Supporting Information

Hierarchical BN@PDA@Co-C/PAM Composites: Synergistic Enhancement of Microwave Absorption and Thermal Conductivity through Heterostructure Design

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Experimental

Materials

2, 5-dihydroxyterephthalic acid (H_4DOBDC) was acquired from Adamas-beta Chemical Reagent Co., Ltd. N, N-methylenebisacrylamide (MBA) were provided by Rhawn Chemical Reagent Co., Ltd. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), tetramethylethylene-diamine (TMEDA), 2-methimidazole, acrylamide (AM) were purchased from Macklin Chemical Reagent Co., Ltd. Ethanol (EtOH), methanol (MeOH) were procured from Xilong Scientific Co., Ltd. Potassium persulfate (KPS), glycerol (Gly) were obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd. All chemicals were used as received without further purification, and deionized (DI) water was used throughout this study.

Characterization

The morphology and microstructure of the synthesized samples were observed by scanning electron microscopy (SEM, FEI Quanta FEG 250). The microstructure of the Co-MOF-74 derivatives was characterized using transmission electron microscopy (TEM, JEOL JEM-F200). Three-dimensional X-ray Microtomograph (SKYSCAN 1272, Al 0.5 + Cu 0.038 radiation) was used to observe the spatial arrangement of the filler inside the composite material. X-ray powder diffraction (XRD, RIGAKU Ultima IV, Cu-Kα radiation, 2θ scan range: 10°-80°) was used to analyze the crystallographic structure and phase composition of the samples. The chemical bond of the material was determined by Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Scientific, Nicolet IS 50/6700) in the range of 400-4000 cm^{-1}. The heat resistance index and exact content of the material were determined by synchronous thermogravimetric analyzer (TG, STA449C/6/G) in N_2 atmopsphere from 50 °C to 750 °C with a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha) was used to determine the composition and valence state of elements on the surface of materials. The thermal image and temperature of the samples were recorded by an infrared thermal imaging instrument (FLIR TG267). Thermal conductivity is studied through by

Sweden HotDisk TPS 2500S thermal constant analyzer. Electromagnetic parameters were measured on a vector network analyzer (VNA, Agilent N5234A) in the frequency range of 2-18 GHz by a transmission-refection mode. The precursor solution was added to mold with Φ_{out} of 7.00 mm and Φ_{in} of 3 mm, and the coaxial rings of PAM-x was obtained by in-situ polymerization under magnetic field. The refection loss (RL) of PAM-x was calculated by transmission-line theory.

Content lists

Equation:

According to Debye theory, the relatively complex permittivity imaginary part (ε'') could be divided into conduction loss (ε_c'') and polarization loss (ε_p'') as following equations:

$$\varepsilon'' = \frac{\omega\tau(\varepsilon_s - \varepsilon_\infty)}{1+\omega^2\tau^2} + \frac{\sigma}{\omega\varepsilon_0} = \varepsilon_p'' + \varepsilon_c'' \quad \text{(S1)}$$

$$\varepsilon_c'' = \frac{\sigma}{\omega\varepsilon_0} \quad \text{(S2)}$$

where ω is angular frequency, ε_s is static dielectric constant, τ is polarization relaxation time, ε_∞ is relative permittivity at high frequency and σ is electrical conductivity.

Debye relaxation (Cole–Cole plots) can be expressed as follows:

$$(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_s - \varepsilon_\infty}{2})^2 \quad \text{(S3)}$$

The eddy current loss is usually described by the following formula:

$$C_0 = \mu''(\mu')^{-2}f^{-1} = \frac{2}{3}\pi\mu_0\sigma d^2 \quad \text{(S4)}$$

If the $\mu''(\mu')^{-2}f^{-1}$ value remains stable as the electromagnetic wave frequency changes, eddy current loss should be the only contribution to magnetic loss.

The RL of the samples can be calculated from the relative permeability and permittivity of a given frequency range and thickness basing on the following equation：

$$Z_{in} = Z_0(\mu_r/\varepsilon_r)^{1/2} tanh(j\frac{2\pi fd}{c}(\mu_r/\varepsilon_r)^{1/2}) \quad \text{(S5)}$$

$$RL = 20log\left|(Z_{in} - Z_0)/(Z_{in} + Z_0)\right| \quad \text{(S6)}$$

where Z_{in} and Z_0 are the input impedance of the absorbing material and the impedance of free space, respectively, μ_r and ε_r repentant the relative complex permeability and the complex permittivity, respectively, f, d and c are the frequency of the microwaves in free space, the thickness of the sample and velocity of light. When RL is lower than -10 dB mean that more than 90% incident electromagnetic wave is absorbed, and its corresponding frequency range is called effective absorption bandwidth (EAB).

The attenuation constant (α) can be calculated through

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}} \quad \text{(S7)}$$

The minimum RL value can be obtained under a certain frequency (f_m) if the matching thickness (t_m) of the Co-C/PAM satisfies the following equation

$$t_m = \frac{n\lambda}{4} = \frac{nc}{4f_m\sqrt{|\mu_r||\varepsilon_r|}} \qquad (n = 1, 3, 5...) \quad \text{(S8)}$$

where $|\mu_r|$ and $|\varepsilon_r|$ are the modulus of the μ_r and ε_r, respectively.

Microwave energy storage efficiency (w_s), microwave conversion efficiency (w_d) and their ratios (w_r) are shown below

$$w_s = \frac{E_1}{E} = \frac{p_1}{p} = \frac{p_1}{p_1 + p_2} \quad \text{(S9)}$$

$$w_r = \frac{E_1}{E_2} = \frac{p_1}{p_2} \quad \text{(S10)}$$

$$w_d = \frac{E_2}{E} = \frac{p_2}{p} = \frac{p_2}{p_1 + p_2} \quad \text{(S11)}$$

The efficiency of converted microwave energy derived from conduction (w_c), polarization (w_p) and magnetic losses (w_m) can be expressed as:

$$w_c = \frac{E_c}{E_2} = \frac{p_c}{p_2} \quad \text{(S12)}$$

$$w_p = \frac{E_p}{E_2} = \frac{p_p}{p_2} \quad \text{(S13)}$$

$$w_m = \frac{E_m}{E_2} = \frac{p_m}{p_2} \quad \text{(S14)}$$

where p_1, p_2, p_c, p_p and p_m represent the power of the storage, converted, conduction, polarization and magnetic losses, respectively.

$$p_1 = \frac{\omega}{2}\mu' H_0^2 + \frac{\omega}{2}\varepsilon' E_0^2 \quad \text{(S15)}$$

$$p_2 = p_c + p_p + p_m \tag{S16}$$

$$p_c = \frac{\omega}{2}\varepsilon_c^{''}E_0^2 \tag{S17}$$

$$p_p = \frac{\omega}{2}\varepsilon_p^{''}E_0^2 \tag{S18}$$

$$p_m = \frac{\omega}{2}\mu^{''}H_0^2 \tag{S19}$$

where the ω stands for the angular frequency. The relationship between the intensity of electric field (E_0) and magnetic field (H_0) is as follows:

$$\left|\frac{E_0}{H_0}\right| = |Z_0| = \left|\sqrt{\frac{\mu_r}{\varepsilon_r}}\right| \tag{S20}$$

CST simulation:

CST Studio Suite 2024 was used to simulate the radar cross sections (RCS) of PAM and PAM-BN_x. The simulation model is made up of the bottom perfect electric conductor (PEC) plate and the upper PAM-x absorber layer. The thickness of the PEC plate is 2.0 mm. The absorber layer has a thickness of 2.3 mm, which corresponds to optimal absorption capability. The length and width of the square shape model are fixed to 200 mm, which is larger than the thickness. The model is placed on the X-O-Y plane, with linearly polarized plane waves incident from the positive to negative Z axes. Electric polarization propagates along the X-axis. Open boundary conditions exist in all directions. The operating frequency is set at 13 GHz, which corresponds to the best absorption qualities. A single station and an integral equation solver are used for calculation. The RCS values can be described using the following equation:

$$\sigma(dBm^2) = 10\log\left[\frac{4\pi S}{\lambda^2}\left|\frac{E_s}{E_i}\right|^2\right] \tag{S21}$$

where S is the area of the simulated plate, λ is the length of the incident microwave, E_s is the electric field intensity of transmitting waves, and E_i is the electric field intensity of receiving wave.

