

Simultaneous modulation of vacancy and heterointerface of double-matrix phosphorus doped NiSe₂/CoSe₂ composite for “dual-core-driven” electromagnetic wave absorption

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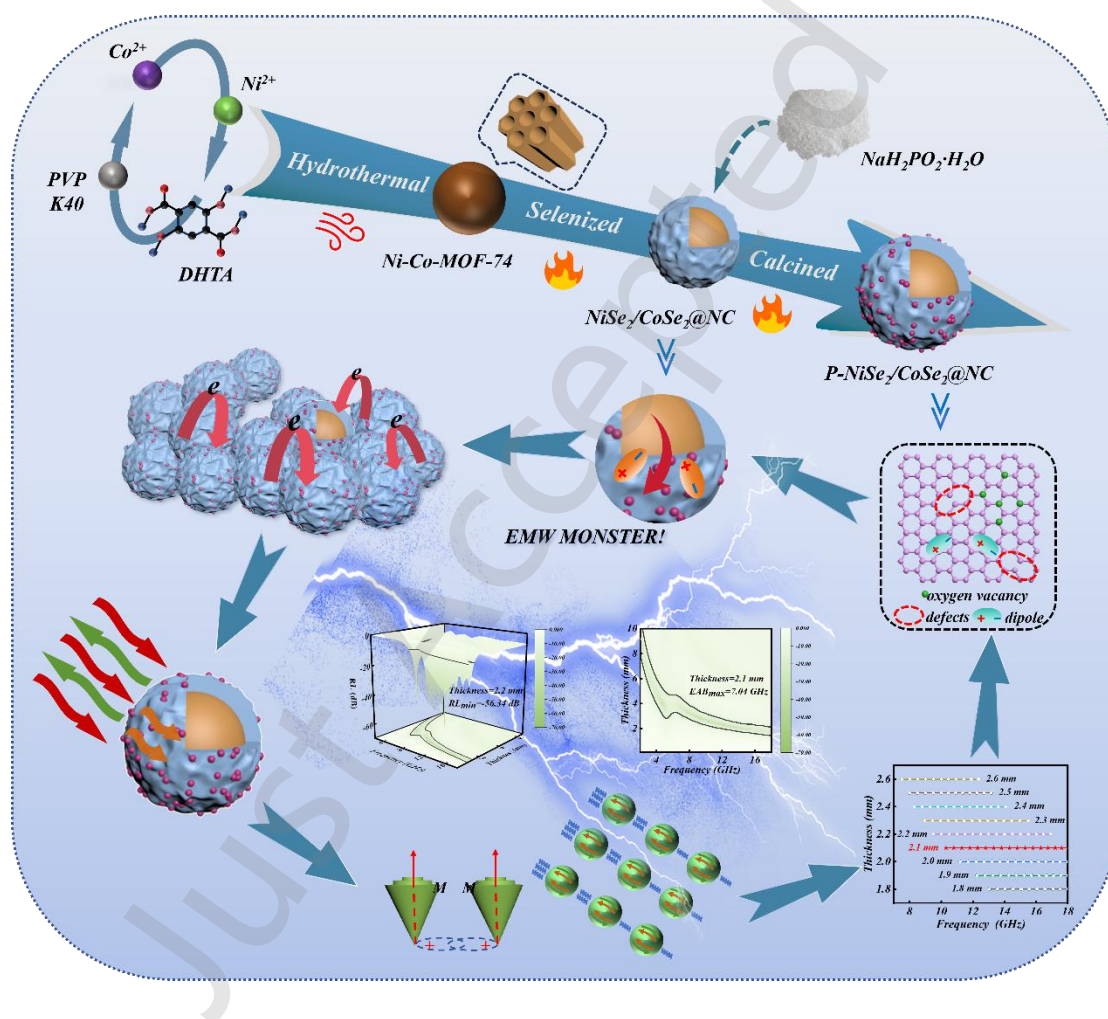
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Graphical abstract



Research Article

Simultaneous modulation of vacancy and heterointerface of double-matrix phosphorus doped NiSe₂/CoSe₂ composite for “dual-core-driven” electromagnetic wave absorption

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Abstract

In order to achieve an efficient response of the absorber to electromagnetic waves (EMW), vacancy modulation and phase optimization of the composites are crucial. In this study, a phosphorus-doped vacancy modulation and phase interface

optimization engineering was designed to prepare nine MOFs-derived metal selenides@carbon double matrix P-doped NiSe₂/CoSe₂@NC (PNCS). The optimal solution of the EMW absorber mechanism was explored by modulating the doping concentration and the calcination temperature. The selection of safeguarded priorities in this work is of constructive significance for the rationalization of EMW absorber preparation is constructive. Upon achieving a ratio of one third of the phosphorus source in the selenide matrix, the calcination temperature of 400 °C introduces moderate defects, thus providing the sample with optimal EMW absorption capabilities. With a maximum effective absorption bandwidth of 7.04 GHz at an ultra-thin matching thickness of 2.1 mm. This value covers the entire X and Ku bands within a usable thickness of 2.6 mm, which is significantly superior to other samples of the same type samples. The “dual-core-driven” strategy of heterogeneous interfaces and oxygen vacancies optimizes dielectric relaxation and polarization, supporting a prospective effect on the development and wide application of novel EMW absorbers.

Keywords: phosphorus doping, vacancy modulation, phase interface, electromagnetic wave absorption, dual-core-driven

1. Introduction

In recent years, with the rapid development of the fifth generation communication technology and the popularization of various electronic devices, substantial electromagnetic waves (EMW) emissions are incurred, and excessive EMW contributes to the escalating environmental pollution^[1-3]. More seriously, it can subconsciously damage the human organs and affect the health of human beings (and even develops cancer)^[4-5]. Therefore, the development and utilization of high-performance EMW absorbing materials should not be delayed.

As it stands, pooling and synergizing the EMW absorption capacity of multiple components is usually used to achieve the overall advantage of composites (1+1>2 or 1+1+1>3, etc.)^[6]. Maxwell-Wagner-Silas theory explains that interface polarization, primarily due to charge redistribution at dissimilar dielectric property and conductivity junctions, amplifies the EMW response and absorption in sample surfaces^[7]. Metal organic frameworks (MOF)-derived carbon-based materials with

unique microstructures, synergistic effects, and ease of modification have been identified as a reasonable choice for the preparation of high-performance EMW absorbers^[8]. Initially, post high-temperature annealing process, MOF-derived EMW absorbers fabricate a carbon matrix augmenting the dielectric loss against EMW through enhanced conductivity.^[9] Secondly, given their expansive specific surface area due to a loose and porous framework, MOFs foster an increased propagation route for EMW within the substance, promoting comprehensive reflections and scattering, thus amplifying electromagnetic energy dissipation^[10]. Thirdly, MOFs primarily comprising of metal ions and organic ligands selectively interact with EMW via electronic transitions and energy level decoupling. Precise control over MOF composition and structure is achieved by manipulating MOF species, doping elements and carbonization temperature, thereby optimizing sample impedance matching characteristics.^[11]

Single MOF components (phase) fall short in meeting contemporary requirements, so transition metal dihalides (TMDCs) gaining interest due to their uniform anchoring on MOFs, exhibiting impressive dielectric properties, flexibility, and chemical stability^[12]. Uniformly dispersed TMDCs can also be densely stacked to form a three-dimensional conductive network, which is regarded as an EMW absorber with great potential^[13]. For the time being, research on TMDCs has mainly focused on elemental sulfur, but the superiority of transition metal diselenides (XSe_2 , $X=Ni, Co, Mo, V, \dots$) has been relatively under-analyzed^[14-15]. In fact, adhering to the Mendeleev's periodic table, elements below the same main group have stronger metal abundance than those above. Their propensity for relinquishing outermost electrons facilitates electron cloud alteration into Lewis acidic null orbitals, promoting free electron mobility and transfer efficiency. Typically, selenium manifest stronger conductivity than sulfur due to its "lower" position, leading to enhanced dielectric loss and improved EMW attenuation and loss resistance^[16].

The manipulation of defects, along with component optimization, has proven to be an effective strategy for enhancing electromagnetic wave absorption performance. Recent involvement with vacancy structures has expanded our understanding of

defect phenomena and has cultivated focused research on anion vacancy engineering^[17]. Typically, dielectric loss constitutes an important part of the EMW attenuation mechanism of absorbers and is commonly associated with conduction loss and polarization^[18]. Regarding conduction loss, it is widely accepted that oxygen vacancies can remodel the energy band structure by narrowing the band gap and act as shallow donors, thereby further increasing the intrinsic conductivity of TMDCs^[19]. The prevailing view is that vacancies serve as primary high-energy metastable defect centers, potentially facilitating electron pair formation around metal atoms and thus enhancing polarization loss under an external electromagnetic field, though relevant studies remain scarce^[20]. The above information provides sufficient theoretical support for the effective response of oxygen vacancies to EMW absorption and is expected to play a more important role in novel absorber systems.

Despite progress through examination of the stated EMW absorbers, persistent constraints persist: i. refinement largely relies on component addition, seldom addressing defectively active site modulation, inhibiting subsequent advancement; ii. composition discussions remain elementary in comparative works, disregarding physical phase transition effects on absorber efficiency; iii. most investigations incorporate multiple absorption mechanisms, however there are scarce studies analyzing the tuning and regulation of diverse mechanisms in multi-component composites.

In order to address the general limitations in the study of novel EMW absorbers, a phosphorus-doped selenide vacancy modulation and phase interface optimization strategy was designed in this work. Different doping environment gradients were prepared to obtain P-NiSe₂/CoSe₂@NC composites using Ni-Co-MOF-74 as a precursor and NaH₂PO₂·H₂O as phosphorus source for the induced generation of oxygen vacancies. The analysis of the samples on the action mechanism of EMW was used to discuss the mechanism of optimization in synthesis schemes. The established of mass ratio and temperature preference secured during preparation is constructive for the industrialization of EMW absorbers. P-NiSe₂/CoSe₂@NC-1:3 as superior EMW absorbing material achieves a strong minimum reflection loss (RL_{min}) of -56.34

dB at an ultrathin thickness of 2.2 mm, while the maximum effective absorption bandwidth ($EAB_{\max}$) stretches to 7.04 GHz when matched with a thickness of 2.1 mm, which covers high-frequency half of the X band and the entire Ku band. In this work, from the inherent advantages of MOFs and XSe_2 materials in TMDCs, together with the controllable tuning of vacancies and crystalline phases, the “dual-core-driven” strategy of $NiSe_2-CoSe_2-NC$ heterointerface polarization and oxygen vacancy polarization is realized. The tailored composite material boasts excellent EMW absorption attributes, offering foreseeable potential for utilization.

2. Experimental Section

2.1 Materials

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), 2, 5 dihydroxyterephthalic acid (DHTA, $C_8H_6O_6$), sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$), and selenium powder (Se) were purchased from Macklin Ltd., anhydrous ethanol (C_2H_5OH) and N, N-dimethylformamide (DMF, C_3H_7NO) were purchased from Sinopharm Chemical Reagent Co. Polyvinylpyrrolidone (PVP K40, $(C_6H_9NO)_n$) was purchased from Shanghai Yuanye Biotechnology Co. All chemicals mentioned in this work were of analytical grade (AR) and were used without further purification.

2.2 Preparation of Ni-Co-MOF-74 precursor

The precursor was prepared by a simple one-step hydrothermal method. In a typical synthesis system, 5 mmol of $NiCl_2 \cdot 6H_2O$, 5 mmol of $CoCl_2 \cdot 6H_2O$ and 1 mmol of DHTA, 4 g of PVP K40 were dissolved in 40 mL of DMF, respectively, and stirred for 0.5 h, labeled as solution A and solution B. Subsequently, solution B was added dropwise to solution A and stirred for 0.5 h. The resulting mixed solution was transferred to a 100 mL Teflon-lined autoclave and reacted at 100 °C for 24 h. Finally, the precipitate was collected by centrifugation, washed alternately with deionized water and ethanol, and the precipitate was dried under vacuum at 60 °C for 12 h. The product was labeled as Ni-Co-MOF-74.

2.3 Preparation of NCS

The Se powder and Ni-Co-MOF-74 precursor were fully ground and mixed in a

mortar at a mass ratio of 1:1, transferred to a porcelain boat and pushed into a tube furnace with Ar atmosphere, and calcined at 400 °C for 2 h (the heating rate was 2 °C · min⁻¹) to obtain the NiSe₂/CoSe₂@NC composites (abbreviated as NCS).

2.4 Preparation of PNCS

Utilizing NaH₂PO₂·H₂O as a phosphorus source, the P-NiSe₂/CoSe₂@NC was fabricated at various doping concentrations and temperatures conforming to the principle of control variables. As a doping raw material, the mass of the phosphide always should be less than that of the selenide. NaH₂PO₂·H₂O and NiSe₂/CoSe₂@NC were thoroughly ground and mixed in a mortar in mass ratios of x (x is symbolized by the numbers 1-5, signifying the doping mass ratio of 1:5, 1:4, 1:3, 1:2.5 and 1:2), transferred to a porcelain boat and pushed into a tube furnace under Ar atmosphere, and calcined at y for 2 h (y is denoted by the letters A-D, representing the calcination temperatures of 300, 400, 500 and 600 °C, the heating rate was 5 °C · min⁻¹), and the resulting product was labeled PNCS-xy.

2.5 Characterization

The physical phase of the samples was analyzed by X-ray diffractometer (XRD) with Cu-K α radiation (Rigaku Ultima IV, λ = 0.15418 nm). A scanning electron microscope (SEM, JEOL JSM-7800F) with elemental spectra was used to take micro-morphologic images of the samples. The crystallization and topography of the absorbers were tested using a transmission electron microscope (TEM, JEOL JEM-2100). The state of existence of elemental bonding was analyzed by an Al K α X-ray source at 1486.6 eV using a Thermo Fisher ESCALAB 250Xi spectrometer. A Renishaw InVia Plus micro-Raman spectroscopy system equipped with a 50 mW 532 nm DPSS laser was used to obtain Raman spectra of the composites over the range of 0-3000 cm⁻¹. Thermogravimetric analysis was performed on a SDT Q600 analyzer (testing range from room temperature to 800 °C with a heating rate of 10 °C · min⁻¹). The electrochemical behaviour of samples were characterized using an electrochemical analyzer employing a standard three-electrode set up (CHI 760e, working electrode: Ni/NiZn@C, counter electrode: Pt foil, reference electrode: Ag/AgCl). EIS tests were conducted at frequencies of 10⁵-10⁻² Hz with a signal

perturbation of 10 mV.

2.6 EMW absorption performance test

The test sample powder was thoroughly mixed with paraffin wax in an appropriate and identical proportion, paraffin wax can neutralize the dielectric properties of the absorber as an insulator, making the impedance of the absorber more similar to that of the air environment. This avoids the problem of excessive conductivity of the selenide, which could lead to impedance mismatch. The mixture was conditioned to form black rings of about 2 mm thickness by means of a kind of cylindrical mold (outer diameter of 7 mm and inner diameter of 3.04 mm). The relative permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and relative permeability ($\mu_r = \mu' - j\mu''$) of the samples in the bandwidth range of 2-18 GHz were tested by the coaxial method on a vector network analyzer (VNA, AgilentN5222A). Using the classical transmission line theory, the $RL_{\min}$ values can be calculated for different matching thicknesses and frequencies to evaluate the absorption and loss capability of the material for EMW. The calculation formula is as follows^[21]:

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

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left| j \left(\frac{2\pi f d}{c} \right) \sqrt{\epsilon_r \mu_r} \right| \quad (2)$$

where Z_{in} and Z_0 denote the input impedance of the standard EMW absorber and the characteristic impedance in free space, respectively, f is the frequency of electromagnetic wave radiation, d is the matched thickness of the sample, and c is the propagation speed of the electromagnetic wave in free space.

Using CST Studio Suite software, the RCS of the sample on a 300 mm $\times$ 300 mm PEC substrate was simulated. The time/frequency-domain solver yielded an optimal thickness of 2.2 mm and absorption frequency of 12.88 GHz. RCS data as functions of angle and frequency were plotted in 2D and polar images, allowing direct comparison with the bare PEC to assess absorption and stealth performance.

3. Results and Discussion

3.1 Design and Preparation

As shown in Fig. 1a, the schematic diagram briefly describes the preparation process of PNCS-xy. As a surfactant and structure-directing agent, PVP K40 selectively adsorbs onto the crystal nucleus surface to inhibit excessive aggregation, promoting the formation of uniform and dispersed microspheres, while regulating the particle size and the regularity of morphology. Utilizing a simple one-step hydrothermal method to synthesize loose and porous Ni-Co-MOF-74 precursor, subsequent phase transformation and recrystallization during selenide annealing produced NCS. Under high-temperature conditions, the organic ligands in the MOF structure escape in the gaseous form. The remaining Ni/Co bimetallic species coordinate with selenium atoms to form diselenides. A mass ratio of 1:1 can uniformly coat a layer of selenide particles on the MOF substrate, ensuring the topological purity of the phase and avoiding the agglomeration of impurities^[22]. Modulation of vacancy defects by using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as a phosphorus source, and the PNCS-xy composites were obtained by controlling different concentration (mass ratio: phosphorus source: selenide=1:5-1:2) of phosphorus elements and doping temperatures (300-600 °C).

3.2 Structural analysis

The XRD spectra of PNCS-xy with different doping concentration are shown in Fig. 2a₁. The diffraction peaks at 29.8°, 33.4°, 36.7°, 42.7°, 50.5°, and 52.9° corresponded to the (200), (210), (211), (220), (311), and (222) crystal planes of NiSe_2 , respectively. Located at 34.7° and 51.8° diffraction peaks are used to represent the (111) and (311) crystal planes of CoSe_2 ^[23] (XRD patterns of the Ni-Co-MOF-74 precursor are shown in Fig. S1^[24]). It can be seen that the trend of the diffraction peaks is basically the same with increasing phosphorus doping at a fixed calcination temperature of 400 °C. The peak positions show a slightly shifted orientation towards lower diffraction angles, which may be attributed to the induced generation of oxygen vacancies. When the doping ratio exceeds 1:2.5, Ni_2P and Co_2P phases begin to appear, which can reduce the conduction and polarization loss of material, and cause impedance mismatch. The authors will elaborate on mechanism in detail later. By the time the mass of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ reaches half of that of selenide, the pristine NiSe_2 and CoSe_2 are no longer present, and are instead replaced by the hexagonal phase of the

phosphide, which mainly attributed to the substitution of selenium sites by excess phosphorus atoms. The additional electron shell of selenium endows metal selenides with metallic or narrow-bandgap semiconducting behavior, facilitating high carrier mobility and conductivity. In contrast, most metal phosphides are wide-bandgap semiconductors with poor conductivity. Furthermore, the high crystal symmetry of Ni_2P and Co_2P restricts defect-dipole responses, thereby suppressing polarization losses^[25].

The effect of doping temperature on the products is discussed in Fig. 2a₂, where the diselenide phase is still maintained unaltered when the temperature is below 400 °C. Whereas the products exist as $\text{P-Ni}_{0.85}\text{Se/Co}_{0.85}\text{Se@NC}$ and $\text{NiSe/Ni}_2\text{P/Co}_2\text{P}$ when the temperature is increased to 500 °C and 600 °C, respectively, which originate from the positive feedback mechanism of temperature increase on the “P-Se” substitution. Calculations of the NCS and PNCS-xy lattice constants in Tab. S1 corroborate the our conjecture about vacancies. At the highest possible phosphorus doping ratio, PNCS-3B exhibits stability in the selenide phase and vacancy induction. A noteworthy average lattice constant of 5.994 signifies a significant amount of lattice defects introduced due to maximized oxygen vacancy insertion^[26]. Observing similar pattern appears in doping temperature, lattice dimensions for PNCS-3A/3C/3D exhibit further shrinkage versus PNCS-3B, indicating a high degree of defects in the main sample again.

In Raman spectra, the blue G band at 1580 cm^{-1} is used to represent the sp^2 hybridization of carbon atoms in ideal graphite, while the red D band at 1350 cm^{-1} characterizes defects, edges, heteroatoms, and disordered structures within the graphite layers^[27]. Therefore, the commonly used values of I_D/I_G are correlated with the degree of graphitization of the sample: the higher I_D/I_G value, the lower the degree of graphitization of the sample and the higher the internal defects density^[28]. It is evident in Fig. 2b that the PNCS-3B has the highest value of I_D/I_G , which implies that it has the highest number of internal defects (later confirmed: oxygen vacancy), matching the results discussed in the XRD patterns. In addition, the Raman spectrum shows a “P Peak” (indicated by the triangle shape) around 700 cm^{-1} , which also

implies the successful introduction of the element phosphorus^[29]. The average lattice constants and the values of I_D/I_G with error bars for each type of samples are visualized in the form of histograms and dotted line plots in Fig. 2c. It is evident that only PNCS-3B achieves “double high” values, superior average lattice constant as well as I_D/I_G , the uniform error bars indicate the statistical accuracy of the data calculation. As shown in Fig. 2d, the temperature-mass change relationship of the samples was examined using a thermogravimetric analyzer (TGA) to evaluate the stability of the EMW absorbers under high-temperature conditions^[30]. The slight decrease in mass in the range of 0-150 °C can be attributed to the loss of water, whereas the combustion of the MOF carbon substrate, selenide-oxide transformation and sublimation of some products at high temperatures led to a significant decrease in the sample mass when the temperature was above 150 °C. Significantly, as temperature rises, the mass losses of absorbers diminish progressively for doping ratios escalation. This is primarily stems from the creation of oxygen vacancies increases the disorder of the atomic arrangement, which in turn induces a change in the group entropy and vibrational entropy, conferring a superior thermodynamic stability to the material, enabling it to operate stably at higher temperatures and maintain excellent performance. The TGA curves of the products with doping ratios exceeding 1:3 and calcined at 500/600 °C, demonstrating significantly more sample loss at high temperatures, and limits its potential for further applications.

XPS spectra are used to accurately reflect the chemical energy bands and chemical state changes^[31]. The XPS full spectrum of PNCS-3B is shown in Fig. 2e₁, labeling the seven major elements, including C, O, N, Ni, Co, Se, and P. Characteristic peaks in the C 1s spectrum (Fig. 2e₂) at 286.3 eV, 284.8 eV, and 282.3 eV correspond to C-Ni/Co, C-C/C=C, and C-O, respectively^[32]. The N 1s and O 1s peaks in the full spectrum respond to the remaining N and O elements after pyrolysis of the samples as well as bound water in air^[33]. The peak at 532.3 eV in Fig. 2e₃ is attributed to oxygen vacancies induced through doping. It should be emphasized that the samples were prepared and treated at high temperature, under which physically adsorbed oxygen and surface hydroxyl groups are generally decomposed and removed. Therefore, the

contribution of adsorbed oxygen and hydroxyl species to the peak at 532.3 eV can be reasonably excluded^[34]. The different chemical states of elemental N are presented in Fig. 2e₄^[35]. Both Ni and Co elements have both +2 and +3 chemical valences as well as weaker satellite peaks (Sat.), which can be found in common in the Ni 2p and Co 2p spectra (Fig. 2e₅-e₆). The slight shift of the metal peak towards lower binding energy once again proves the existence of the vacancy structure: oxygen vacancies cause the system to generate additional free electrons, and increase the density of the metal valence electron cloud. This is attributed to the loss of O²⁻ ions results in an excess of local electrons, which tend to transfer to adjacent metal sites. Electron enrichment increases the density of electrons around the metal cations, weakening the attraction of the atomic nucleus for the inner electrons^[36]. The Se 3d spectra (Fig. 2e₇) are composed of three peaks at 59.3 eV (Se 3d_{5/2}), 55.7 eV (Se 3d_{3/2}), and 55.0 eV (SeO_x), where SeO_x mainly originates from the partial oxidation of selenides exposed to air^[37]. As shown in Fig. 2e₈, the multiple bonding of P elements in the P 2p spectra also verified the rationality of the doping process^[38]. The XPS spectra of the comparison samples with different doping ratios and calcination temperatures are detailed in Fig. S2-S9. With the increase of the ratio and temperature, phosphorus dominance in composites emerges. The subsequent diminution and absence of P-Se peaks signifies the accomplishment of phosphide substitution within selenium. In addition, it can be found that the peaks of P-Ni/Co are shifted to the direction of high binding energy with the increase of the doping mass ratio, implying more phosphorus element occupies the position of selenium atoms, and the presence of metal phosphide tends to be stabilized. The authors indeed observed variations in the full width at half maximum (FWHM) and peak shape of the P-Ni/Co peaks under different doping ratios and calcination temperatures. With increasing P doping, the P 2p peaks of Ni/Co phosphides exhibit progressively narrower FWHM and higher symmetry, indicating a more uniform phosphide phase and ordered local chemistry^[39]. In contrast, lower doping or calcination temperature yields broader, asymmetric peaks, suggesting coexistence of P-Se/P-Ni/Co species along with amorphous regions or defect sites. These trends align with the phase evolution of the XRD patterns in the previous text,

and SEM, TEM images in the following text.

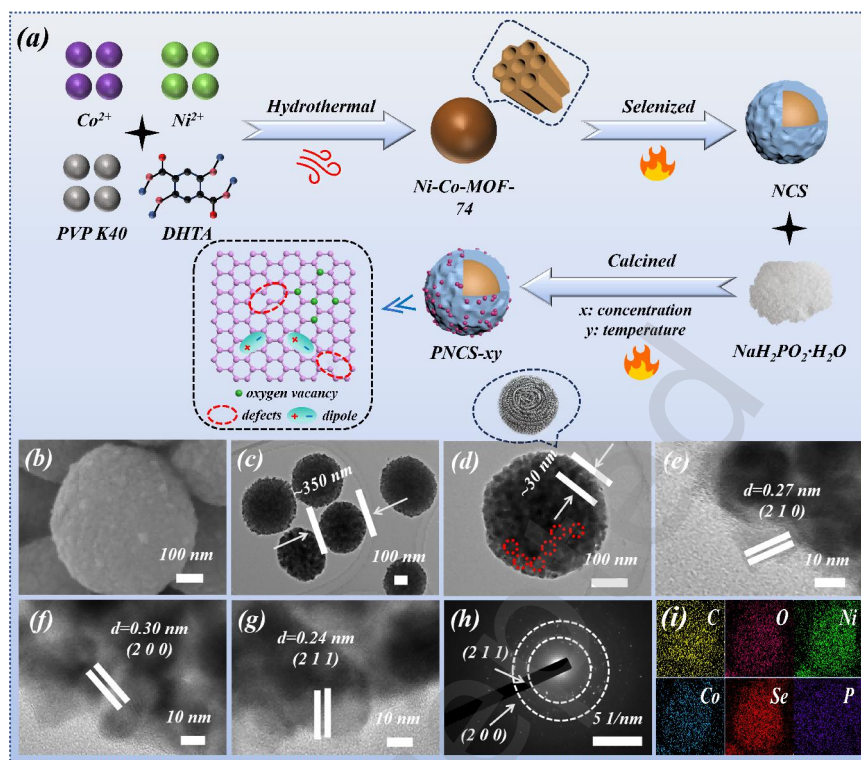


Fig 1. a) Schematic illustration of the synthesis process for PNCS-xy. b) SEM, c-d) TEM, e-g) HRTEM, h) SAED images and i) EDS element mapping of PNCS-3B.

In the field of view of the scanning electron microscope, Ni-Co-MOF-74 presented as uniformly dispersed microspheres with sizes around 330 nm (Fig. S10). After high temperature selenization, the microsphere surface started to become rough and the particle size slightly increased to obtain NCS (Fig. S11). The morphological evolution is attributed to the interspaces among in-situ formed selenide nanocrystals, as well as the wrinkles and lattice distortion induced by high-temperature pyrolysis. Subsequently, phosphorus was introduced into the interior of the particles by the calcination process to form oxygen vacancy defects. Oxygen vacancies can lead to unsaturated coordination of surface atoms, triggering local stress release and surface reconstruction, thereby forming abundant nanoscale uneven, steps and pores. The surface roughness was further increased, resulting in “wire-like spheres” PNCS-3B with a size of about 350 nm and abundant vacancy defects (Fig. 1b). The EDS images in Fig. 1i show the elemental species and distribution of the composites, in agreement with the results obtained in the XPS spectra described previously. SEM images of the

samples with doping ratios of 1:5, 1:4, 1:2.5 and 1:2 are displayed in Fig. S12-S15, where it can be seen that the roughness of the microsphere surfaces is enhanced with the increase of the doping ratio. The effect of calcination temperature on the sample morphology is more obvious, as shown in Fig. S16-S18, it is difficult to ensure the stable morphology of PNCS at too high or too low temperature. Especially at 600 °C, the microspheres exhibited extensive fragmentation and size irregularities. Surface impurities were evident concurrently, closely related to the crystalline state transformation and significantly influenced the EMW absorption of the samples^[40].

The low magnification TEM images (Fig. 1c-d) show the core-shell structure of the PNCS-3B microspheres with dimensions almost identical to those of the SEM images. The spheres comprise an exterior coating 30 nm in thickness, while the loose and porous core structure originates from the internally interlocked “metal-DHTA” framework with abundant micropores and open metal site of the bimetallic MOF. The porous structure is a product of inherent porosity, template effect, and gas escape during conversion. Owing to its long molecular length and high rigidity, DHTA forms coordination bonds with metal that support channels, which can not collapse at high temperatures, and endow it with ample active sites for EMW multiple reflections and scattering^[41]. Furthermore, the author considers that the oxygen vacancies induced by phosphorus doping cause the surface atoms to be in an unsaturated coordination state, leading to the release of local stress and surface reconstruction, resulting in a nanoscale “wire-like” morphology. Under high power transmission electron microscopy, the connected stripes are uniformly arranged around the lattice edge region of the composite, and the measured crystal spacing of 0.27 nm, 0.30 nm and 0.24 nm corresponds to the (210) (200) and (211) crystal planes, respectively (Fig. 1e-g)^[42]. Since both NiSe₂ and CoSe₂ belong to the cubic crystal system and possess similar lattice constants, they are difficult to fully distinguish by HRTEM. Therefore, these lattice fringes are generally considered to originate from bimetallic selenides phases, which is consistent with the overlapping diffraction peaks observed in XRD patterns. Fig. 1h shows the analysis of the selected area electron diffraction (SAED) pattern, where the diffraction spots are clearly visible and connected to each other to

form concentric rings indicated by dashed lines, which represent the (211) and (200) crystal planes^[43]. Different shades and fonts signify alterations in crystallographic phases, derived from changes in doping concentration and calcination temperature, subsequently influencing differing types of crystalline planes and lattice fringes (Fig. S19-S20)^[44-45]. Yellow denotes the $\text{Ni}_2\text{P}/\text{Co}_2\text{P}$ phases [e.g., (111) and (210) crystal planes in Fig. S19d₃-e₃], green for the $\text{Ni}_{0.85}\text{Se}/\text{Co}_{0.85}\text{Se}$ phase [e.g., the (101) facet in Fig. S20b₃], red for the NiSe phase [e.g., the (200) facet in Fig. S20c₃], and the most abundant white color denotes the presence of large amounts of the $\text{NiSe}_2/\text{CoSe}_2$ phase.

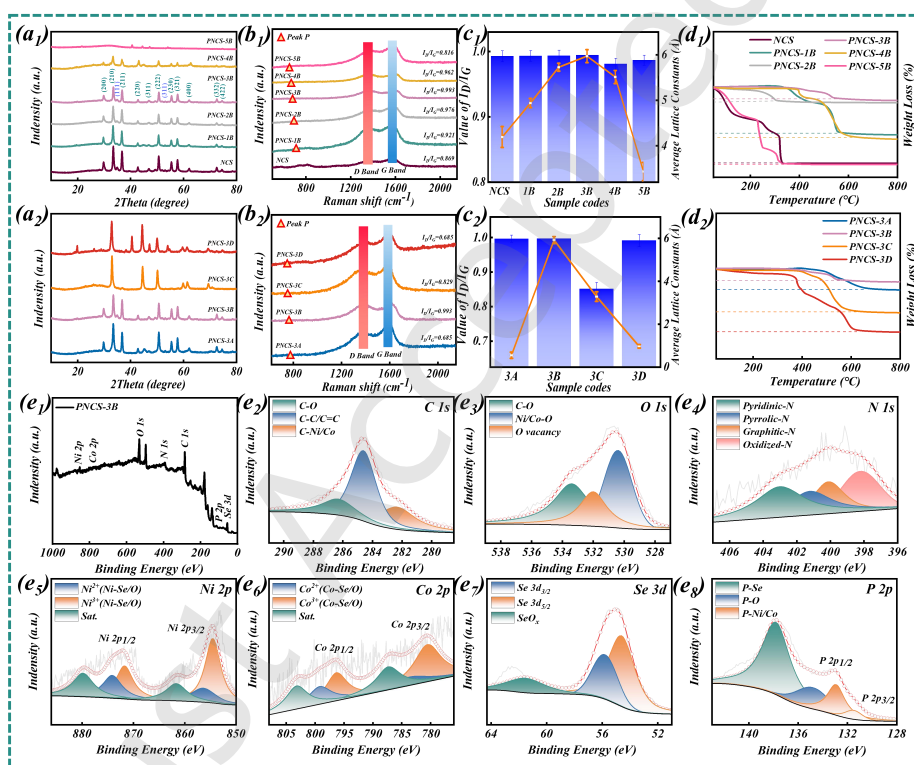


Fig. 2 a) XRD patterns, b) Raman spectra, c) value of I_D/I_G and average lattice constants graph with error bars, d) TGA curves of NCS and PNCS-xy. e) XPS spectra of PNCS-3B.

3.3 Electromagnetic response properties

The complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and complex permeability ($\mu_r = \mu' - j\mu''$) are commonly used to characterize the ability of a material to absorb and attenuate EMW. Both are relative to the vacuum constants under an alternating electric field^[46]. The real parts ϵ' and μ' correspond to the ability of the sample to store EMW, and the imaginary parts ϵ'' and μ'' are often regarded as related to the dissipation ability of

EMW^[47]. As shown in Fig. 3a, ϵ' of the samples with different doping ratios all decrease with increasing frequency. PNCS-3B exhibits a particularly pronounced decrease (from 9.7 to 5.6), which is attributed to the fact that the Debye polarization behavior of the dipole lags behind the frequency change of the incident EMW, showing a typical dielectric relaxation phenomenon^[48]. In the low-frequency region, the contribution of interface polarization is significant; as the frequency increases, the dipole polarization gradually lags behind, and the interface polarization also weakens due to the limited space charge mobility. The decrease in ϵ' is the result of the combined effect of Debye relaxation and the response of interface polarization. ϵ'' in Fig. 3b exhibits a similar trend to ϵ' and is accompanied by multiple resonance peaks, which is characteristic of dielectric loss. Especially when the frequency increases above 13 GHz, the slight increase in ϵ'' is the result of dipole reorientation, multiple distinct relaxation peaks correspond to the abundant polarization relaxation process^[49]. Accordingly, the high electrical conductivity, a large number of heterogeneous interfaces, and doping-induced vacancy defects together confer the highest dielectric loss angular tangent $\tan\delta_\epsilon$ ($\tan\epsilon''/\epsilon'$) for PNCS-3B (Fig. 3c), contributing to the highly efficient absorption and attenuation of the EMW. Compared to other comparison samples doped at 300, 500 and 600 °C, calcination of the ideal sample at 400 °C entitles it higher ϵ' , ϵ'' and $\tan\delta_\epsilon$ values, similar trends are shown for doping mass ratios above 1:2.5, the strong superiority of PNCS-3B is unquestionable.

Significant fluctuations observed across μ' and μ'' of all the samples reveal highlights in Fig. 3e-f, while the variation curves of the magnetic loss angular tangent $\tan\delta_\mu$ ($\tan\mu''/\mu'$) are shown in Fig. 3g. It is a remarkable fact that the curves of both $\tan\delta_\epsilon$ and $\tan\mu_\epsilon$ are consistent with the trend of the corresponding imaginary part due to the synergistic influence promoting the loss capability of the samples^[50]. Typically, the magnetic interactions between the components inside the nanoparticles constitute a complex network of magnetic losses leading to natural resonant dissipation, which mainly occurs in the low-frequency region (2-8 GHz)^[51]. Whereas the oscillations in the high-frequency region (8-18 GHz) imply that the exchange resonance starts to dominate under the interaction between the electric and magnetic fields^[52]. In addition,

in order to further investigate the magnetic loss mechanism, we calculated the C_0 value using Eq. (3)^[53]:

$$C_0 = \mu''(\mu')^{-2} f^{-1} = 2\pi\mu_0 d^2 \sigma \quad (3)$$

where μ_0 is the vacuum permeability, d is the matching thickness, and σ is the electrical conductivity.

It is well known that a strong eddy current loss effect occurs when the value of C_0 is not affected by frequency^[54]. The curve of PNCS-3B at high frequencies is almost parallel to the x-axis (Fig. 3h), which means that the authors attribute the eddy current loss also in the context of the magnetic loss mechanism of the samples. As mentioned before, the change patterns of magnetic property parameters of comparison samples are not essentially different from that of the PNCS-3B, which may be related to the intrinsic properties of selenides/phosphides.

The Cole-Cole theory expression is derived by applying the Debye relaxation model to correct the non-uniformity of the relaxation process in actual materials, which lies in introducing a relaxation distribution index to describe the dispersion of relaxation times. It is usually calculated using the following equation^[55]:

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2} \right)^2 \quad (4)$$

where ε_s is the static dielectric constant and ε_∞ is the optical dielectric constant.

As shown in Fig. S21, with the doping environment transitions from mild to extreme, the polarization density of the products first increases and then decreases. When the bimetallic diselenide phase remains stable, the polarization semicircle is significantly larger than that after selenium substitution, serving as a semi-quantitative indicator to evaluate the respective contributions of vacancy polarization and interfacial polarization to EMW absorption performance. The inherent advantage of selenides in tunable defects plays a greater role than heterointerfaces. The high density “semicircle” facets observed in PNCS-3B illustrate its superior polarization properties compared to the reference samples. These unique sites effectively alter local electrostatic potential leading to multiple polarization relaxation mechanisms^[56].

Consequently, the polarization “semicircle” with a relatively regular radius of optimal PNCS-3B are believed to correlate with synergistic effect of multiple dielectric loss mechanisms (e.g., oxygen vacancy-induced dipole polarization and interfacial polarization occurring at heterogeneous interfaces, etc.)^[57].

Accordingly, the polarization relaxation process of the material is evaluated using the Debye theory, calculated as shown in Eq. (5)^[58]:

$$\varepsilon' = \frac{1}{2\pi\tau} \frac{\varepsilon''}{f} + \varepsilon_{\infty} \quad (5)$$

where τ is the polarization relaxation time.

According to the Eq. (5), ε' is a primary function with respect to ε''/f with a slope of $1/2\pi\tau$ and an intercept of ε_{∞} . In other words, the linear relationship between ε' and ε''/f usually represents the only correlation between dipole polarization and dielectric loss^[59]. As shown in Fig. S22, the tails of the ε' - ε''/f curves for all the samples can be fitted to a long straight line segment, while presenting a nonlinear state in the low-frequency region from 2 to 8 GHz. Therefore, dipole polarization does not exclusively contribute to dielectric loss. Rather, it is an interplay between interfacial polarization and other mechanisms that induce significant conduction loss, aligning with our prior examination of polarization “semicircle” radius.

Attenuation constant is one of the important indexes to evaluate the effective EMW absorption performance of composite materials. A higher α generally means stronger dielectric and magnetic loss, which is beneficial for energy attenuation. However, an excessively large α may lead to poor impedance matching, causing serious surface reflection and weakening absorption. Conversely, an overly low α results in insufficient EMW dissipation. Therefore, excellent EMW requires a moderate and stable α value that can balance impedance matching and attenuation. The α value of effective EMW absorber needs to be above 200 generally. The values of α were calculated for different samples using Eq. (6)^[60]:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu'\varepsilon'' + \mu''\varepsilon')^2 + (\mu''\varepsilon'' - \mu'\varepsilon')^2}} \quad (6)$$

The unique advantage of PNCS-3B can be clearly seen in Fig. 3d: the α value

shows a steady upward trend with increasing frequency, exceeding 150 at 12.8 GHz and reaching 305.8 at high frequencies. The PNCS-3B exhibits strong attenuation even in the low frequency region. The attenuation capability in the low frequency range of the S band is even comparable to that of other samples in the high frequency range of the Ku band. Doping concentration markedly influences product attenuation capacity, except when maintaining a fixed doping mass ratio of 1:3. Beyond this ratio, the maximum α value reaches a maximum around 100 (Fig. 3d₁). Conversely, fluctuations in temperature exhibit marginal impact on attenuation capability, with maximum α values exceeding 200 for doping at 200, 400, and 600 °C (Fig. 3d₂). Fig. 3i portray the average propagation constants for the nine identical sample sets. They underscore that PNCS-3B exhibits higher EMW attenuation than all other comparison samples across an extensive bandwidth of 2-18 GHz, demonstrating its promising potential as an effective EMW absorber.

The normalized characteristic impedance $Z(|Z_{in}/Z_0|)$ is another important index for evaluating the performance of the EMW absorber. The current consensus among researchers is that when the Z value tends to be 1, EMW goes more into the interior of the sample rather than being reflected^[61]. Fig. S23 present the 2D impedance match maps for diverse doping levels PNCS-xy. The area enclosed by the solid and dashed lines signify Z parameters within the range of 0.8 to 1.2. It is obvious that the normalized characteristic impedance first tends to match and subsequently mismatch as the amount of introduced phosphorus element increases. The PNCS with doping ratios of 1:5, 1:4, and 1:3 have superior impedance matching properties with a maximum impedance matching area of $\approx 13\%$ (Fig. S23b-d). And the impedance matching of the doped samples at 300 °C was also maintained at a high level when the fixed doping ratio was 1:3 (Fig. S23g). However, due to the synergistic effect of multiple mechanisms and parameters, such as interfacial polarization, dipole polarization, attenuation constant, and conductivity (metal abundance), PNCS-3B should achieve the most outstanding EMW absorption performance, which the authors will discuss in detail later. In addition, a clear fluctuating trend of first increasing and then decreasing can be observed in the Z - f curves (Fig. S24).

Combined with the previous analysis of the variation in α , the authors consider that an excessively high α is often accompanied by a significant increase in the imaginary part of the electromagnetic parameters, which enlarges the discrepancy between the Z_{in} and Z_0 , thereby preventing incident electromagnetic waves from effectively entering the material for attenuation. Therefore, an ideal EMW absorbing material requires a balance between a high value of α and good impedance matching^[62]. The impedance matching of the pure precursor is shown in Fig. S25g. The region with impedance matching less than 10%, which mainly originates from the carbon framework and the loose and porous internal structure. The obvious disadvantages compared to NCS and PNCS-xy are due to their lower dielectric loss and magnetic loss (Fig. S25a-b). Moreover, the single component results in insufficient heterointerfaces, and there are almost no defects such as vacancies, which prevent it from achieving effective attenuation of EMW (Fig. S25c-d).

The authors picked out four samples (PNCS-3A/3B/3C/4B) with relatively optimal EMW absorption parameters and examined their electrochemical properties, which further validated the viability of employing PNCS-3B as an outstanding EMW absorber, and revealed the intrinsic mechanism from an electronic perspective. As depicted in Fig. 3j₁, because of the difference in dielectric properties among the constituents of the composite material, the space charge amassed at the micro-nano interface polarize under the applied magnetic field. PNCS-3B exhibits the largest real and imaginary parts of dielectric capacitance (C_d' and C_d''), signifying that the fabricated P-doped selenide/carbon double matrix composites possess the strongest polarization loss. The comparatively low electrolyte capacitance (C_e' and C_e'') value of PNCS-3B, might predominantly stem from its remarkable charge transfer efficiency, which aligns with the dielectric capacitance analysis (Fig. 3j₂). Dielectric polarization and conduction loss collectively enhance the EMW effective attenuation of absorbers, serving as key evidence for the synergistic effect that improves EMW absorption performance^[63]. The analysis of the electrochemical properties of the absorbers not only further clarify the intrinsic EMW absorption mechanism by revealing the electronic structure, charge transport behavior, and polarization

characteristics of PNCS, but also endows the absorber with great application potential beyond EMW. More importantly, such multifunctional exploration is expected to broaden its practical applications in fields of energy, including supercapacitors, fuel cells, electrocatalysis, and other interdisciplinary areas.

As a general principle, the quarter-wavelength theory is used for optimizing the thickness of absorbing materials. Based on the propagation characteristics of EMW in the medium and the principle of destructive interference. Since the losses incurred by the absorbent during the EMW absorption process can be disregarded, the core formula and related derivations are as follows^[64]:

$$t_m = \frac{n\lambda}{4} = \frac{nc}{4f_m \sqrt{|\mu_r||\epsilon_r|}} (n = 1, 3, 5 \dots) \quad (7)$$

where t_m is the matching thickness and f_m is the peak frequency, $|\epsilon_r|$ and $|\mu_r|$ are the modulus of the relative dielectric constant and the relative permeability, respectively.

When the phase difference between the reflected and absorbed waves is $\pi/2$ (i.e., 180°), t_m and f_m satisfy the functional relationship of the above equation. The two EMWs cancel each other inside the absorber and produce the minimum return loss value accordingly. The total intensity of reflected waves has significantly decreased, and a large amount of EMW can enter the material interior for further loss and attenuation^[65]. The t_m - f_m curves of PNCS-3B are simulated based on the $\lambda/4$ matching model, and the fitted data are in high agreement with the experimental results (Fig. S24). Corresponding thickness and frequency aligned with the point of minimum reflection loss, suggesting that the quarter-wavelength theory is satisfied for the EMW absorption of PNCS-3B. Notably, the relationship between incident wave frequency and characteristic impedance is shown in the bottom of Fig. S24. The frequency at which the best EMW absorption performance occurs for all samples corresponds to the position of $Z \approx 1$. The Z value of the ideal sample PNCS-3B fluctuates in the range of 0.8 to 1.2 within the bandwidth of 9.0-15.8 GHz (8.96-18 GHz), which matches with the position where $RL_{\min}$ (12.8 GHz) and $EAB_{\max}$ are demonstrated to occur.

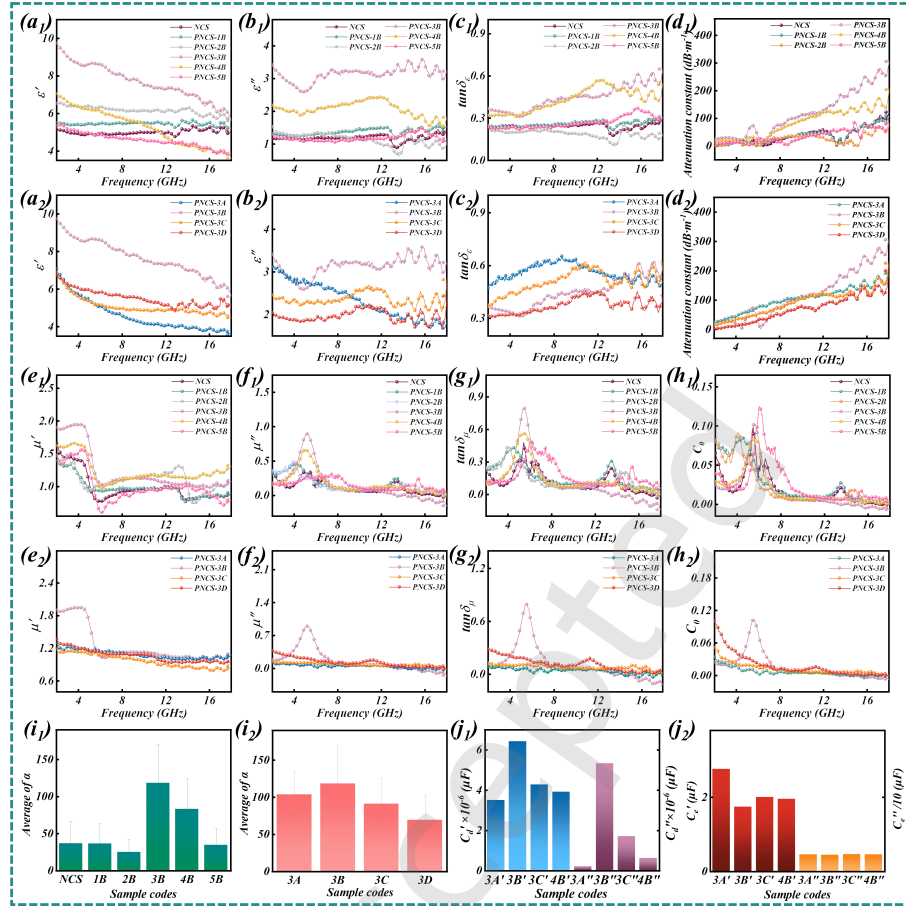


Fig 3. a) real part and b) imaginary part of the dielectric constant, c) tangent to the dielectric loss angle, e) real part, f) imaginary part of the permeability constant, g) tangent to the magnetic loss angle, h) C_0 curves, d) attenuation constant (α), and i) average of α for NCS and PNCS-xy. j) dielectric capacitance and electrolyte capacitance of PNCS-3A/3B/3C/4B.

3.4 EMW absorption performance

The EMW absorption performance of PNCS with different doping ratios were calculated using the classical transmission line theory. Single component Ni-Co-MOF-74 suffers from extremely weak EMW absorption performance due to the lack of stable attenuation mechanisms such as interfacial polarization and defect-induced dipole polarization. Although it can achieve 6.72 GHz of EAB, the corresponding matching thickness of 6.4 mm is hardly applicable in practical scenarios (Fig. S25e). Furthermore, its $RL_{\min}$ is only -16.35 dB, which is far below the criterion for conventional EMW absorbers (Fig. S25f). The 2D EAB and 3D RL images are shown in Fig. 4a₁-a₆ and S26 a-f. The pure NCS contains a large number

of TMDCs heterogeneous interfaces. Compared with the homogeneous interfaces, the differences in electronic properties and bonding states in the heterogeneous interfacial regions lead to inhomogeneous spatial charge distribution, which generate electric dipole moments^[66]. The carrier aggregation and polarization relaxation process, resulting in interfacial polarization within an alternating electromagnetic field, exhibit potential for EMW absorption efficiency (-42.14 dB, 5.36 GHz). However, its mechanism for EMW attenuation mainly originates from the isolated bimetallic selenide interfaces, excessive matched thickness also exhibits practical limitations on the use of these types (6.7 mm, 7.7 mm)^[67]. Phosphorus significantly intensifies the attenuation and decay rates of pristine selenide samples due to lattice distortions and the proliferation of oxygen vacancy defects, thereby optimizing the polarization effect and the impedance matching properties of the samples. Meanwhile, by optimizing the energy band structure, the conductivity of the material has been improved, and the intrinsic mechanism affecting EMW absorption has been refined. Trace phosphorus doping induces oxygen vacancies, yet the poor synergy between vacancy polarization and interfacial polarization leads to negligible enhancement in EMW absorption^[68]. The EMW absorption capability peaks at sufficiently doped PNCS-3B: the $RL_{\min}$ is -56.34 dB when the matching thickness is 2.2 mm (Fig. S26d); while the $EAB_{\max}$ below -10 dB extends to 7.04 GHz when the sample thickness is 2.1 mm (Fig. 4a₄). As the old proverb says: “too much is not enough”, when the doping ratio of more than 1:3, the composition of the crystal phase changes. The generated Ni_2P and Co_2P phases exhibit lower electrical conductivity than the corresponding transition metal selenides, which directly reduces the overall dielectric properties and conduction loss of the composite. The weakened conduction loss and dielectric polarization behavior further impair the EMW attenuation capacity, while the balanced impedance matching condition established in the selenide-based system is also disturbed.

Although both have constructed relatively sufficient heterojunctions of bimetallic compounds, then triggered by the “butterfly effect” caused by the sample conductivity reduction, impedance mismatch, attenuation ability, polarization ability, and a series of negative effects. The phosphorus atom is small in size and has a dense lattice,

quickly filling the lattice voids and being hard to escape, making it difficult to induce defects; and strong electronegativity results in high ion bond energy when forming ionic bonds with metals, reducing the ionic conductivity of the product, while also preventing the occurrence of polarization, which is devastating to the performance of the absorber^[69]. In addition, the authors set the doping ratio of 1:3 as a fixed amount and the calcination temperature as a variable, and explored the mechanism of the calcination temperature on the absorption ability of EMW (Fig. 4a7-a9 and S26 g-i). The observation indicates that the doping products tested at 300 °C, 500 °C, and 600 °C exhibit a degree of EMW absorption capabilities, but there is still a big gap compared with the ideal sample PNCS-3B. In a side-by-side comparison of the samples obtained by calcination at the three temperatures, the EMW absorption of PNCS-3B is relatively strong, which may be attributed to the fact that the material still maintains the main phase of the diselenide unchanged at 300 °C. Calcinating at 500 °C and 600 °C, NiSe₂/CoSe₂ transformed into Ni_{0.85}Se/Co_{0.85}Se and NiSe/Ni₂P/Co₂P structures devoid of transition metal diselenides, thereby diminishing their efficacy as TMDCs and EMW absorption properties are weakened. By comparing the RL_{min} values of the absorbers before and after the reaction threshold, it can be seen that the inherent advantage of selenides remains significant. After introducing a sufficient amount of phosphorus source to induce oxygen vacancies, the RL_{min} of the samples remains consistently below -50 dB, with a relatively low matching thickness.

For the sake of further analyzing the EMW absorption characteristics of PNCS, we selected four samples with better performance to draw 2D RL curves and demonstrate the unique advantages of PNCS-3B (Fig. 4b). Fig. 4c elucidates the correspondence between the matching thickness, RL_{min}, and incident wave frequency, with the most outstanding RL_{min} value of PNCS-3B achieved at 2.2 mm, and the location where RL_{min} appears begins to move towards the lower frequency region as the thickness increases. The analysis of the similarity law for EAB_{max} in Fig. 4d is more intuitive, the 2.1mm thickness sample obtained high-frequency half of the X band and the entire Ku band EAB_{max}. The EAB range of PNCS-3B covers the entire X

and Ku bands in the available matching thickness range below 2.6 mm. The EMW absorption properties of the samples at different ratios are depicted in histograms in Fig. 4e. The highest prism corresponds to the PNCS-3B, demonstrating efficient attenuation and loss of EMW. The superiority of the present study over other similar works is demonstrated in Fig. 4f^[70-77]. The similarities are mainly in the application areas, research directions, microstructures, morphologies and paraffin filling proportion, etc. It is corroborated that authors organically integrates the unique structure, defect advantages and interfacial synergy, and regulates the PNCS-3B composite absorber based on other classic works, thereby achieving the unification of the strong reflection loss and the wide effective absorption bandwidth, particularly the thinner matching thickness meets the engineering requirements of modern society, which demonstrates a strong potential for application. Vacancy-induced dipolar polarization exhibits a more pronounced promotion effect on EMW absorption: it yields a thinner matching thickness, a wider effective bandwidth, and a shift of the effective absorption band toward lower frequencies, better meeting current engineering demands. In contrast, after the selenide is converted into phosphide, despite the retention of abundant heterointerfaces, the absorption performance deteriorates significantly.

As discussed above, the superior EMW absorption performance of the material is closely correlated with the heterointerface. To further analyze the correlation between the evolution of space charge behavior and EMW absorption, density functional theory (DFT) calculations were performed to investigate the discrepancies in electrostatic potential and charge density of PNCS-xy. Fig.4g₁ depicts the electrostatic potential distributions of NiSe₂ and CoSe₂ over the shared (200) crystal plane; the intrinsic potential discrepancy between the two phases gives rise to a bipolar interfacial electric field (BIEF) near the heterointerface, which effectively modulates charge transfer dynamics. The distinction of interfacial charge is visually manifested in the charge density difference mapping (Fig. 4g₂), revealing that the Co-based domain exhibits higher charge density relative to the Ni-based domain, corresponding to a charge accumulation state. Such divergent charge densities favor the induction of

dipole pairs to strengthen polarization effects, thereby facilitating EMW energy dissipation. Moreover, Fig 4g₃ illustrates the distinct band structures of single-phase NiSe₂ and CoSe₂, which undergo strong coupling at the heterointerface, resulting in staggered electronic energy level distributions in the density of states (DOS) curves. Notably, the DOS near the Fermi level for the NiSe₂/CoSe₂ dual-semiconductor heterostructure is markedly higher than that of the single phase counterparts (Fig. 4g₄), further corroborating that the construction of the heterojunction narrows the band gap compactly and accelerates charge transfer kinetics.

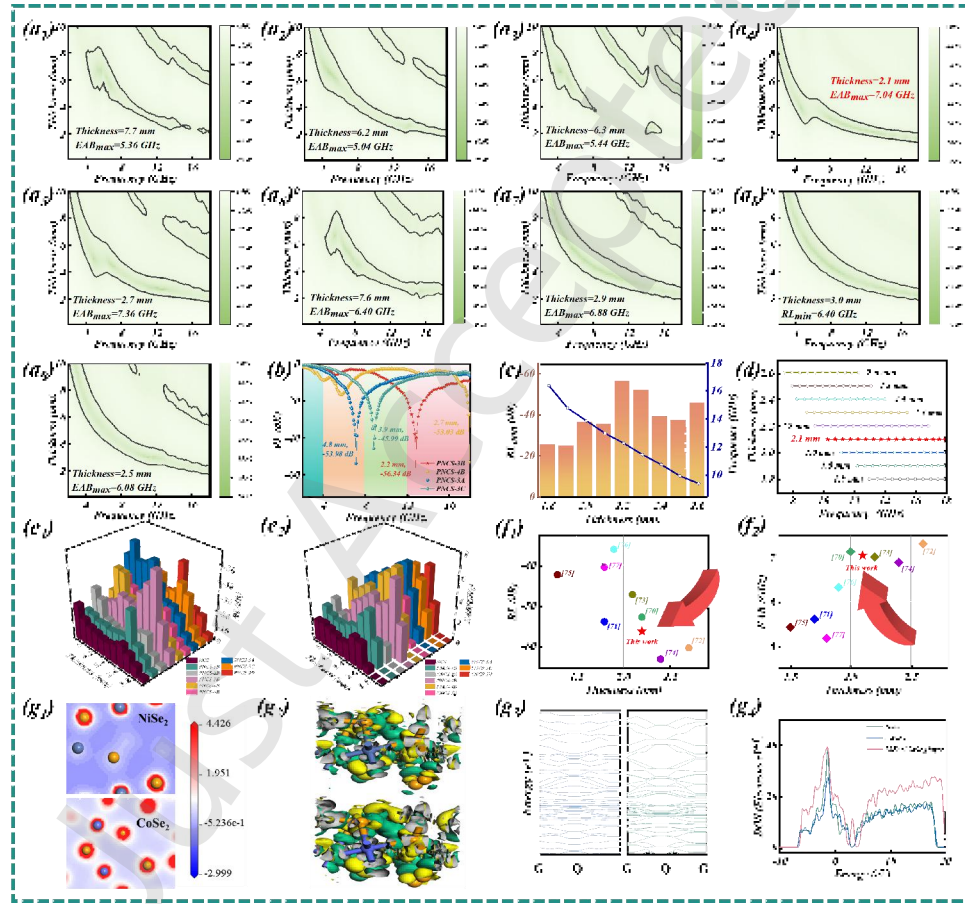


Fig 4. a₁-a₉) 2D EAB of NCS and PNCS-xy. b) RL and corresponding matching thickness of PNCS-3A/3B/3C/4B. c) RL and d) EAB of PNCS-3B at 1.8-2.6 mm, 3D histograms of e₁) RL and e₂) EAB for above samples, f₁) RL and f₂) EAB are compared with other similar absorbers. g₁) charge density images of NiSe₂ and CoSe₂, g₂) charge density difference mapping of the NiSe₂/CoSe₂ heterointerface, g₃) band structure and g₄) density of states curves of NiSe₂, CoSe₂, and NiSe₂/CoSe₂.

3.5 EMW absorption mechanisms

In order to assess the practical application potential of NCS and PNCS-xy, we utilized CST Studio Suite software at 12.88 GHz to simulate radar reflection cross section (RCS) of samples. Our experimental platform features a Planar Electric Conductivity substrate (PEC) measuring 300mm×300mm and an EMW coating. Fig 5a₁-e₁ and S27a₁-e₁ show the 3D RCS signals of the PEC substrate and nine different samples. In comparison to the pristine PEC substrate, the 3D RCS values of the coated absorbers exhibit varying degrees of reduction, with the PNCS-3B demonstrating the most significant decrease, thereby validating its superior EMW absorption capabilities. Fig. 5a₂-e₂, a₃-e₃ and Fig. S27a₂-e₂, a₃-e₃ illustrate the suppressive effects of various samples on RCS signals across the incident angle spectrum spanning from -90° to 90°. Notably, the RCS value of PNCS-3B exhibits a precipitous decline at 0° incidence angle, signifying enhanced EMW absorption and loss capacity, making it particularly adept for intricate military electromagnetic environment. As supplementary, the simulated RCS plots of Ni-Co-MOF-74 precursor are detailed in Fig. S25h-j.

Meanwhile, the authors explored the mechanism of PNCS-xy on EMW and constructed an EMW absorption model (Fig 5f). Phosphorus doping induces lattice stress that facilitates the formation of oxygen vacancies. These vacancies serve as donors, leading to charge rearrangement at heterointerfaces. The consequent local charge imbalance strengthens interfacial and dipolar polarization, thus substantially boosting dielectric loss. The efficient integration of multiple mechanisms provides a positive feedback effect on the loss and attenuation of EMW. First of all, on the basis of the inherent advantages of selenides, the abundant heterostructure inside PNCS-xy enhances the interfacial polarization^[84]. Secondly, the introduction of phosphorus atoms induces local charge imbalance, driving the material to spontaneously form vacancy structures to maintain electrical neutrality. The difference in atomic radii between phosphorus and oxygen gives rise to lattice expansion and stress accumulation. To relieve the excessive stress, oxygen atoms are expelled to relax the lattice distortion. The formation of oxygen vacancies significantly enhances the defect-induced dipole polarization and dielectric relaxation^[85]. Thirdly, abundant

uniformly dispersed PNCS-xy microspherical network acts as a three-dimensional conductive matrix by physical contact, facilitating free-electron leaps and induced current transport. Oxygen vacancies introduce defect levels within the bandgap, which effectively narrow the bandgap, facilitate the excitation of electrons from the valence band to the conduction band, and enhance both the carrier concentration and conduction loss capacity^[86-87]. In addition, the incorporation of magnetic NiSe₂ and CoSe₂ nanoparticles induces magnetic loss through resonance and eddy current interaction resulting in the conversion of electromagnetic energy into thermal energy^[88-89].

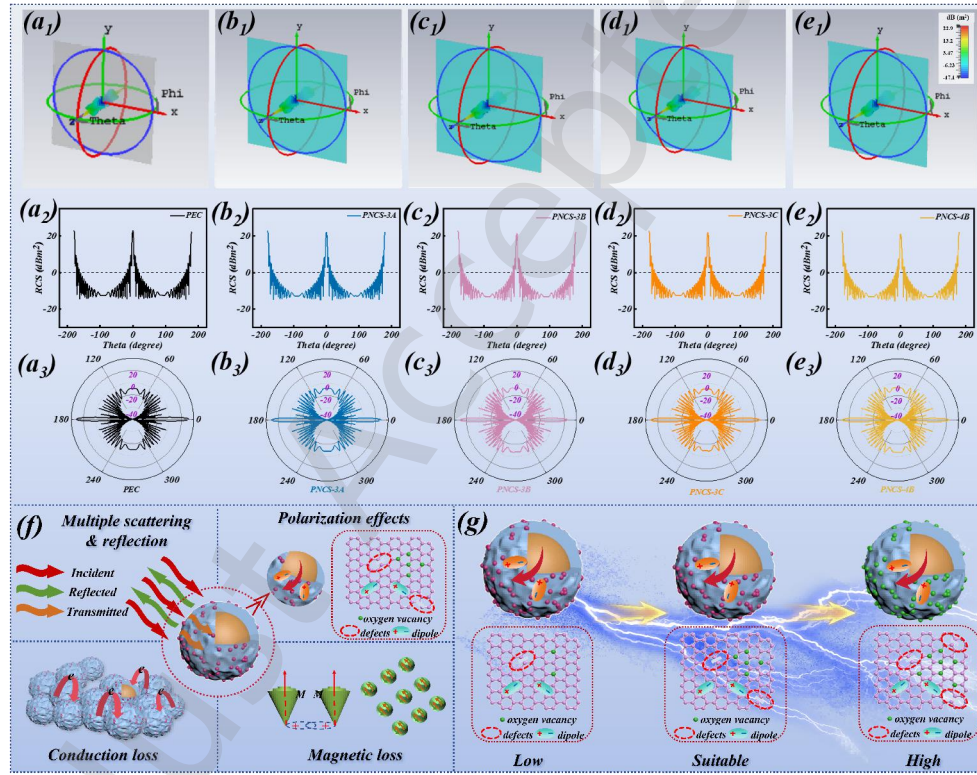


Fig 5. a₁-e₁) 3D radar wave scattering signals, a₂-e₂) RCS simulation curves, and a₃-c₃) RCS simulation results of polar coordinates of PEC, PNCS-3A, PNCS-3B, PNCS-3C and PNCS-4B. f-g) EMW absorption mechanism of PNCS-xy.

Controllably inducing defects and reasonably optimizing the phase interface are crucial facets that warrant emphasis. Within reduced doping concentration and temperature ranges, the interface polarization effect between the bimetallic selenide and the MOF substrate plays a dominant role, but the EMW absorbency capacity exhibited by the sample fell short of our anticipations due to the inadequate structure

of the defect. As the reaction condition reaches extreme thresholds, the phase makeup of the PNCS-xy becomes unmanageable, thereby forfeiting the inherent benefits of the selenide compound, excessive phosphorus occupies the selenium atomic sites, disrupting the energy band structure of the material and weakening the conductive loss. Only under suitable reaction parameters, the maximum defect concentration be achieved while maintaining the stability of the phase, realizing the organic coordination of interfacial polarization under mild conditions, as well as defect-induced dipole polarization and conduction loss under severe conditions. The “dual-core driven” of defects and interface polarization engineering can be actualized to endow the material with optimal EMW absorption capabilities (Fig. 5g).

4. Conclusions

In summary, using Ni-Co-MOF-74 as a precursor, the researchers designed a phosphorus-doped selenide vacancy modulation and phase interface optimization engineering, and discussed optimal solution of regulating defect and interface polarization in multi-component composites. The PNCS-3B demonstrates excellent EMW absorption performance, achieving $RL_{\min}$ of -56.34 dB at an ultrathin matching thickness of 2.2 mm, alongside a substantial $EAB_{\max}$ of 7.04 GHz achieved at 2.1 mm, realizing a complete coverage of the X and Ku bands within available 2.6 mm. The remarkable enhancement of the absorber is attributed to its unique core-shell loose porous microstructure, abundant heterogeneous interfaces, phosphorus-induced oxygen vacancy polarization, relaxation, strong conduction loss, and excellent impedance matching properties, meeting contemporary requirements for the application of advanced EMW absorbers effectively. This work provides a potential reference for modeling the response of novel absorbers to EMW.

Declaration of competing interest

The authors declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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CRedit authorship contribution statement

Yuhao Dong, Guangrong Wu and Zhenguo Gao: Writing - original draft, Validation, Methodology. Hua Qiu: Data curation. Di Lan, Zirui Jia and Guanglei Wu: Writing - review & editing, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Supplementary materials

Supplementary material associated with this article can be found, in the online version.

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Electronic Supplementary Material

Simultaneous modulation of vacancy and heterointerface of double-matrix phosphorus doped NiSe₂/CoSe₂ composite for “dual-core-driven” electromagnetic wave absorption

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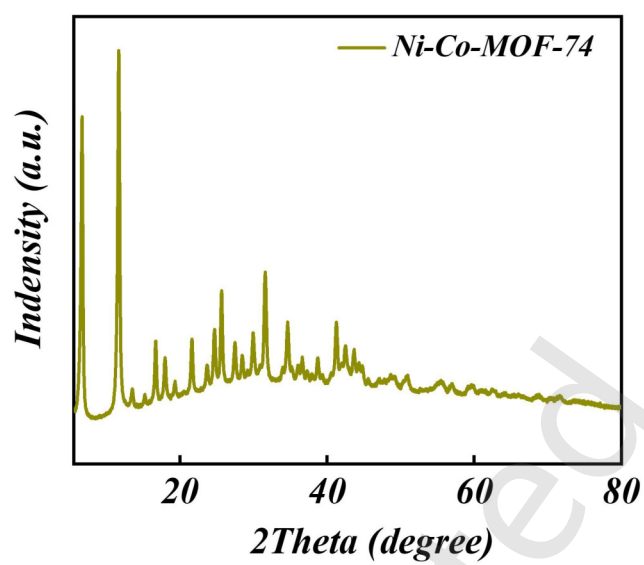


Fig S1. XRD pattern of Ni-Co-MOF-74 precursor.

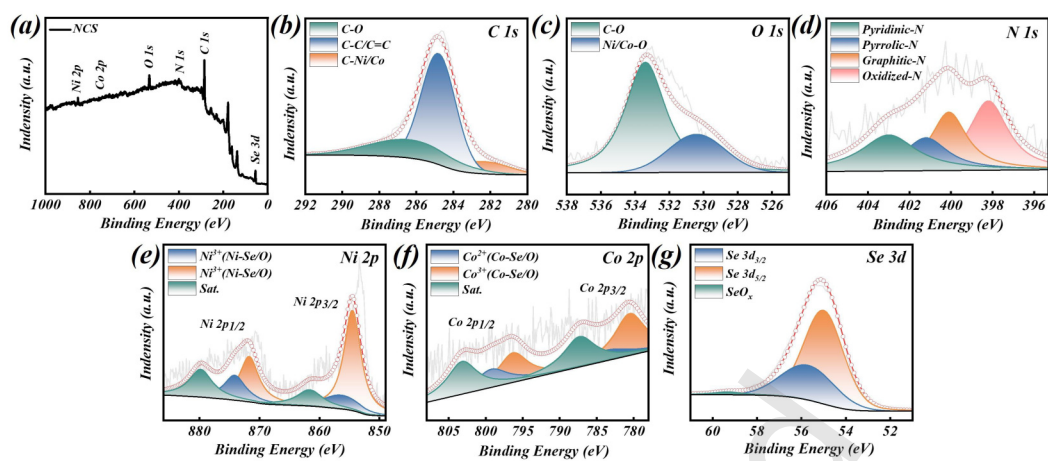


Fig S2. XPS spectra of NCS.

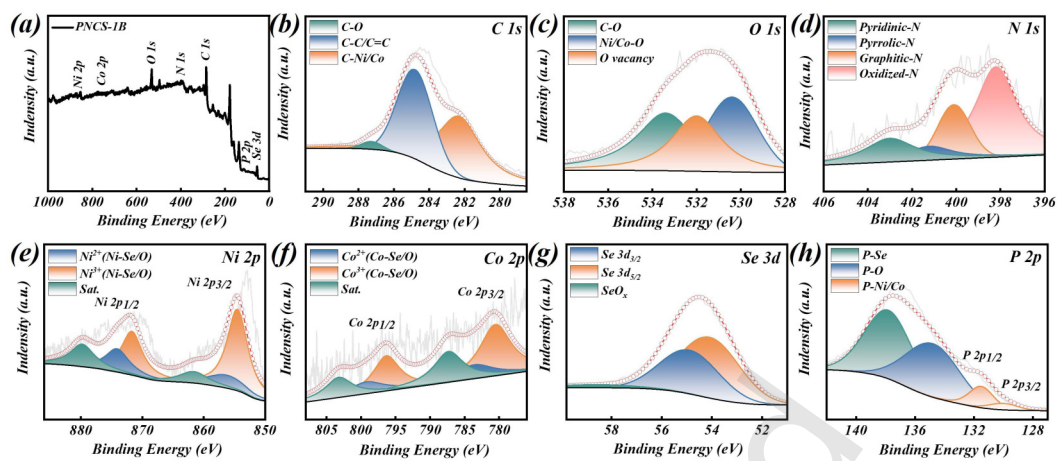


Fig S3. XPS spectra of PNCS-1B.

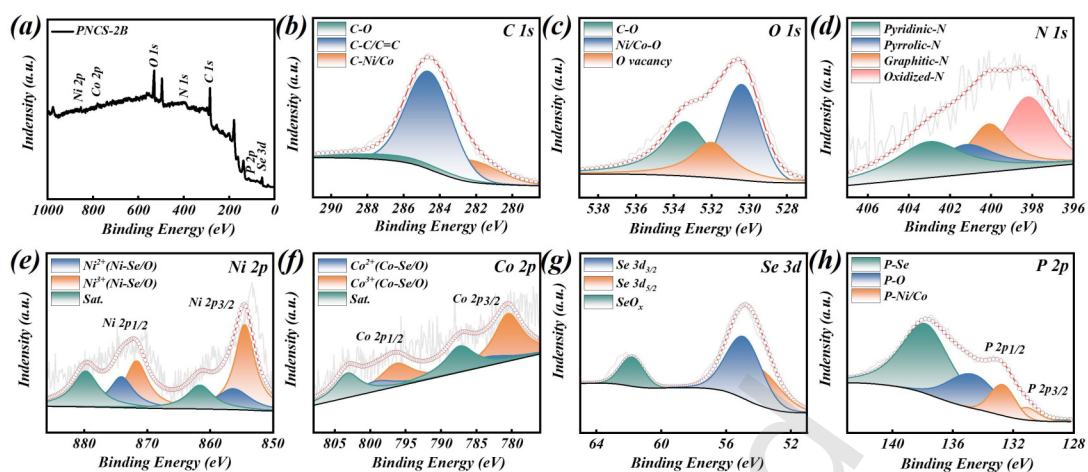


Fig S4. XPS spectra of PNCS-2B.

