Neural network-inspired hybrid aerogel boosting solar thermal storage and microwave absorption

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ABSTRACT

In response to the rapid development of highly integrated multifunctional electronic devices, developing advanced multifunctional composite phase change materials (PCMs) that integrate thermal management, solar-thermal conversion and microwave absorption has become increasingly essential. Herein, we propose a bionical strategy to design neural network-like (carbon nanofiber) CNF@Co/C aerogels by growing ZIF-67 in situ on bacterial cellulose (BC) and subsequent calcination strategies. After the encapsulation of thermal storage unit (paraffin wax, PW), the obtained multifunctional composite PCMs (PW-CN斐@Co/C aerogel) are composed of “soma” (Co/C polyhedra), “axon” (porous CNF) and thermal storage unit (PW). Importantly, the composite PCMs show a high solar-thermal conversion efficiency of 95.27% benefiting from the synergism of “soma” with strong local surface plasmon resonance (LSPR) effect and “axon” with enhanced photon transmission path. More attractively, the composite PCMs also display good microwave absorption capacity with a minimum reflection loss (RL) of -26.8 dB at 10.91 GHz owing to the synergy of magnetic and dielectric components along with abundant polarization and multiple reflections. Our developed functionally integrated composite PCMs provide a prospective application of highly integrated and miniaturized electronic devices in complex and changeable outdoor environments.

KEYWORDS

phase change materials, bionic design, thermal energy storage, solar-thermal conversion, microwave absorption

1 Introduction

Modern electronic devices are evolving towards multifunctionality, high integration, miniaturisation and high frequency in the 5G era [1]. However, electronic devices inevitably generate plenty of heat, causing severe instantaneous thermal shock to weaken the efficiency and working life of electronic devices [2, 3]. In addition, the operational efficiency of electronic devices dramatically drops at low temperatures, even failing to be activated. Simultaneously, numerous electromagnetic waves generated by electronic devices within a limited space can cause mutual interference and damage to human health [4, 5].

Overheating or overcooling can drastically reduce the operating efficiency of electronic devices [6]. Thermally enhanced composite phase change materials (PCMs) have the ability to store and release massive energy as latent heat, which are widely acknowledged for the ability to ensure precise temperature control in electronic devices [7, 8]. Consequently, developing high-performance composite PCMs has become crucial for improving the thermal management capability of electronic devices. Additionally, it is also important to introduce solar-thermal conversion function into composite PCMs to maintain the stability of electronic devices in outdoor low temperature environments [9, 10]. However, Pure PCMs exhibit a notably low light absorption capacity [10, 11]. Solar-thermal materials with broadband absorption can help PCMs convert and store solar energy [12]. Bacterial cellulose (BC) is a highly desirable natural biomass due to its numerous advantages including biodegradability, low cost, high purity, renewability, easy modification and functionalization. BC-derived carbon nanofiber (CNF) by high temperature carbonization has been considered as a promising solar-thermal material [5, 13, 14].

Except thermal management of electronic devices, it is also
imminent to solve mutual electromagnetic interference (EMI) and electromagnetic wave pollution caused by highly integrated electronic devices [15]. Recent interest in microwave absorption has focused on organometallic frameworks (MOFs) due to their exceptional porosity, adjustable pore structure and high specific surface area [16–18]. MOFs as self-sacrificing precursors can be converted in situ into porous magnetic metal/carbon nanostructures. Consequently, MOF-derived nanostructures with electric loss and magnetic loss can effectively modulate impedance matching to enhance microwave absorption. For instance, Qiu et al. synthesized Ni-MOF derived hollow Ni/C microsphere with excellent microwave absorption of a reflection loss (RL) of −57.25 dB and a bandwidth of 5.1 GHz at 1.8 mm [19]. Moreover, Zhang et al. synthesized CoZn-containing nitrogen-doped carbon nanotube spheres on graphene nanosheets using MOFs and graphene as precursors, which exhibited excellent microwave absorption of a RL of −47.31 dB and a −10 dB bandwidth of 4.01 GHz [20]. Unfortunately, utilizing a multilayer design consisting of thermal management layer and microwave absorbing layer cannot ensure normal and efficient operation of electronic devices due to limited narrow space and high interface thermal resistance. Therefore, developing advanced multifunctional composite materials integrating thermal management and microwave absorption is significant to promote the cutting-edge applications of composite PCMs.

