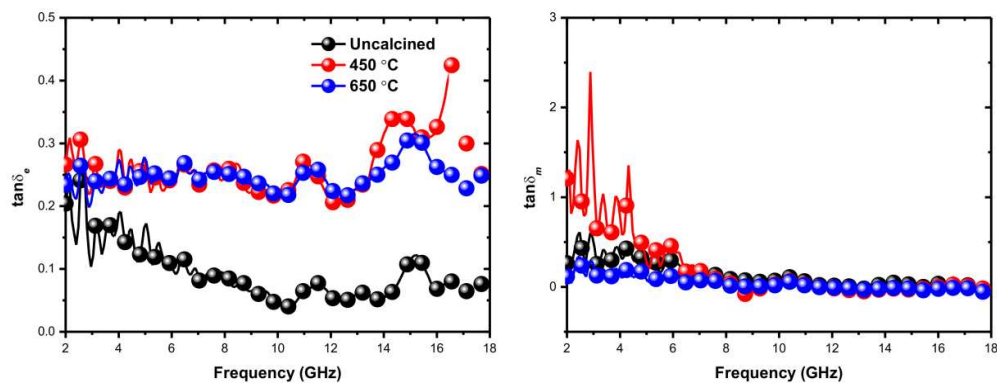


Fig. 10 The frequency dependence of dielectric loss tangent and magnetic loss tangent for the hierarchical $\text{NiCo}_2\text{O}_4\text{-CoNiO}_2$ hybrids.

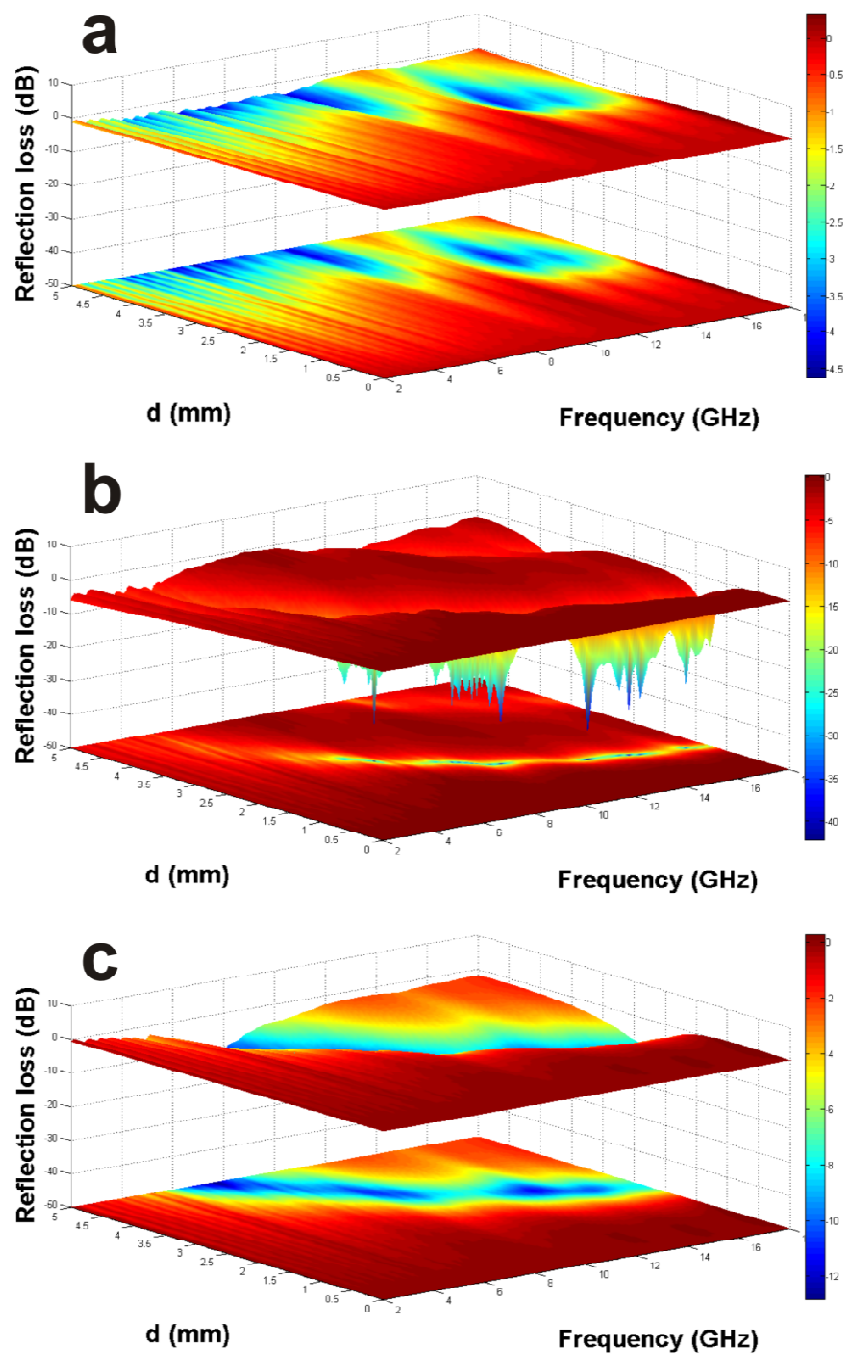


Fig. 11 Three-dimensional representation of RL values for the paraffin wax composites (50 wt.%): (a) uncalcined sample, (b) calcined sample at 450 °C, and (c)

calcined sample at 650 °C.