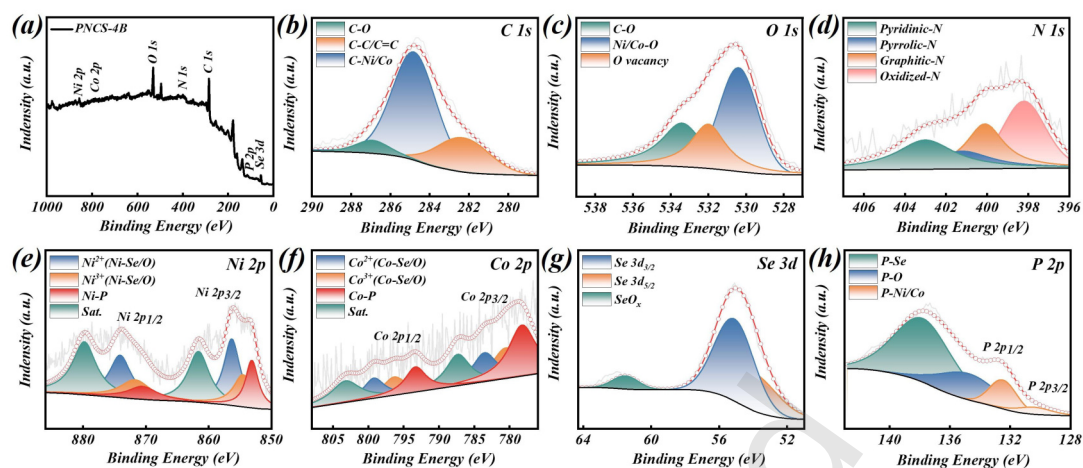


Fig S5. XPS spectra of PNCS-4B.

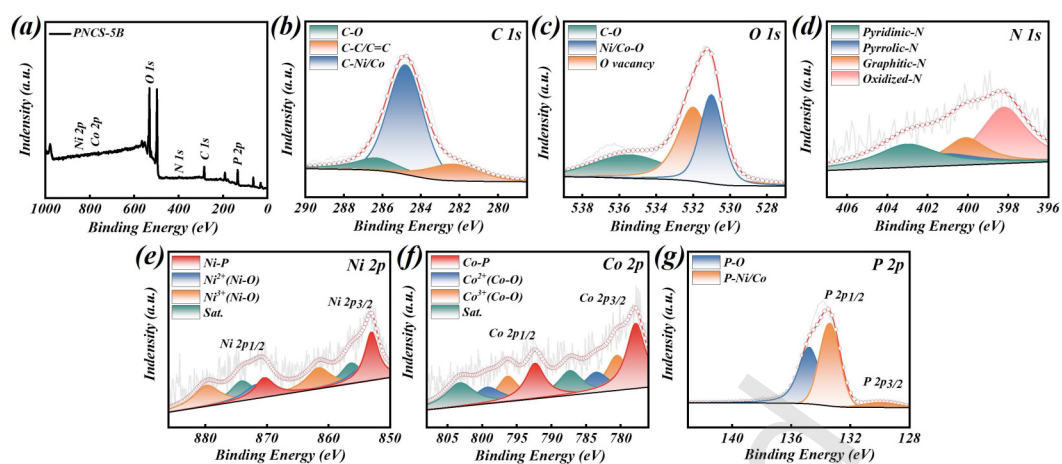


Fig S6. XPS spectra of PNCS-5B.

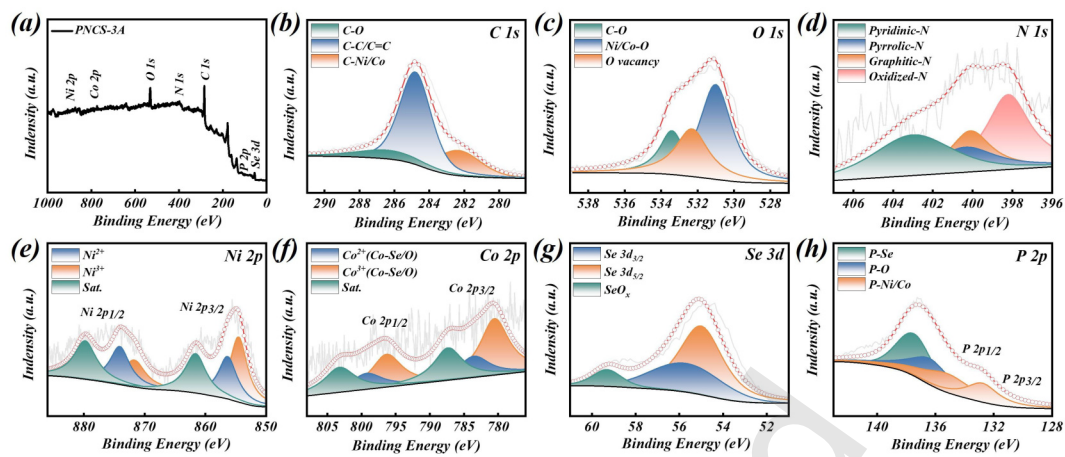


Fig S7. XPS spectra of PNCS-3A.

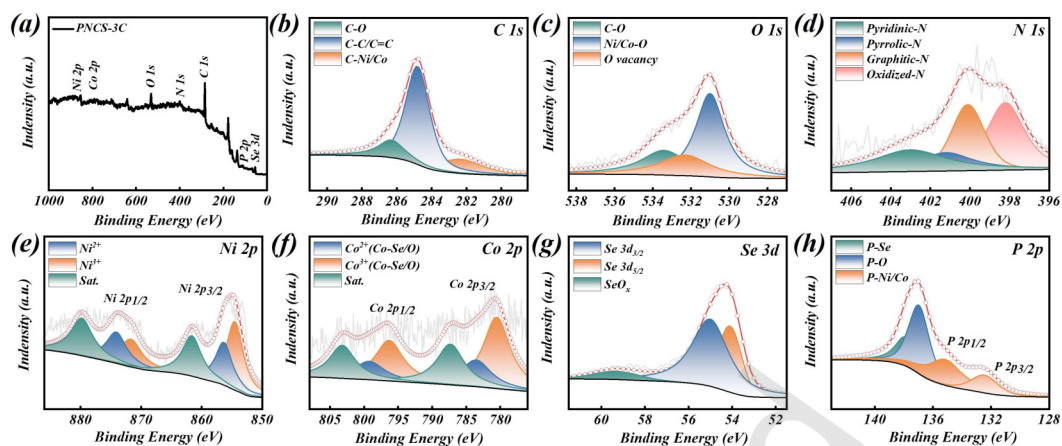


Fig S8. XPS spectra of PNCS-3C.

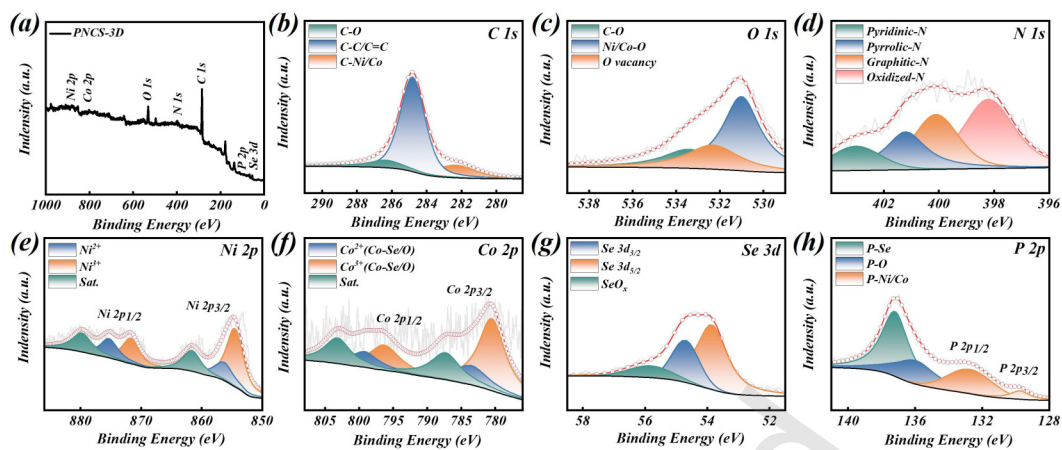


Fig S9. XPS spectra of PNCS-3D.

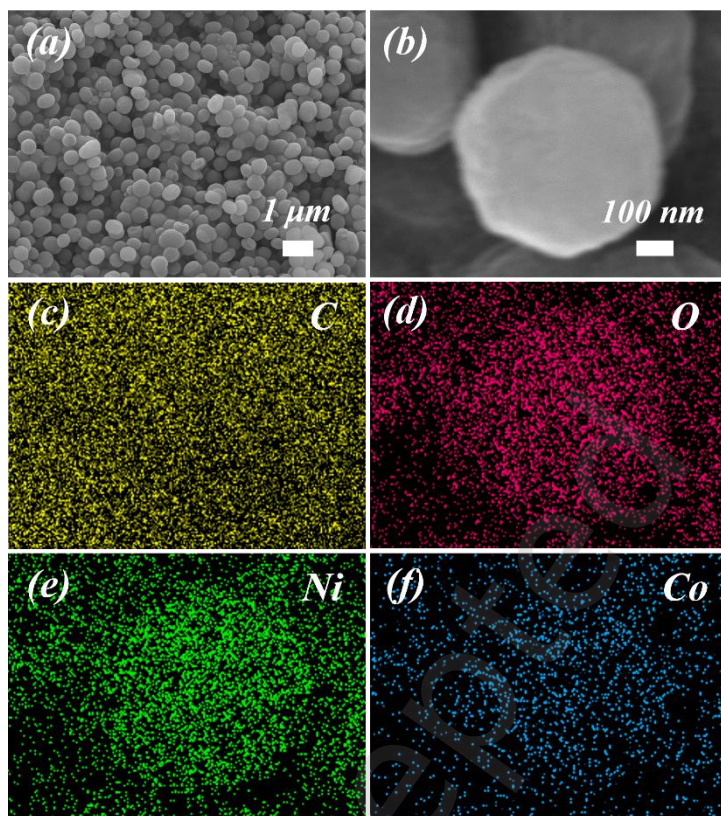


Fig S10. SEM images of Ni-Co-MOF-74 precursor.

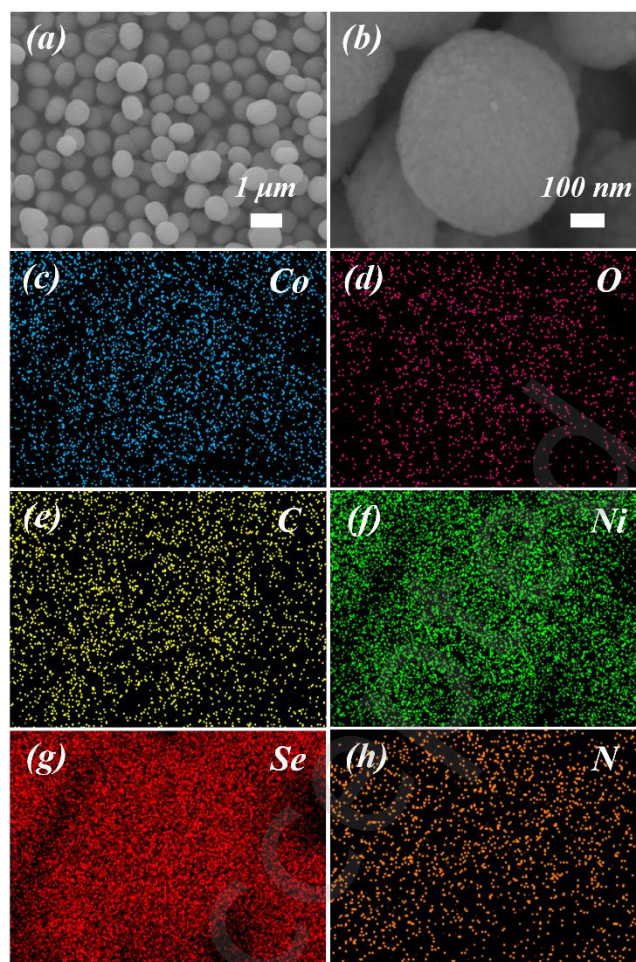


Fig S11. SEM images of NCS.

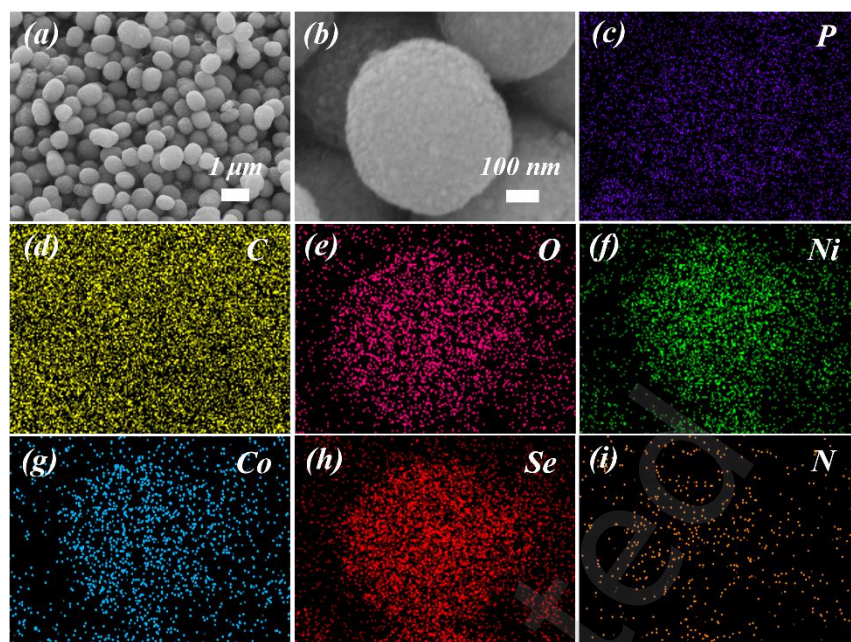


Fig S12. SEM images of PNCS-1B.

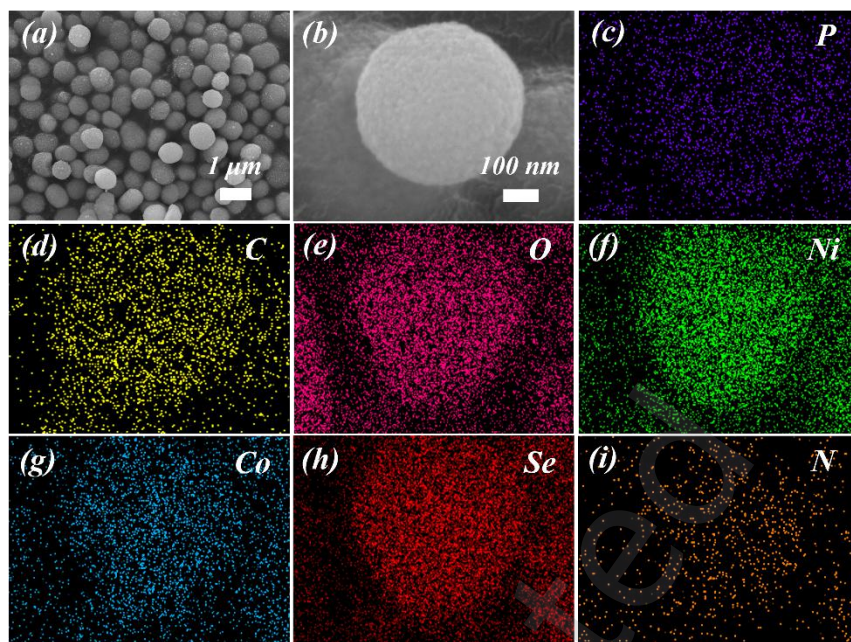


Fig S13. SEM images of PNCS-2B.

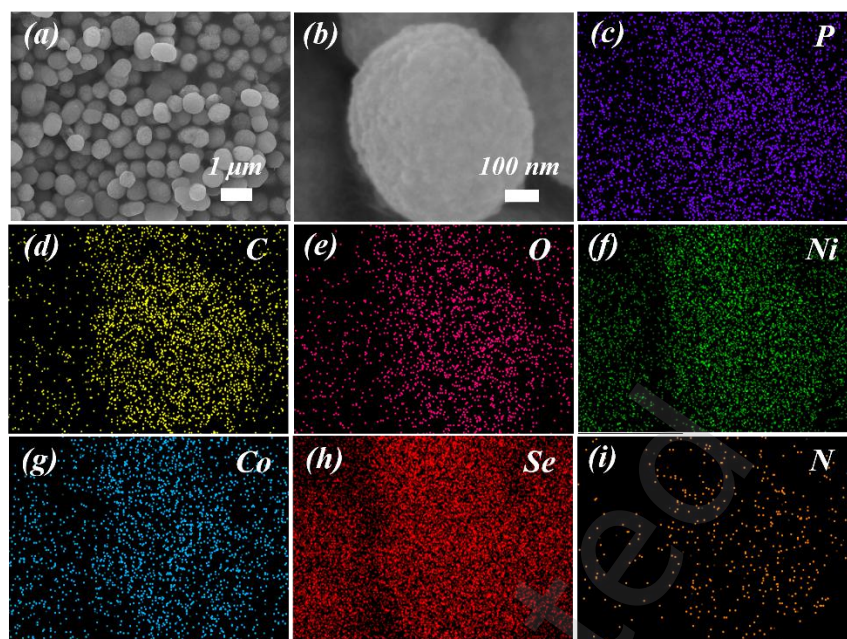


Fig S14. SEM images of PNCS-4B.

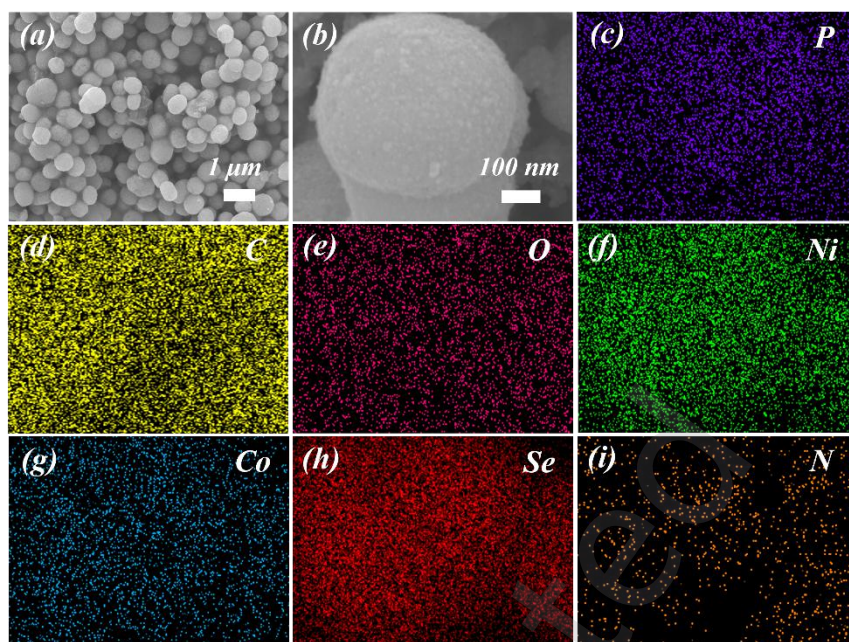


Fig S15. SEM images of PNCS-5B.

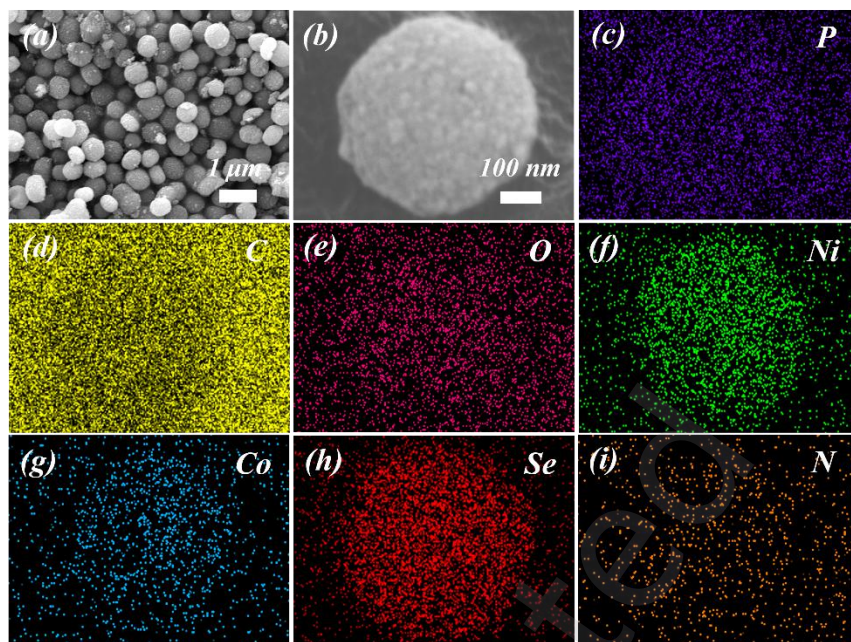


Fig S16. SEM images of PNCS-3A.

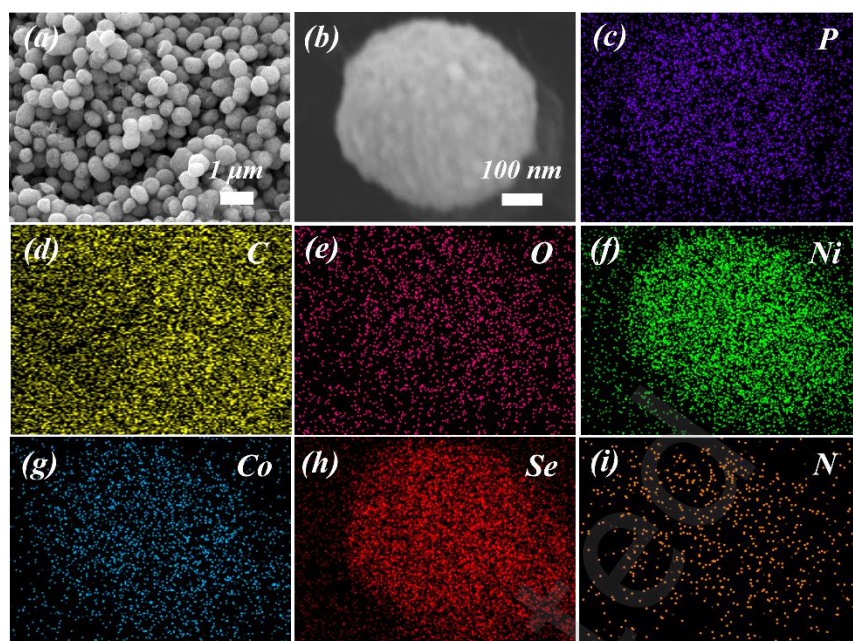


Fig S17. SEM images of PNCS-3C.

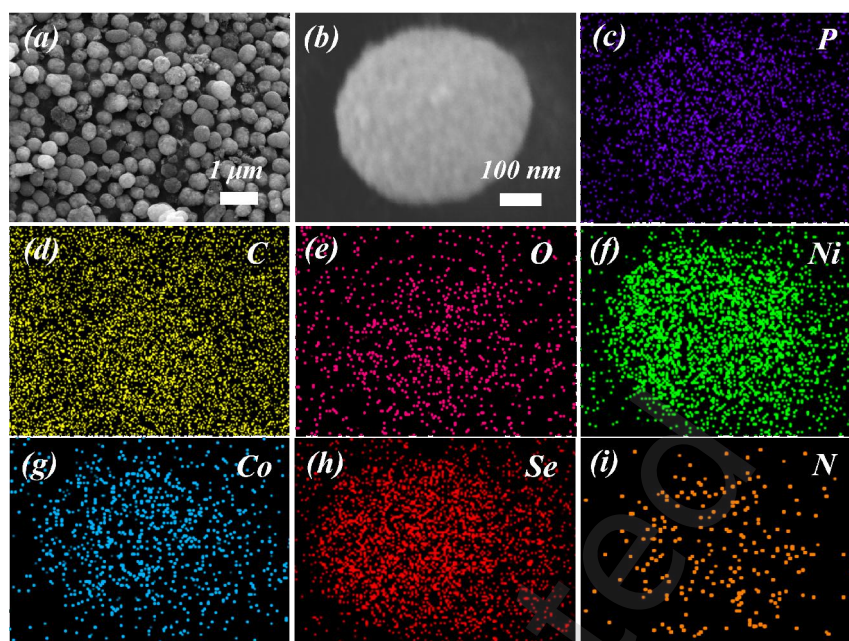


Fig S18. SEM images of PNCS-3D.

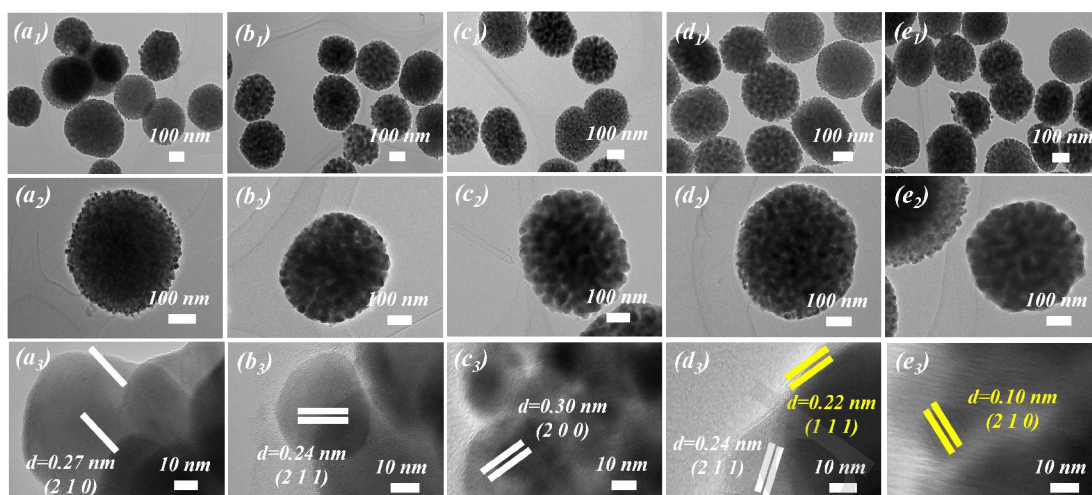


Fig S19. a₁-e₁), a₂-e₂) TEM and a₃-e₃) HRTEM images of NCS and PNCS-1B/2B/4B/5B.

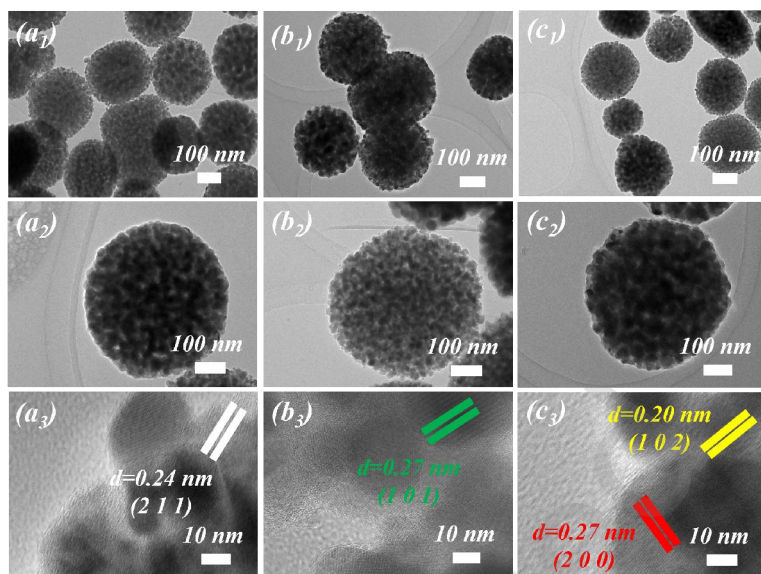


Fig S20. a₁-c₁), a₂-e₂) TEM and a₃-c₃) HRTEM images of PNCS-3A/3C/3D.

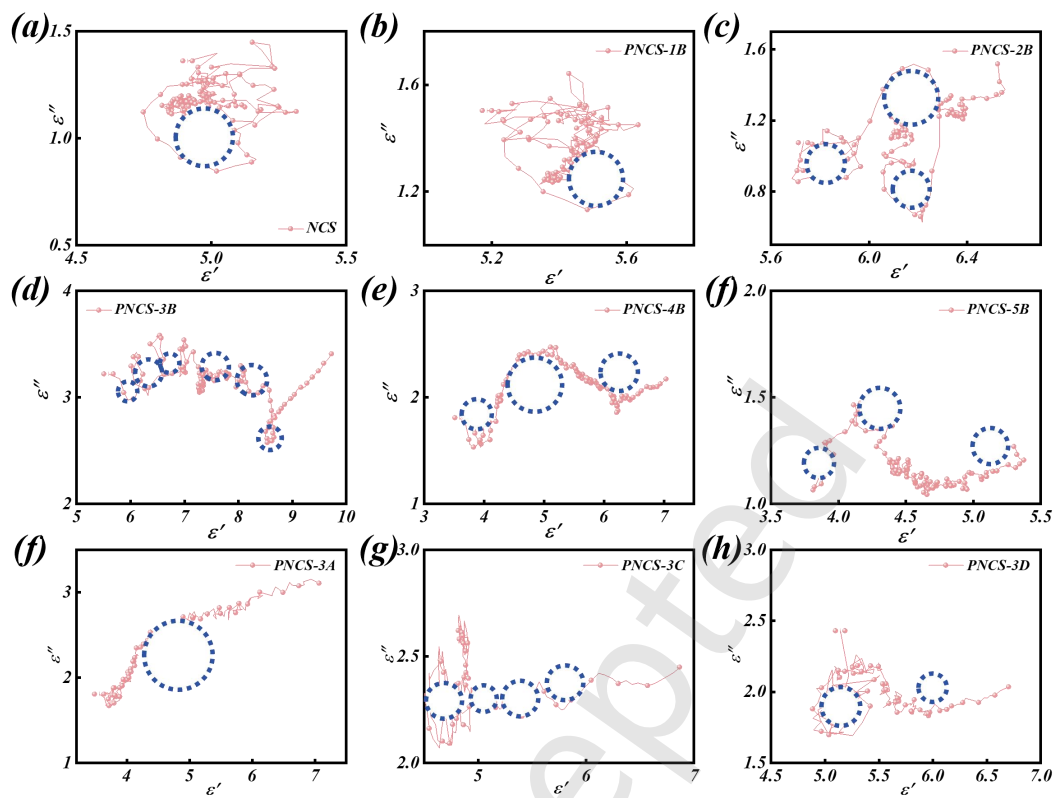


Fig S21. Cole-Cole plots for NCS and PNCS-xy.

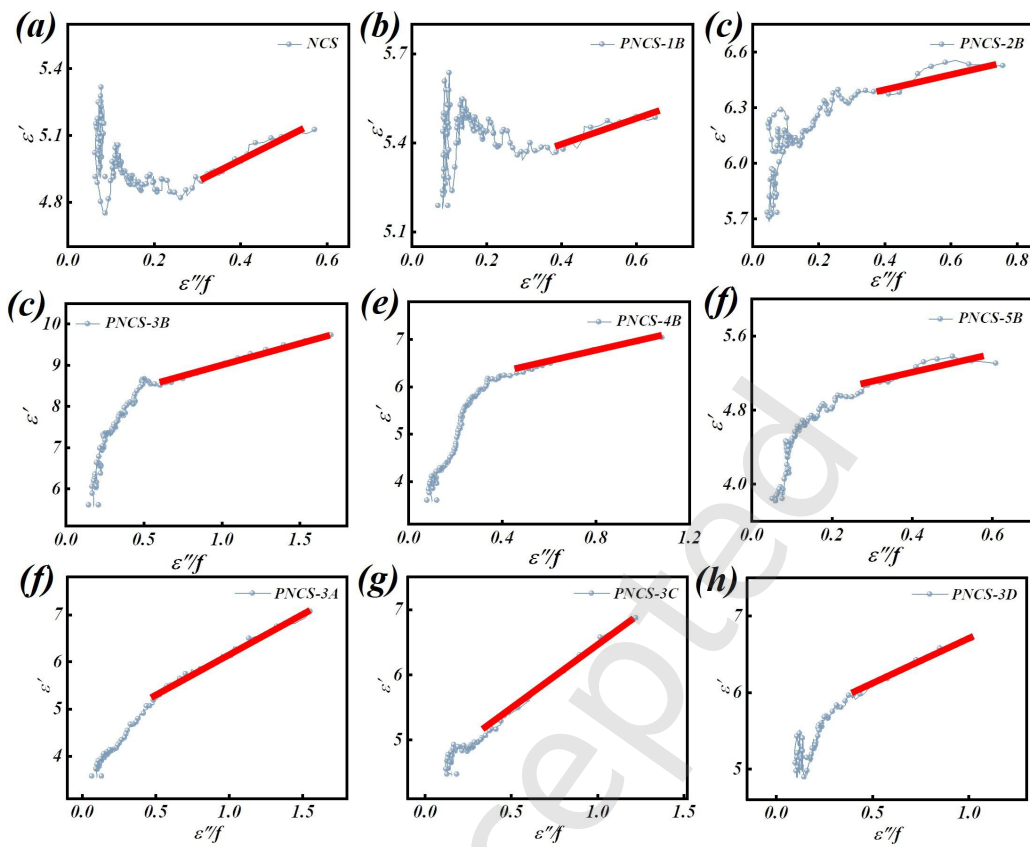


Fig S22. ϵ' - ϵ''/f curve for NCS and PNCS-xy.

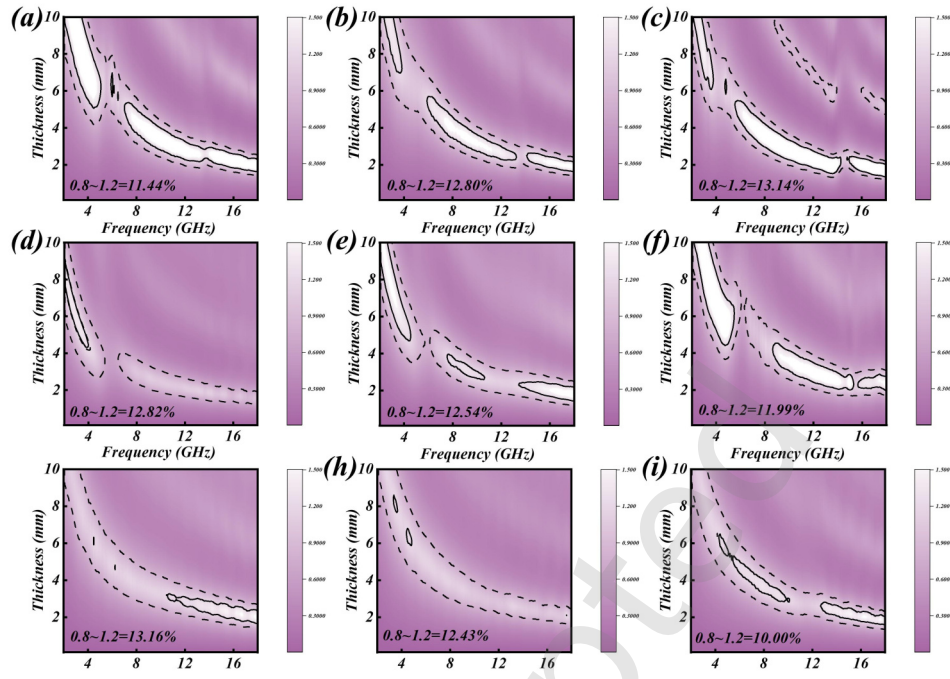


Fig S23. impedance matching area plots of NCS and
PNCS-1B/2B/3B/4B/5B/3A/3C/3D.

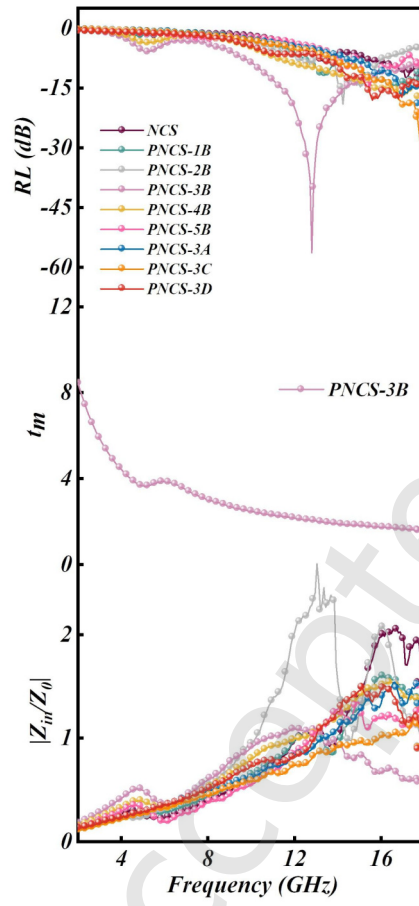


Fig S24. dependence of $\lambda/4$ matching thickness vs RL peak vs $|Z_{in}/Z_0|$ plots for all nine samples, and t_m - f_m curves of PNCS-3B.

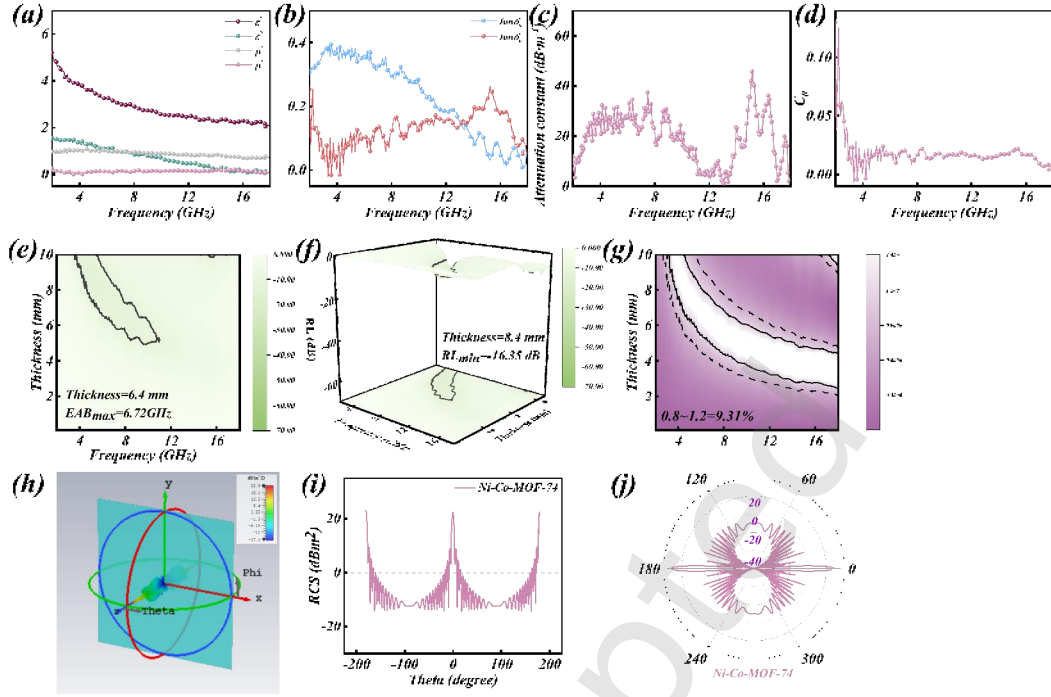


Fig S25. a-d) electromagnetic parameters, e) 2D EAB, f) 3D RL, g) impedance matching area plots and h-j) RCS simulation results of pure Ni-Co-MOF-74 precursor.

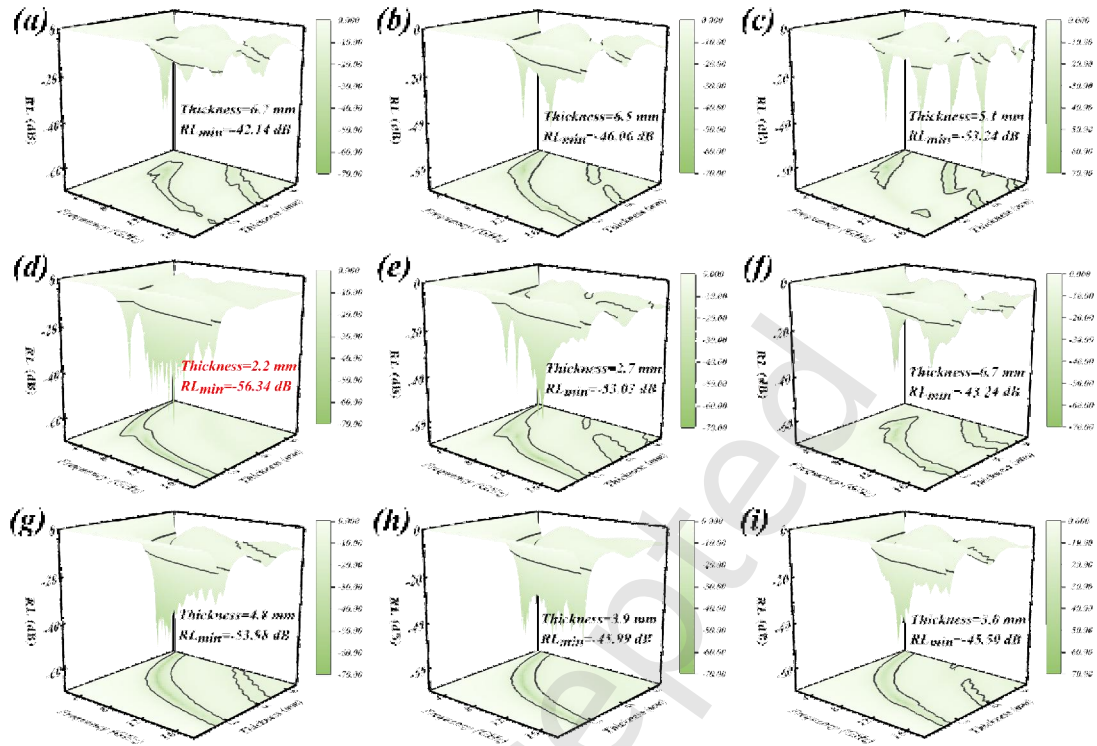


Fig S26. 3D RL of NCS and PNCS-1B/2B/3B/4B/5B/3A/3C/3D.

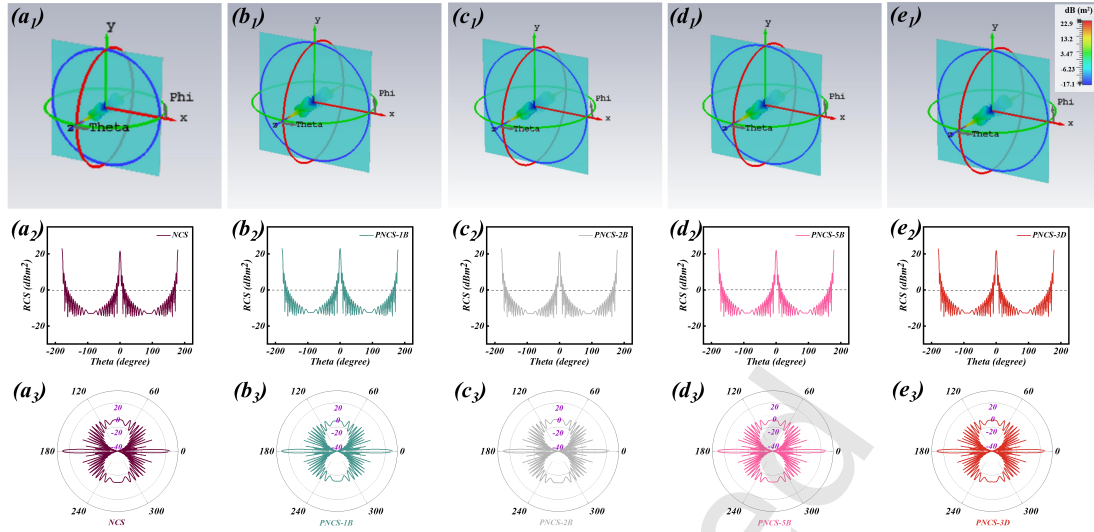


Fig S27. a₁-e₁) 3D radar wave scattering signals, a₂-e₂) RCS simulation curves, and a₃-e₃) RCS simulation results of polar coordinates of NCS, PNCS-1B, PNCS-2B, PNCS-5B and PNCS-3D.

The average lattice constants of NCS and PNCS-xy.

Sample	Symmetry	Average Lattice Constants/Å
NCS	Cubic	5.967
PNCS-1B	Cubic	5.973
PNCS-2B	Cubic	5.980
PNCS-3B	Cubic	5.994
PNCS-4B	Cubic/Hexagonal	5.976
PNCS-5B	Hexagonal	5.881
PNCS-3A	Cubic	5.984
PNCS-3C	Hexagonal	3.645
PNCS-3D	Hexagonal	5.900

Tab S1. Table of average lattice constants for NCS and PNCS-xy.