Herein, we bionically designed a neural network-like CNF@Co/C aerogels using self-assembly and high temperature carbonization strategies. As neurons, Co/C polyhedra display excellent light capture capability. As soma, CNF connecting the polyhedra can efficiently hasten the transmission of electrons and photons. After paraffin wax (PW) encapsulation, as-prepared PW/CNF@Co/C aerogel composite PCMs exhibit outstanding solar-thermal conversion and microwave absorption performance. In addition, the composite PCMs also exhibit long-term thermal cycle stability. Our bionically fabricated high-performance and functional integrated aerogel-based composite PCMs with thermal management, solar-thermal conversion and microwave absorption functions show a good prospective application in overcoming overheating or overcooking and EMI of electronic equipments.

2 Experimental

2.1 Materials

Bacterial cellulose (BC) was purchased by Guilin Qi Hong Technology Co., Ltd. Methanol, ethanol and were purchased from Sinopharm Chemical Reagents Beijing Co. Ltd. NaOH, 2-Methylimidazole (2-MI), paraffin wax (PW), and Co(NO₃)₂·6H₂O were provided from Shanghai Aladdin Biochemical Technology Co., Ltd. All the chemicals used have not been further purified.

2.2 Preparation of BC@ZIF-67 aerogel

The pretreatment of BC involved immersing the hydrogels in 1% NaOH (w/v) at 80 °C for 6 h. The hydrogels underwent 48-hour deionized water wash to remove acetic acid derived from BC during fermentation. Following that, the pretreated BC was placed in a 30 mL methanol solution with 2 mmol of Co(NO₃)₂·6H₂O and stirred for 20 h at room temperature. Following this, 60 mL methanol solution containing 1.64 g 2-MI was gradually added to the mixture solution under stirring. The gels underwent stirring for 2 h and then aged silently for 12 h at 25 °C. At last, purple gels were washed with deionized water and frozen dried to yield BC@ZIF-67 aerogels.

2.3 Preparation of CNF@Co/C aerogels

BC@ZIF-67 aerogels were directly calcined at 600, 800, and 1000 °C for 6 h under N₂ atmosphere with 5 °C/min to yield metal Co-embedded carbon nanofiber (CNF@Co/C) aerogels.

2.4 Preparation of PW-CNF@Co/C aerogel composite PCMs

PW-CNF@Co/C aerogel composite PCMs were synthesized using vacuum impregnation. In a standard procedure, CNF@Co/C aerogel was initially added to hexane solution containing PW. PW-CNF@Co/C aerogel composite PCMs were acquired by vacuum after stirring 3 h at 80 °C, drying at 80 °C for 24 h to remove the hexane solution.

2.5 Characterizations

Scanning electron microscope (SEM, Regulus 8100) and transmission electron microscope (TEM, FEI TF200) were used to analyze the morphology. X-ray diffraction (XRD, Bruker D8-Advance) was employed to determine the crystal structure. Fourier transform infrared spectrometer (FT-IR, Nicolet 6700) was used to evaluate the functional groups. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+) was used to study the surface state characteristics. The degree of graphitization was determined by Raman microscope (Horiba Hr Evolution). Ultraviolet-visible-near infrared spectrometer (Shimadzu UV-3600) was used to evaluate the light absorption ability. Vibrating sample magnetometer (VSM, Quantum Design) was used to assess the magnetic properties. The enthalpy and phase change temperature were determined by differential scanning calorimetry (Mettler Toledo DSC3). Thermal stability properties are assessed using Thermogravimetric Analysis (TGA, Netzsch Sta449F3). Infrared thermography is captured by an infrared thermal imager (Fluke Ti450). Solar-thermal conversion performance was tested by infrared thermometer (R2100) and a simulated solar xenon lamp (AM 1.5, 100 mW/cm²). Vector network analyzer (Agilent E5071C) in 2–18 GHz was carried out to measure the complex permittivity and complex permeability. Differential charge calculations were conducted by density functional theory (DFT) and Quantum Espresso software and were modeled using the Perdew-Burke-Ernzerhof (PBE).

3 Results and discussion

3.1 Structural and chemical analysis

Nature has created a magical world and inspired the whimsy of scientists [21]. Herein, we propose a neural network bionic strategy for the preparation of PW-CNF@Co/C aerogel composite PCMs, which is schematically illustrated in Fig. 1. ZIF-67 attained numerous nucleation centers for in situ self-assembly benefiting from abundant hydroxyl groups in BC. Firstly, to initiate the growth of ZIF-67 crystals, the NaOH pre-treatment of BC gel was employed to generate nucleation centers. Then, hydroxylated BC was penetrated into the Co(NO₃)₂·6H₂O solution to uniformly absorb Co⁺ onto the BC surface through electrostatic interaction and coordination between numerous –OH groups and Co⁺. Subsequently, 2-methylimidazole (2-MI) solution was introduced
into the system to facilitate heterogeneous crystal nucleation. Thus, ZIF-67 polyhedra were uniformly grown on BC by the coordination between Co$^{2+}$ and 2-MI. Resultantly, ZIF-67 polyhedra were strung on BC skeleton to synthesize BC@ZIF-67 aerogels after undergoing high temperature calcination.期间，BC@ZIF-67 aerogels were transformed into black CNF@Co/C aerogels after being subjected to high temperature calcination. During the calcination, BC skeleton was converted into three-dimensional (3D) interconnected CNF network and ZIF-67 was converted into metallic Co-embedded carbon [22]. Importantly, ultralight CNF@Co/C aerogels can stand gently on petals without collapsing them (Fig. S1 in the Electronic Supplementary Material (ESM)). Finally, PW was physically infiltrated into CNF@Co/C aerogels to prepare PW-CNFAerogel composite PCMs through the capillary force and van der wals force between PW and CNF@Co/C aerogels [23].

The BC hydrogels with pristine monolithic structure exhibit a 3D porous network (Fig. 2(a)). Figure 2(b) demonstrates that the alkali-treated BC facilitates the in situ assembly of large-area uniform ZIF-67 polyhedra that are effectively penetrated and inserted into the BC skeleton. After carbonization, CNF@Co/C aerogels maintain their polyhedral structure similar to ZIF-67 and also retain a 3D porous interconnected network (Fig. 2(c)). CNF@Co/C aerogels are structurally similar to a neural network, where CNF and Co/C serve as the axon and neuron, respectively (Figs. 2(d) and 2(g)) [24]. The pyrolysis process causes the polyhedral surface of CNF@Co/C aerogels to become rougher. TEM images further confirm the neural network structure of CNF@Co/C aerogels, in which CNF fibers are observed to be embedded in the polyhedra (Fig. 2(e)). In addition, HRTEM images demonstrate that Co nanoparticles are wrapped by multiple carbon layers, attributing to the (002) of graphitic carbon with a crystalline spacing of 0.34 nm. The EDS images reveal that the C, N elements are uniformly distributed in CNF@Co/C aerogels composed of porous carbon nanofibers coated with a carbon layer doped with Co and N. In particular, Co element is uniformly distributed on the nanoparticles.

XRD confirms the crystal structure of BC@ZIF67 aerogels and CNF@Co/C aerogels. BC@ZIF-67 maintains characteristic peaks of ZIF-67, indicating that ZIF-67 is successfully grown on BC in situ (Fig. S2(a) in the ESM). After high temperature carbonization, the diffraction pattern for CNF@Co/C aerogels has three broad peaks at 44.2°, 51.6° and 76.4°, corresponding to (111), (200) and (220) of Co crystal (JCPDS No. 15-0806), respectively [22]. A faint yet distinct diffraction peak gradually emerges at 26.1°, indicating the presence of graphitic carbon with a (002) crystal plane, which is in line with HRTEM results (Fig. 3(a), Fig. S2(b) in the ESM and Fig. 2(f)). According to XRD analysis, the CNF@Co/C encapsulated PW exhibits noticeable PW characteristic peaks at 21.3° and 23.5°, affirming the retention of high crystallinity of PW molecules (Fig. 4(a)) [25].

Figure 3(b) demonstrates the FT-IR spectra of BC@ZIF-67 aerogels and CNF@Co/C aerogels. The occurrence of peaks at approximately 1570 cm$^{-1}$ can be associated with the stretching vibration of C=N. Additionally, the presence of peaks at approximately 758 and 691 cm$^{-1}$ can be attributed to the out-of-plane bending of C=N. The positions of all distinctive peaks in PW-CNFAerogel composite PCMs correspond well with those detected in CNF@Co/C aerogels and pure PW [26]. No new peaks or peak shifts indicate that CNF@Co/C aerogels have excellent compatibility with PW (Figs. S4 and S5 in the ESM).

Raman spectra are detected to assess the graphitization degree...
Figure 2  SEM images of (a) BC, (b) BC@ZIF-67 aerogel, (c) and (d) CNF@Co/C-1000 aerogel. (e) TEM image, (f) HRTEM image of CNF@Co/C-1000 aerogel. (g) Neural network-inspired design of CNF@Co/C aerogel, and (h) TEM-EDS of CNF@Co/C-1000 aerogel.

Figure 3  (a) XRD patterns; (b) FTIR spectra. (c) Raman spectra of CNF@Co/C aerogel. (d)–(f) XPS spectra of CNF@Co/C-1000 aerogel. (g)–(i) N2 adsorption-desorption isotherms and pore size distributions of CNF@Co/C aerogel.
of CNF@Co/C aerogels (Fig. 3(c)). Generally, D-band (1339.4 cm$^{-1}$) typically indicates disordered carbon structure and atomic crystal defects, while G-band (1592.1 cm$^{-1}$) represents the in-plane stretching vibration from sp$^2$ hybrid carbon atoms. The intensity ratio of D-band and G-band ($I_D/I_G$) intensity ratio serves as a reference standard for evaluating the graphitization degree of the carbon components in CNF@Co/C aerogels. As the pyrolysis temperature increases, $I_D/I_G$ values show an upward trend from 0.92 (CNF@Co/C-600 aerogel) to 0.99 (CNF@Co/C-1000 aerogel). This trend may benefit microwave absorption associated loss ability and thermal conductivity (Table S1 in the ESM).

XPS is employed to investigate the surface chemical composition and valence state of CNF@Co/C-1000 aerogel (Fig. S3 in the ESM). Figures 3(d)–3(f) show the presence of C, Co and N elements in CNF@Co/C-1000 aerogel, which is consistent with the elemental mapping (Fig. 2(h)). As for C 1s spectrum of CNF@Co/C-1000 aerogel, C=C/C-C, C-N and C=O appear at 284.8, 285.6 and 287.4 eV, respectively, indicating successful doping of nitrogen heteroatoms in carbon network (Fig. 3(d)). N-doped element can serve as hopping centers allowing CNF@Co/C-1000 aerogels to possess electric dipoles, thereby generating dipole polarization relaxation to cause related dielectric loss [27]. The N 1s spectrum of CNF@Co/C-1000 aerogel displays graphitic-N (401.1 eV), pyrrolic-N (399.6 eV), and pyridinic-N (398.6 eV) (Fig. 3(e)). Furthermore, the Co 2p spectrum of CNF@Co/C-1000 aerogel is shown in Fig. 3(f). In detail, metallic Co peak and Co-O bond appear at 778.8 and 780.8 eV for CNF@Co/C-1000 aerogel [21]. Considering the sensitivity of metallic Co to oxygen in the air, the observed Co-O peak may be attributed to the existence of cobalt oxide on the metallic Co surface.

To further study the porous properties of CNF@Co/C aerogels, we measured nitrogen adsorption-desorption isotherm curves. The results reveal that all CNF@Co/C aerogels exhibit type IV isotherms having a hysteresis loop of H3 type at higher relative pressures, indicating that mesopores were constructed in the aerogels. Brummer-Emmett-Taylor (BET) equation and Barrett-Joyner-Hallenda (BJH) method were used to determine specific surface area and pore size distribution, respectively (Figs. 3(g)–3(i)) [28]. The sequential increase in the specific surface area of CNF@Co/C aerogels is contingent on the carbonization
temperature. In detail, the specific surface areas of CNF@Co/C-600 aerogel, CNF@Co/C-800 aerogel and CNF@Co/C-1000 aerogel are 168, 278, and 338 m$^2$·g$^{-1}$, respectively. The average pore sizes of CNF@Co/C-600 aerogel, CNF@Co/C-800 aerogel and CNF@Co/C-1000 aerogel are 6.2, 4.8, and 4.8 nm, respectively, further confirming the existence of mesopores (Table S4 in the ESM). Numerous studies have demonstrated that a porous network structure not only provides large specific surface area for adsorbing PCMs, but also dissipates microwave energy through scattering or multiple-reflection. Thus, PW-CNf@Co/C can be expected to become excellent microwave absorbing composite PCMs [29].

3.2 Thermal properties

PW was fully adsorbed in the pores of CNF@Co/C aerogel through capillary force and surface tension (Figs. S7 and S8 in the ESM). Thermal properties of composite PCMs are evaluated depending on their melting/freezing enthalpy and temperature (Figs. 4(b) and 4(c)) [30]. These properties of PW-CNf@Co/C aerogel composite PCM are summarized in Fig. 4(d) and Table S2 in the ESM. In detail, PW-CNf@Co/C-1000 aerogel composite PCMs exhibit a melting point of 59.67 °C and a melting enthalpy of 122.19 J/g, as well as a freezing point of 54.48 °C and a freezing enthalpy of 120.95 J/g. Similarly, PW-CNf@Co/C-800 aerogel composite PCMs display a melting point of 59.96 °C and a melting enthalpy of 122.04 J/g, whereas a freezing point of 55.14 °C and a freezing enthalpy of 120.87 J/g. Likewise, PW-CNf@Co/C-600 aerogel composite PCM exhibit a melting point of 59.46 °C and a melting enthalpy of 121.60 J/g, as well as a freezing point of 55.31 °C and a freezing enthalpy of 120.61 J/g. The thermal stability analysis showed that the composite PCMs is suitable for application at medium-low temperature scenarios (Fig. S6 in the ESM).

Thermal cycling stability is an important factor limiting cutting-edge applications of composite PCMs [31]. Thermal cycling stability is evaluated by multiple heating-cooling cycles. As shown in Fig. 4(e) and Fig. S9 in the ESM, the peak positions and relative areas of DSC curves of PW-CNf@Co/C-1000 aerogel composite PCMs almost overlap before and after multiple cycles, demonstrating excellent thermal energy storage durability. Likewise, the FT-IR and XRD spectra are nearly similar after 100 heating-cooling cycles (Fig. S10 in the ESM), demonstrating excellent thermal cycling reliability in functional groups and crystal structures.

3.3 Solar-thermal energy conversion and mechanism

Black low-reflective PCMs are effective at capturing solar energy and transforming it into thermal energy [32]. To determine the photo-absorption capabilities of pure PW and PW-CNf@Co/C aerogel composite PCMs, UV–Vis–NIR absorption spectra were recorded. Pure PW only exhibits relatively strong absorption around 1700–1800 nm, and the absorption is very weak at other wavelength ranges, especially in the ultraviolet region (200–380 nm) and visible light range (380–780 nm) even below 20%. Interestingly, PW-CNf@Co/C aerogel composite PCMs exhibit broadband and strong full-spectrum light absorption (>90%) (Fig. 5(a)).

To assess the solar-thermal potential of PW-CNf@Co/C
aerogel composite PCMs, a corresponding test system is designed to real-time monitor the temperature variation curves of the composite PCMs under simulated solar conditions [33]. The photosensitive CNF and Co/C in PW-CNF@Co/C aerogel composite PCMs can immediately capture and absorb the irradiated solar energy, simultaneously converting it into thermal, causing the temperature rises rapidly. The temperature of the sample gradually increases until it reaches the platform period of the melting phase change of PW. Subsequently, the temperature rises rapidly again. After removing the light, the temperature decreases rapidly and tends to be stable, accompanied by latent heat release, corresponding to the solidification of PW (Fig 5(b)). The temperature change trend of the solar-thermal curves in different PW-CNF@Co/C aerogel composite PCMs are consistent. However, PW-CNF@Co/C-1000 aerogel composite PCMs tend to reach the same temperature faster compared to PW-CNF@Co/C-600 and PW-CNF@Co/C-800 aerogel composite PCMs.

The solar-thermal conversion efficiency ($\eta$) of PW-CNF@Co/C-600, PW-CNF@Co/C-800 and PW-CNF@Co/C-1000 composite PCMs are calculated to be 90.96%, 92.76%, and 95.27%, respectively (Fig 5(c) and Table S3 in the ESM) [34]. Comparing with other composites, the solar-thermal conversion of PW-CNF@Co/C aerogel composite PCMs is above average (Table S5 in the ESM).

$$\eta = \frac{m \Delta H}{PS(t_2-t_1)}$$  \hspace{1cm} (1)

The equation demonstrates the relationship between the mass ($m$), phase change enthalpy ($\Delta H$), irradiation intensity of the simulated solar source ($P$), surface area ($S$), and the starting ($t_1$) and terminating ($t_2$) times of the phase change process.

Figure 5(d) illustrated the solar-thermal conversion and storage mechanism of PW-CNF@Co/C aerogel composite PCMs. The PW-CNF@Co/C aerogel composite PCMs exhibit enhanced solar-thermal conversion capacity benefiting from efficient phonon transportation, multiple solar reflection and broad-band intense solar absorption of composite PCMs [35]. Furthermore, ZIF-67 derived highly dispersed Co nanoparticles with LSPR effect further enhance solar-thermal conversion. In our designed interconnected hierarchical neural-like solar-thermal network structure (CNF@Co/C aerogel), the axon-like CNF and soma-like Co/C work together as solar-thermal capturers and molecular heaters [36]. The carbon network skeleton embedded with Co nanoparticles facilitates efficient phonon diffusion, enhancing the rate of heat transfer by prolonging the mean free paths of phonons. Simultaneously, interconnected hierarchical neural-like solar-thermal network structure in the PW-CNF@Co/C aerogel composite PCMs can increase photon transmission path and promote light absorption due to multiple reflection and scattering of solar. Additionally, soma-like Co nanoparticles with LSPR effect further enhances the solar absorption ability of PW-CNF@Co/C aerogel composite PCMs. Therefore, PW-CNF@Co/C aerogel composite PCMs display broadband and strong solar absorption (over 90%) over the full spectrum, thus yielding excellent solar-thermal conversion performance [7].

### 3.4 Microwave absorption and mechanism

In order to prevent mutual EMI between electronic devices, the electronic devices need not only have good thermal management performance, but also show high electromagnetic wave absorption capacity. However, Traditional microwave absorbers typically use PW as a supplemental wave transmitter when evaluating their performance. Interestingly, our designed composite PCMs by directly encapsulating PW into CNF@Co/C aerogel in advance exhibit efficient functional coupling of thermal management and microwave absorption.

To assess microwave absorption capacity of PW-CNF@Co/C aerogel composite PCMs, we explored their electromagnetic parameters. Specifically, the complex permittivity ($\varepsilon$) and permeability ($\mu$) of these composite PCMs are investigated. $\varepsilon$ and $\mu$ are the real and imaginary components of the complex permittivity, while $\varepsilon'$ and $\varepsilon''$ are the real and imaginary components of the complex permittivity, respectively. The real components of both permittivity and permeability reflect ability to store electromagnetic energy, whereas the imaginary components and indicate their ability to dissipate it (Fig S1 in the ESM). RL can be calculated to visually evaluate the microwave absorption performance [37, 38].

In these equations, $Z_c$ and $Z_o$ represent the impedance of free space and the input impedance of absorber, respectively. $c, f$ and $d$ represent free space microwave velocity, microwave frequency and absorption thickness, respectively [39].

As is displayed in Fig. 6(a), these composite PCMs exhibit distinct hysteresis loop and characteristic ferromagnetic behavior, enhancing magnetic loss ability. The saturation magnetic value of the PW-CNF@Co/C-1000 aerogel composite PCMs is measured at 52.8 emu/g, indicating a significant magnetic capacity. As can be seen in Fig. 6(b) and Fig. S14 in the ESM, PW-CNF@Co/C-600 aerogel composite PCMs show a poor microwave absorption of $\sim 10.5$ dB at 5.97 GHz. With pyrolysis temperature increasing, the microwave absorption ability of PW-CNF@Co/C aerogel composite PCMs improved [40]. The minimum RL values of PW-CNF@Co/C-800 aerogel composite PCMs and PW-CNF@Co/C-1000 aerogel composite PCMs are $\sim$15.80 dB at 8.11 GHz and $\sim$26.8 dB at 10.91 GHz, respectively. Compared with other microwave absorption functionalized composite PCMs, the microwave absorption performance of PW-CNF@Co/C aerogel composite PCMs is above average (Table S6 in the ESM).

Furthermore, the effective bandwidth of PW-CNF@Co/C-1000 aerogel composite PCMs can cover both X-band (8‒12 GHz) and Ku-band (12‒18 GHz) through the regulation of thickness (Fig. 6(c)). The strategy has broad applications across multiple industries, including climate satellite, broadcast satellite, communications satellite, military radar, and wireless communication systems. The versatility of the strategy extends applicability to various industries, such as climate satellite, wireless communications, broadcast satellite, communications satellite and military radar systems.

Figure 6(d) illustrates microwave absorption mechanism of PW-CNF@Co/C aerogel composite PCMs. Firstly, 3D interconnected CNF/C network structure increases the propagation path of microwaves, while the porous matrix structure effectively enhances the scattering and reflection of microwave. Both of these factors contribute to an overall improvement in microwave absorption efficiency. Simultaneously, 3D conductive CNF/C network skeleton can efficiently enhance electronic migration, leading to conduction loss and conversion of electromagnetic energy into thermal energy, ultimately absorbing electromagnetic waves [41]. Furthermore, CNF@Co/C aerogel can facilitate interfacial polarization and effectively adjust impedance matching. To calculate differential charge density by DFT, optimized geometric models of Co crystal/ nitrogen doped carbon skeleton and CNF are constructed (Figs. 6(e)–6(g)) [5, 42].
disappearance. The electrons on the metal Co crystal transfer to the nitrogen doped carbon skeleton and accumulate in the interface, generating strong interfacial polarization [43]. Simultaneously, the electrons on the polyhedra transfer to CNF and accumulate in the interface, further enhancing interfacial polarization. In addition, dipole polarization and defect polarization are enhanced by the abundant defects in nitrogen doped carbon skeletons. The consumption of incident waves is promoted by metallic Co crystals consisting of natural resonance and exchange resonance under an alternating electromagnetic field[39]. Therefore, PW-CNF@Co/C aerogel composite PCMs are promising microwave absorption materials, which can effectively absorb the microwave signals emitted from target aircraft to solve electromagnetic detection and further realize radar stealth [44].

3.5 Integrated application

To visually evaluate microwave absorption property of PW-CNF@Co/C-1000 aerogel composite PCMs, bluetooth signal interruption tests between Huawei smartphone (named as BNU-Thermal management) and Xiaomi smartphone (named as BNU-Microwave absorption) are conducted (Fig. 7(a) and Fig. S11 in the ESM) [45]. The bluetooth signals of Huawei smartphone and Xiaomi smartphone connect successfully under normal bare conditions (Fig. 7(a1)). While when Xiaomi smartphone is completely covered by a commercial microwave absorbing film, bluetooth signals cannot be properly connected because of the excellent microwave absorbing property of the film (Fig. 7(a2)). After digging a tiny hole on the commercial microwave absorbing film, the bluetooth signal is successfully reconnected again (Fig. 7(a3)).
7(a3)). Surprisingly, the bluetooth connection is destroyed when this tiny hole is covered by our developed PW-CNFeCo/C-1000 aerogel composite PCMs (Fig. 7(a4)). These findings indicate that PW-CNFeCo/C-1000 aerogel composite PCMs exhibit excellent microwave absorption capability, showing enormous potential in solving mutual interference of electronic devices.

Furthermore, to further evaluate thermal management property of composite PCMs, the tabletting ones is located on the motherboard of smartphone (Xiaomi, Max1, 5G, China, Fig. S12 in the ESM) [46]. After running the game continuously for approximately 30 min under the 5G signal (Beijing Normal University, Beijing, China), the maximum temperature of the bare smartphone motherboard is constantly about 44.7 °C (the purple circular area in Fig. 7(b1)). A distinct low temperature region (25.2 °C) is observed when the PW-CNFeCo/C-1000 aerogel composite PCM is tableted on the purple circle area of the mobile phone motherboard (Fig. 7(b2)). After 2 min of continuous operation of the mobile phone again, the temperature of the tabletting is nearly 36.6°C (Fig. 7(b3)), which is still lower than initial temperature (44.7 °C). Upon removal of the tabletting of composite PCMs, the temperature of the smartphone motherboard is approximately 41.9 °C (Fig. 7(b4)), and subsequently rapidly returns to a temperature of 44.8 °C (Fig. 7(b5)) close to the original temperature. This analysis indicates that PW-CNFeCo/C-1000 aerogel composite PCMs can effectively absorb heat generated during smartphone operation and ensure stable operation of the smartphone at a relatively stable temperature [47].

Considering the integrated application potential of composite PCMs, our designed microwave absorbing PW-CNFeCo/C aerogel composite PCMs with enhanced solar-driven energy storage can be applied in outdoor activities [48] (Fig. 8). When the temperature of electronic devices is excessively high, PW-CNFeCo/C aerogel composite PCMs also exhibit superior microwave absorption capability. Therefore, our designed microwave absorbing composite PCMs with enhanced solar-driven energy storage show a promise in solving the problems that electronic devices cannot work normally due to excessive heating or cooling and EMI [50].

4 Conclusion

In brief, inspired by a unique neural network, we prepared neural network-like CNF@Co/C aerogels through self-assembly and high temperature carbonization. After PW encapsulation, the prepared PW-CNFeCo/C aerogel composite PCMs combine solar-thermal conversion and microwave absorption functions. Specifically, PW-CNFeCo/C aerogel composite PCMs exhibit extensive and powerful light absorption capability (surpassing 90%) across the entire spectrum, as well as exceptional effectiveness in converting solar energy into thermal energy with an efficiency of 95.27%. Furthermore, PW-CNFeCo/C aerogel composite PCMs also exhibit substantial thermal storage capacity reaching 122.19 J/g and excellent thermal cycling reliability.
Besides, PW-CNF@Co/C aerogel composite PCMs display outstanding microwave absorption with a –26.8 dB RLmin at 10.91 GHz. Therefore, our designed PW-CNF@Co/C aerogel microwave absorbing composite PCMs with enhanced solar-driven energy storage present great potential in the thermal management and anti-EMI of electronic devices.

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**Electronic Supplementary Material:** Supplementary material (macroscopic digital photos, SEM images, XRD patterns, FT-IR spectra, XPS spectra, TGA curves, leakage test results, microwave absorption properties, cyclic test results, and tables about graphitization degree, photothermal efficiency, thermal performance, pore volume, and the comparison of photothermal conversion and microwave absorption) is available in the online version of this article at https://doi.org/10.26599/NRE.2024.9120120.

**Declaration of conflicting interests**

The authors declare no conflicting interests regarding the content of this article.

**Data availability**

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

**References**


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