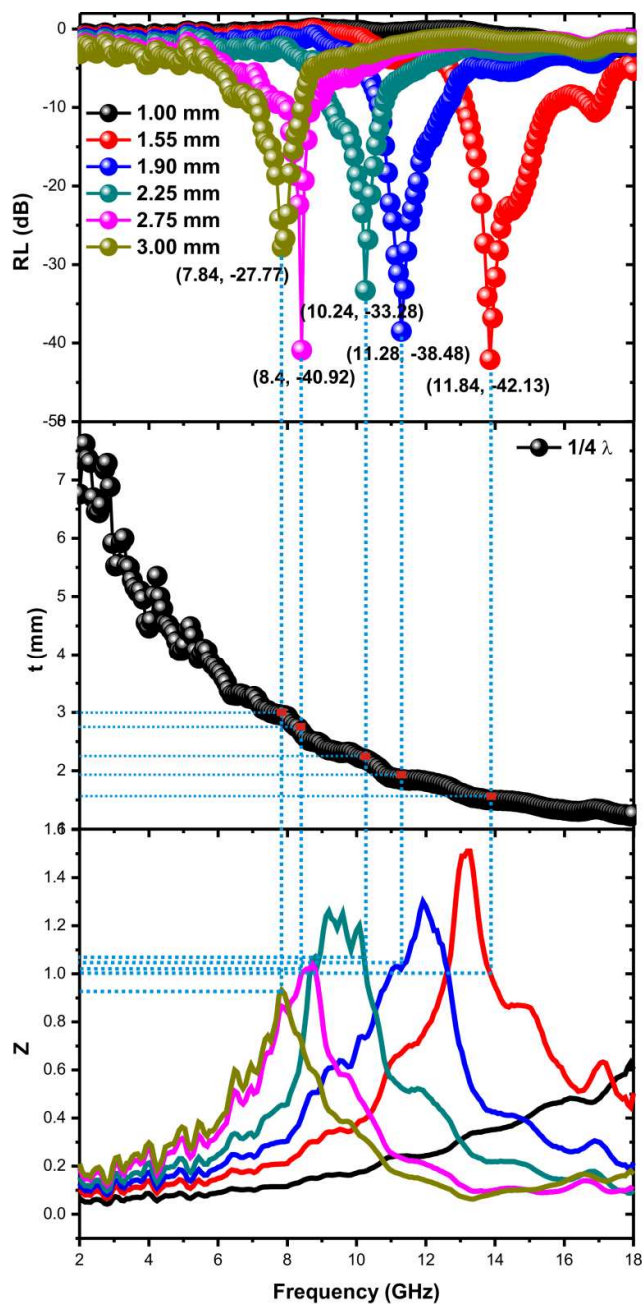


Fig. 12 The frequency dependence of RL values for the calcined sample at 450 °C; simulations of the absorber thickness vs peak frequency for the calcined sample at

450 °C under $\lambda/4$ condition; the modulus of normalized input impedance ($|Z_{in}/Z_0|$) for the calcined sample at 450 °C.

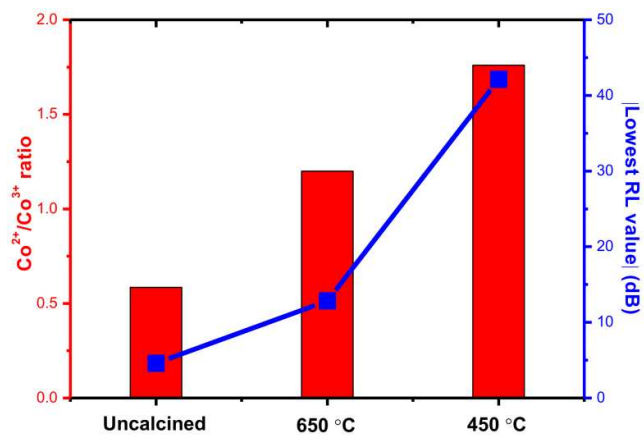


Fig. 13 The relationship between the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio and the absolute lowest RL value.

Table 1 Textural properties of the hierarchical NiCo₂O₄-CoNiO₂ hybrids.

Samples	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
Uncalcined	154.84	0.31	8.32
450 °C	36.84	0.20	3.30
650 °C	23.47	0.10	4.33

Table 2 Binding energies (eV) and surface atomic ratios of the samples.

Samples	Ni2p _{3/2}		Co2p _{3/2}		Ni/Co	Co ²⁺ /Co ³⁺
	Ni ²⁺	Ni ³⁺	Co ³⁺	Co ²⁺	(atomic ratio)	(atomic ratio)
Uncalcined	852.7 (54.8%)	853.8 (45.2%)	778.1 (63.0%)	780.0 (37.0%)	0.24	0.59
450 °C	851.0 (34.2%)	852.8 (65.8%)	776.6 (36.2%)	778.0 (63.8%)	0.69	1.76
650 °C	850.8 (40.3%)	852.6 (59.7%)	776.5 (45.4%)	778.0 (54.6%)	0.63	1.20

Table 3 EM absorption of some representative spinel absorbers.

Samples	Minimum RL value (dB)	Frequency coverage (GHz) (RL < -10 dB)	Thickness (mm)	Percentage (wt.%)	Matrix	Ref.
NiCo ₂ O ₄	-35.76	4.18	1.50	50	paraffin	36
NiFe ₂ O ₄	-22.5	~1.5	3.00	25	paraffin	25
NiFe ₂ O ₄	-24	4.5	3.50	25	paraffin	26
CoFe ₂ O ₄ /G P	-18.5	3.70	2.00	60	paraffin	27
RGO-MnF e ₂ O ₄ /PVF	-29.0	4.88	3.00	5	paraffin	3
NiFe ₂ O ₄ /G P	-29.2	4.40	2.00	60	paraffin	28
NiCo ₂ O ₄ -C oNiO ₂	-42.13	3.92	1.55	50	paraffin	This work

TOC:

