Dual-surfactant templated hydrothermal synthesis of CoSe₂ hierarchical microclews for dielectric microwave absorption

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Abstract: Cobalt diselenide (CoSe₂) hierarchical clew-like structure is synthesized via a dual-surfactant templated hydrothermal process, and for the first time, its microwave absorption capability has been established. Specifically, the as-synthesized hierarchical interconnected structure is assembled by numerous dense nanobelts. Meticulous tuning of the synthetic conditions which could influence the hierarchical architecture indicates that, in this system, cetyltrimethylammonium bromide (CTAB) plays a dominate role of “balling” while protonated diethylenetriamine (DETA) plays the role of “stringing”. As a novel absorbent, the microwave absorption performance of CoSe₂ microstructure is evaluated in 2–18 GHz band. Particularly, 3D hierarchical CoSe₂ microclews exhibit superior minimum reflection loss of −26.93 dB at 7.28 GHz and effective absorption bandwidth of 3.72 GHz, which are ~120% and ~104% higher than those of simple CoSe₂ nanosheets, respectively. Such drastic enhancement could be attributed to the large specific surface area, and more dissipation channels and scattering sites enabled by the unique clew-like microstructure. The versatile dual-surfactant templated assembly of hierarchical CoSe₂ microstructure, along with its appreciable dielectric microwave absorption performance, provides new inspirations in developing novel microwave absorbents for mitigation of electromagnetic pollution.

Keywords: hierarchical structure; cobalt diselenide; surfactant; assembly; microwave absorption

1 Introduction

Hierarchical micro/nano-architecture has recently drawn much attention due to its combination of the advantages from both nanoscale building blocks and

advanced structural design, which offers unique properties and enhanced performance compared to pristine micro/nanoparticles [1]. Precise control of the hierarchical assembly of building blocks with tunable dimension and structure is the prerequisite for dominating its applications in various fields such as photocatalysis [2–4], electrocatalysis [5,6], sensing devices [7–9], biomedicine [10], and microwave absorption [11–14]. There have been numerous reports on various kinds of hierarchical nanomaterials by

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different methods. However, these methods usually suffer from tedious and harsh synthetic conditions, which would result in substantial difficulty in precise control and reliable reproducibility of the synthesis process towards practical applications. In this regard, a solution-phase process is considered to be a more controllable and cost-effective alternative for synthesis of nanomaterials, which requires relatively low temperature and facile operation.

Cobalt diselenide (CoSe_2), as a typical pyrite-type metallic transition metal chalcogenide, is known as an exchange-enhanced Pauli paramagnet in magnetic ground state with a Curie temperature T_C of 124 K [15]. Besides, in recent years, CoSe_2 has attracted tremendous interest for its high electrocatalytic activity for hydrogen evolution reaction (HER) [16], oxygen evolution reaction (OER) [17], oxygen reduction reaction (ORR) [18], H_2O_2 electrosynthesis and activation [19,20], metal-ion batteries [21–23], Li–S batteries [24], supercapacitors [25,26], etc. However, despite its moderate electrical and dielectric properties, the promising capability of CoSe_2 as a novel microwave absorbent has never been explored till now. Generally, for fabrication of high-performance dielectric microwave absorption materials, especially the single-component absorbent, the structural design of hierarchical architectures with improved porosity [27], impedance matching, interface polarization [28–30], relaxation intensity, and conducting state [31,32] is essential, and very recently, these interfacial phenomena have been revealed by some new techniques such as off-axis electron holography [12–14], which provides new fundamental insight into the underlying mechanisms of the dielectric microwave absorption.

In this study, a unique clew-like CoSe_2 microstructure is synthesized via a hydrothermal approach which is templated by both diethylenetriamine (DETA) and cetyltrimethylammonium bromide (CTAB). The hierarchical microclews are built by numerous networks of CoSe_2 nanobelts, which are primarily composed of ultrafine nanocrystals. The size, morphology, and structure of the 3D hierarchical CoSe_2 microstructures synthesized under different reaction conditions are systematically studied, based on which a unique dual-surfactant templated assembling mechanism for the formation of hierarchical CoSe_2 microclews is proposed. More importantly, the capability of such CoSe_2 microclew as a novel microwave absorption material has been confirmed. Owing to the large surface area

and the porous structure-derived abundant dissipation channels and scattering sites, these CoSe_2 microclews display improved microwave absorption properties compared with pristine CoSe_2 nanosheets obtained via a single-surfactant process. This work not only gives insight into the dual-surfactant templated growth behavior of hierarchical CoSe_2 microclews in a hydrothermal process, but also suggests new opportunities in developing novel CoSe_2 -based high-performance dielectric microwave absorption materials.

2 Experimental

2.1 Chemicals

Cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), selenium dioxide (SeO_2), DETA, CTAB, and anhydrous ethanol are obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd., China, which are all of analytical reagent (AR) grade. Deionized (DI) water produced by the Milli-Q Integral System (Millipore, Bedford, USA) is used in all experiments.

2.2 Synthesis of CoSe_2 hierarchical microstructures

The CoSe_2 hierarchical microstructures are synthesized via a facile hydrothermal route. Typically, 1 mmol $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ along with 1.5 mmol CTAB are dissolved in 11 mL DI water at 40 °C. Then, 26 mL DETA is added under vigorous stirring. After stirring for 30 min, 2 mL of aqueous solution which contains 1 mmol SeO_2 is added dropwise into the solution, keeping the volume ratio of DETA/ H_2O at 2:1. The obtained slurry is then transferred into a 50 mL Teflon-lined stainless-steel autoclave. Afterwards, the autoclave is heated to 180 °C and maintained for 16 h, and then allowed to cool down naturally to room temperature. Finally, the generated black precipitate is rinsed several times with DI water and anhydrous ethanol separately, and dried at 60 °C in vacuum overnight.

2.3 Characterization and measurement

The size, morphology, and microstructure of the samples are revealed by a field-emission scanning electron microscope (SEM; Hitachi S4800, Japan) and a field-emission transmission electron microscope (TEM; JOEL JEM-2100F, Japan) equipped with a post-column GIF-tridium imaging filter system (Gatan, USA) operated at 200 kV. X-ray diffraction (XRD) measurements are

carried out using a Bruker D8 X-ray diffractometer (Germany) with Ni-filter Cu K α radiation (40 kV, 40 mA). Raman spectroscopy is studied with a laser confocal Raman micro-spectrometer (inVia reflex, Renishaw, UK) with a 632.8 nm He–Ne laser as the excitation source. Electrochemical impedance spectroscopy (EIS) data are acquired on a PGSTAT302N electrochemical workstation (Metrohm Autolab, the Netherlands) with the frequency recording from 10^5 to 10^{-1} Hz at 10 mV amplitude. Specific surface areas and porosity data of the samples are obtained by measuring N₂ adsorption–desorption isotherms on Micromeritics ASAP-2020 (USA) after degassing of the samples at 180 °C for 12 h.

Microwave absorption properties are examined by dispersing as-synthesized CoSe₂ powder in epoxy resin with a weight ratio of 1:5. Then the mixture is coated on an aluminum substrate (180 mm $\times$ 180 mm) with a thickness of 2 mm to measure the reflection loss (RL) of the samples. Afterwards, the remained sample is molded into the hollow pipe of a rectangular wave

guide cavity (10.2 mm $\times$ 2.9 mm $\times$ 1.2 mm) for complex permittivity and permeability measurement. The above-mentioned measurements are carried out on a HP8510C vector network analyzer (Agilent Technologies, USA) in the range of 2–18 GHz range.

3 Results and discussion

3.1 Structure and morphology characterization

Figure 1 shows the morphology, phase identification, and chemical composition of the synthesized hierarchical microstructure. The sample exhibits a clew-like shape with an average diameter of around 1–2 μ m and consists of many interlaced nanobelt and nanosheet networks (Figs. 1(a) and 1(b)). Figures 1(c) and 1(d) show the corresponding selected area electron diffraction (SAED) pattern and high-resolution TEM (HRTEM) image of the marked region in Fig. 1(b). It can be

Fig. 1 (a) Low- and high-resolution SEM images, (b) TEM image, (c) SAED pattern, (d) HRTEM image, (e) XRD pattern, and (f) EDS spectrum of the hierarchical clew-like CoSe₂ microstructure, which is prepared with 1.5 mmol CTAB in 40 mL solvent ($V_{\text{DETA}}/V_{\text{H}_2\text{O}} = 2:1$) at 180 °C for 16 h (Sample C).

observed from Fig. 1(d) that the nanobelts are assembled from large numbers of irregularly shaped nanoparticles with an average size of about 10 nm, while the growth orientation of these particles is not uniform, as indicated by the red dashed circles. The identified interplanar spacing values of ~ 2.15 , ~ 2.42 , and ~ 2.93 Å correspond to the (220), (211), and (200) crystal planes of CoSe_2 , respectively. These nanoparticles accumulate together to form individual nanobelts with the presence of structure-directing agents, and further assemble into 3D hierarchical microclews. Figure 1(e) shows the XRD pattern of the hierarchical microstructures. It is clear that all distinct diffraction peaks could be well indexed to the cubic CoSe_2 phase with a lattice constant $a = 5.858$ Å (PDF#09-0234), which matches well with the SAED and HRTEM results and is also consistent with Ref. [33]. The broadened diffraction peaks could be attributed to the small size of primary nanoparticles and templating effects of organic surfactants. Meanwhile, EDS analysis also reveals that the sample contains only Co and Se elements with an atomic ratio approximating to Co/Se of $\sim 1:2$ (Fig. 1(f)), which confirms the formation of CoSe_2 as well.

During the hydrothermal synthesis, the templating effect of capping agent can significantly influence the morphology and structure of as-resulted CoSe_2 products. In order to study the influence of CTAB on the morphology, the addition amount of CTAB is varied while keeping the mixed solvent unchanged (40 mL, $V_{\text{DETA}}/V_{\text{H}_2\text{O}} = 2:1$). Figure 2 shows the SEM images of the as-obtained samples. It can be seen from Fig. 2(a) that the nanosheets with uneven edges are obtained when there is no CTAB added in the reaction system. In contrast, when 0.75 mmol CTAB is introduced into the reaction, the clew-like microstructure can be observed (Fig. 2(b)), and as the amount of CTAB increases to 1.5 (Fig. 1(a)) and 3 mmol (Fig. 2(c)), the hierarchical microclews grow larger to 1–2 μm and

further ~ 3 μm , respectively. It is obvious that the morphology of CoSe_2 transforms from 2D nanosheets to 3D microclews after the addition of CATB, and meanwhile, the fundamental units of the microstructure transform from nanosheets to nanobelts as well. However, the 3D microclews become looser and more irregular as the addition amount of CTAB exceeds 1.5 mmol, as indicated by Fig. 2(c) compared to that of Fig. 1(a). The formation of the fundamental sheet- or belt-like units follows the solvent-coordination molecular template mechanism [34]. In particular, DETA is protonated by water molecules during the hydrothermal reaction at 180 °C and form positively charged ammonium ions. Then, the protonated amine molecules are incorporated into neighboring CoSe_2 atomic layers via the coordination with Se sites, generating sheet- and belt-like morphology of CoSe_2 as a result.

Further, the influence of reaction temperature (Fig. 3) and time (Fig. 4) on as-resulted microstructure of CoSe_2 is also investigated. It can be observed that highly porous sponge-like microclews are obtained at a relatively lower temperature of 160 °C (Fig. 3(a)), while the less porous microspheres which seem to be aggregated by lots of small nanoparticles are synthesized at a higher temperature of 200 °C (Fig. 3(b)). Meanwhile, the extension of reaction time seems to have a similar effect with the increase of hydrothermal reaction temperature, as shown in Fig. 4. TEM images (Figs. 4(c) and 4(d)) reveal that the microspheres tend to become increasingly compact and exhibit higher crystallinity as reaction time and temperature increase, due to the occurrence of Ostwald ripening process. In particular, there is also a thermodynamic driving force for such agglomeration growth and ripening as the total surface energy can be substantially reduced when the interface is eliminated and thus the microspheres become less porous [35,36]. Specifically, the specific surface areas and porosity data of these samples are obtained by Brunauer–Emmett–Teller (BET) and

Fig. 2 SEM images of the CoSe_2 samples synthesized in a mixed solvent (40 mL, $V_{\text{DETA}}:V_{\text{H}_2\text{O}} = 2:1$) with different amounts of CTAB: (a) 0 mmol (Sample A), (b) 0.75 mmol (Sample A), and (c) 3 mmol (Sample A).

Fig. 3 SEM images of the CoSe₂ samples synthesized at different hydrothermal reaction temperatures: (a) 160 °C (Sample B) and (b) 200 °C (Sample D).

Fig. 4 (a, b) SEM and (c, d) TEM images of the CoSe₂ samples synthesized under the same condition except prolonged hydrothermal reaction time: (a, c) 24 h (Sample E) and (b, d) 48 h (Sample F).

Barrett–Joyner–Halenda (BJH) analyses [37,38], which are presented in Table S1 in the Electronic Supplementary Material (ESM), indicating that the prolonged hydrothermal reaction time (> 16 h) and increased reaction temperature (> 180 °C) are unfavorable for the formation of porous CoSe₂ microstructure with large specific surface area (SSA_{BET}). Notably, the highly porous Sample B shows the largest SSA_{BET} of about $14.89 \text{ m}^2 \cdot \text{g}^{-1}$ as well as the largest pore volume of about $0.079 \text{ mL} \cdot \text{g}^{-1}$, which are *ca.* 7 times and 5 times higher than those of the pristine CoSe₂ nanosheets (Sample A) of about 2.06 and $0.016 \text{ m}^2 \cdot \text{g}^{-1}$, respectively.

3.2 Morphological evolution and possible mechanism

To better unveil the formation process of the CoSe₂

microclews, the time-dependent experiments are carried out, with the results displayed in Fig. 5. Generally, the formation of nanocrystals in solution phase could be divided into nucleation and growth stage. The nuclei generated at the initial stage usually follow the shape-determinant rule [4,39–41]. It can be known from Fig. 5(a) that $\sim 2 \mu\text{m}$ large spheres are obtained when the reaction has been maintained at 180 °C for 15 min. These spheres are amorphous according to TEM identification. Then, these spheres continue to dissolve into numerous torus-like intermediates with the size of 80–100 nm as the reaction proceeds to 1 h (Fig. 5(b)). Intriguingly, when the reaction is further prolonged to 4 h (Fig. 5(c)), ~ 500 nm microspheres with numbers of small nanoparticles distributing on the rough surface randomly are obtained. Notably, TEM

observation verifies that the microspheres obtained at this time point are crystalline phase of CoSe_2 , implying that the growth stage via Ostwald ripening has become dominant instead of initial nucleation. Next, the “stringing” occurs as the reaction time is further prolonged to 6 h (Fig. 5(d)), resulting in the prototype of microclew morphology. Consequently, more and more interlaced nanobelts form and assemble into clew-like hierarchical microstructure accompanied with the dissolution of the original solid spheres, as exhibited in Fig. 5(e). Afterwards, the resulted microclews of CoSe_2 keep growing larger and becoming more porous, and when the reaction time finally reaches 16 h, the CoSe_2 microclews with relatively uniform size of $\sim 1.2 \mu\text{m}$ are obtained (Fig. 5(f)).

Based on the above results, a dual-surfactant templating process is proposed to describe the formation of hierarchical CoSe_2 microclews (Fig. 6), which could be summarized as the following three steps.

1) “Balling” by CTAB. CTAB, as a cationic surfactant, tends to coordinate with Co^{2+} at the initial

stage of the reaction, and thereafter amorphous microspheres of Co(CTAB)^{2+} with large particle size form as the nuclei of cobalt precursor in aqueous solution, as indicated in Fig. 5(a).

2) Formation of CoSe_2 nanograins. SeO_2 dissociates in water to generate SeO_3^{2-} at the same time as Co(CTAB)^{2+} nuclei form. Then SeO_3^{2-} gets reduced to highly reactive Se^0 species to generate Se^{2-} through disproportionation reaction. Consequently, Se^{2-} ions would combine with Se atoms to release Se_2^{2-} ions ($\text{Se} + \text{Se}^{2-} = \text{Se}_2^{2-}$). Because of the much stronger binding force between Co^{2+} and Se_2^{2-} than that between Co^{2+} and CTAB, as-formed Se_2^{2-} ions are coordinated to Co^{2+} immediately, and hence CoSe_2 nanograins form. Notably, as-formed CoSe_2 nanograins actually grow on the surface of Co(CTAB)^{2+} nuclei particles, as revealed in Fig. 5(c). As the reaction proceeds, Co(CTAB)^{2+} nuclei keep dissolving and recrystallizing successively, and thus nuclei microspheres become smaller and smaller while the amount of crystalline CoSe_2 nanoparticles keep increasing.

Fig. 5 SEM images of the CoSe_2 samples synthesized at 180°C in a mixed solvent (40 mL, $V_{\text{DETA}}:V_{\text{H}_2\text{O}} = 2:1$) with 1.5 mmol CTAB at different time points of the hydrothermal reaction: (a) 15 min, (b) 1 h, (c) 4 h, (d) 6 h, (e) 12 h, and (f) 16 h.

Fig. 6 Schematics of the formation mechanism of hierarchical CoSe_2 microclews.

3) “Stringing” by DETA. Meanwhile, during hydrothermal reaction, DETA is protonated by water molecules to release positively charged ammonium ions, which are subsequently incorporated into CoSe₂ nanograins by coordination at Se sites. Protonated DETA, due to its linear configuration, acts as a linear template to direct the accumulation of CoSe₂ nanograins linearly. Such “stringing” effect turns out to be dominant as the reaction proceeds to ≥ 12 h, and thus the clew-like structure becomes distinct in Figs. 5(e) and 5(f).

Notably, the original nuclei spheres also act as a template for subsequent microclews; therefore, it is rational that only nanosheets can form if no CTAB is introduced in the reaction (Fig. 2(a)). Neither the “balling” effect of CTAB nor the “stringing” effect of DETA is negligible for construction of the microclews, and such dual-surfactant templating strategy is expected to be a versatile method for assembly of various 3D hierarchical microstructures.

3.3 Complex permittivity and microwave absorption property

To reveal the microwave absorption properties of as-synthesized hierarchical CoSe₂ microstructures, the relative complex permeability and permittivity are measured, based on which RL values are calculated according to Eqs. (1) and (2) (i.e., transmit line theory) [42–45]:

$$Z_{in} = \sqrt{\mu_r / \varepsilon_r} \tanh(-j(2\pi/c)\sqrt{\mu_r / \varepsilon_r}fd) \quad (1)$$

$$RL(\text{dB}) = -20\log_{10}(|(Z_{in} - 1) / (Z_{in} + 1)|) \quad (2)$$

where ε_r and μ_r are the relative complex permittivity and permeability of the absorber, respectively. f is the frequency of microwave in free space, c is the velocity of light, d is the coating thickness, and Z_{in} is the input impedance of the absorber. Detailed information of the

selected samples for measurement is summarized in Table 1.

Figure 7(a) shows the RL of the CoSe₂ powder/epoxy resin composites. The minimum RL values ($RL_{\min}$) for Samples A and D are -12.24 and -15.47 dB at 9.43 GHz, respectively, while the $RL_{\min}$ for other samples are -26.93 dB for Sample B, -17.70 dB for Sample C, -23.75 dB for Sample E, and -25.69 dB for Sample F at ~ 7.28 GHz. It is distinct that the morphology of CoSe₂ will greatly affect its microwave absorption property. Basically, $RL_{\min}$ becomes much stronger and shifts to lower frequency as CoSe₂ microstructure transforms from simple nanosheet to hierarchical microclew. Amazingly, the $RL_{\min}$ of microclew Sample B is $\sim 120\%$ higher than that of Sample A, and its effective absorption bandwidth (EAB, the bandwidth of $RL \leq -10$ dB) is also improved for $\sim 104\%$ compared with Sample A, as presented in Table 1. As the highly porous structure of CoSe₂ microclew significantly increases its surface area ($14.89 \text{ m}^2 \cdot \text{g}^{-1}$ vs. $2.06 \text{ m}^2 \cdot \text{g}^{-1}$, Table S1 in the ESM), the interfacial dipole polarization and dielectric relaxation effects get enhanced compared with pristine CoSe₂ nanosheets. Moreover, abundant dissipation channels within the interconnected pores ($0.079 \text{ mL} \cdot \text{g}^{-1}$ vs. $0.016 \text{ mL} \cdot \text{g}^{-1}$ of the pore volume) bring about extended microwave

Table 1 Detailed information of the selected CoSe₂ samples for electromagnetic measurements, as well as the absorption performance of the CoSe₂/epoxy resin composites

Sample	CTAB	Temperature (°C)	Time (h)	Morphology	$RL_{\min}$ (dB)	EAB (GHz)
A	0	180	16	Nanosheet	-12.24	1.82
B	1.5 mmol	160	16	Microclew	-26.93	3.72
C		180	16		-17.70	2.14
D		200	16	Particle-agglomerated microsphere	-15.47	2.87
E		180	24		-23.75	3.15
F		180	48		-25.69	3.46

Fig. 7 (a) RL curves of the selected CoSe₂ microstructure composites at a thickness of 2 mm. (b, c) Relative complex permittivity of the samples: (b) real and (c) imaginary parts.

propagating time and pathway, resulting in promoted multiple scattering and reflection, and consequently the dissipation of microwave energy [46–48]. On the other hand, it is found that the $RL_{\min}$ for the samples changes from -17.70 to -25.69 dB as the reaction time is prolonged from 16 to 48 h, suggesting that stronger spontaneous polarization is achieved as longer reaction time brings about higher crystallinity [49,50].

Notably, the highly porous microclew Sample B obtained at a relatively lower temperature of 160°C exhibits enhanced absorption performance in terms of both $RL_{\min}$ and EAB values compared with Sample C which possesses similar clew-like morphology. This may be owing to its larger surface area ($14.89\text{ m}^2\cdot\text{g}^{-1}$ vs. $13.37\text{ m}^2\cdot\text{g}^{-1}$, as indicated in Table S1 in the ESM) and abundant surface defects resulted from the lower synthetic temperature, which generate more dissipation sites and more interface contributing to promoted interface polarization [51]. Possible defects which might exist in these CoSe_2 products include surface dangling bonds, amorphous species in the $[\text{Se}]_n$ chain, stacking faults, and lattice mismatch derived from the cubic–orthorhombic phase transition of CoSe_2 . The boosted surface defective sites in Sample B are evidenced by the greatly eliminated characteristic scattering band intensity in as-recorded Raman spectra (Fig. S3 in the ESM) [52], with the detailed band assignment described in the ESM. Moreover, these defects can also help improve the electrical conductivity of the CoSe_2 composite [39,52–54]. EIS Nyquist plots [55–57] are acquired to reveal the interfacial charge transfer resistance (R_{CT}), which corresponds to the diameter of the arc of as-obtained CoSe_2 composites (Fig. S4 in the ESM). Generally, the R_{CT} value is inversely proportional to the conductivity, which means that lower R_{CT} value indicates higher conductivity. Therefore, the lowest R_{CT} value of Sample B ($47.52\ \Omega$) helps to verify its improved electrical conductivity compared with other CoSe_2 samples, which consequently results in promotion of the conductivity loss, as depicted in Fig. 8.

CoSe_2 is known as a semiconductor, in which magnetic loss is almost negligible and hence dielectric loss dominates the overall microwave loss mechanism. The real (μ') and imaginary (μ'') parts of relative complex permeability are 1 and 0.01 for all samples, respectively, and remain constant throughout 2–16 GHz. Hence in this regard, the real (ϵ') and imaginary (ϵ'') parts of relative complex permittivity of all CoSe_2

Fig. 8 Schematics of microwave absorption mechanisms of the CoSe_2 microclew system.

samples are recorded in the frequency range of 2–16 GHz, as displayed in Figs. 7(b) and 7(c). Generally, the real part of complex permittivity represents the storage ability of microwave energy, while the imaginary part stands for loss ability [42,58]. It is intriguing that the variation of ϵ' for Samples A–F is almost opposite to that of ϵ'' . It is known that materials possessing larger ϵ'' and dielectric loss tangent of complex permittivity usually show stronger absorption, and thus the tendency of ϵ'' variation is consistent with that of RL . The ϵ' curve of each sample exhibits a decrease within 2–16 GHz range with some small fluctuations, and no resonance peak is observed for Samples B and F. In contrast, ϵ'' curves exhibit mild increase at low-frequency band of < 8 GHz and then decrease along with the frequency. Particularly, the ϵ'' curves of Samples B, E, and F display obvious fluctuations within the range of 2–10 GHz, implying the existence of relatively strong dielectric resonance. Based on these results, a spatial conductive network model could be proposed for explanation of the dielectric loss performance of these hierarchical porous CoSe_2 absorbents. Pristine nanosheets have only one stable propagation pathway for incident microwave, whilst the hierarchical CoSe_2 microclews composed of numerous nanobelt/nanoparticle units could create a 3D interconnected conductive network, which provides more microwave propagation channels for dielectric loss [37].

Specifically, Sample B exhibits the largest ϵ'' values throughout the band of 2–16 GHz, which could be attributed to its strongest relaxation polarization of incident microwave considering its improved electrical conductivity and the lowest R_{CT} , as well as the largest

interior pore volume and specific surface area affording the most abundant interfaces. Finally, impedance matching characteristics in terms of the impedance coefficient (M_Z), and the attenuation constant (α) are calculated according to Eqs. (3) and (4) [32,37], with the resulted M_Z and α curves presented in Fig. S5 in the ESM.

$$M_Z = \frac{2Z'_{in}}{|Z_{in}|^2 + 1} \quad (3)$$

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\varepsilon'\mu'' + \varepsilon''\mu')^2}} \quad (4)$$

where Z' represents the real part of normalized input impedance. It is obvious that α curves (Fig. S5(b) in the ESM) show similar tendency with ε'' curves (Fig. 7(c)), and the regularity of M_Z curves (Fig. S5(a) in the ESM) is also in good agreement with the RL curves (Fig. 7(a)), among which Sample B demonstrates the closest M_Z value to 1. Both the impedance matching characteristics and attenuation constants further confirm the best dielectric loss performance of highly porous and hierarchical microclew Sample B.

4 Conclusions

In summary, we propose a facile hydrothermal strategy for controlled synthesis of hierarchical CoSe₂ microclews. The formation mechanism of such unique microclew morphology is attributed to the dual-surfactant templating effects mediated by both CTAB and DETA, where CTAB plays a dominant role of “balling” and DETA plays the role of “stringing”. Owing to the highly porous and hierarchical structure, as-obtained CoSe₂ microclews display ~120% enhanced absorption intensity and ~104% increased EAB compared to simple CoSe₂ nanosheets, with RL_{min} reaching −26.93 dB at 7.28 GHz. Overall, for the first time, the CoSe₂ microclews have been established as a new promising microwave absorption material. Besides, the dual-surfactant templating route could also be extended for constructing more hierarchical structures with designed morphology and surface architecture towards various applications like catalysts, sensors, energy conversion and storage devices, microwave absorbents, etc.

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Electronic Supplementary Material

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