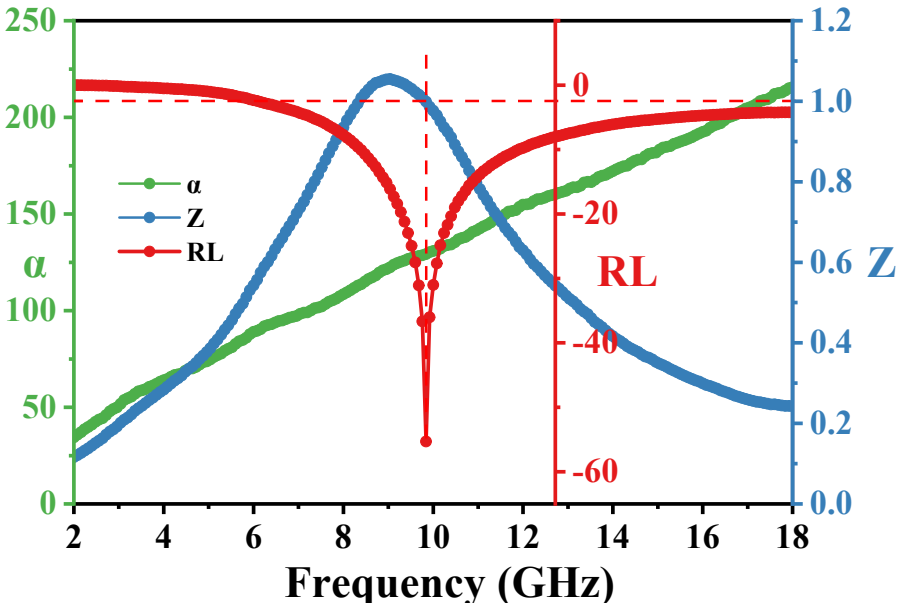

Fig. S1 Frequency-dependent α, Z, and RL values of PAM-BN_5 at 2.8 mm

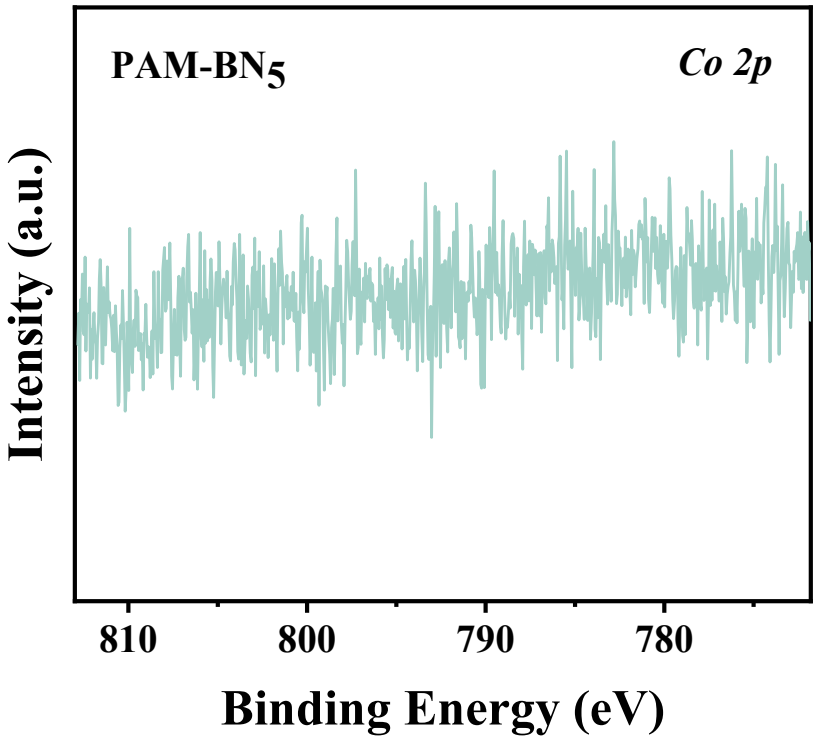

Fig. S2 XPS spectra of Co 2p of PAM-BN_5

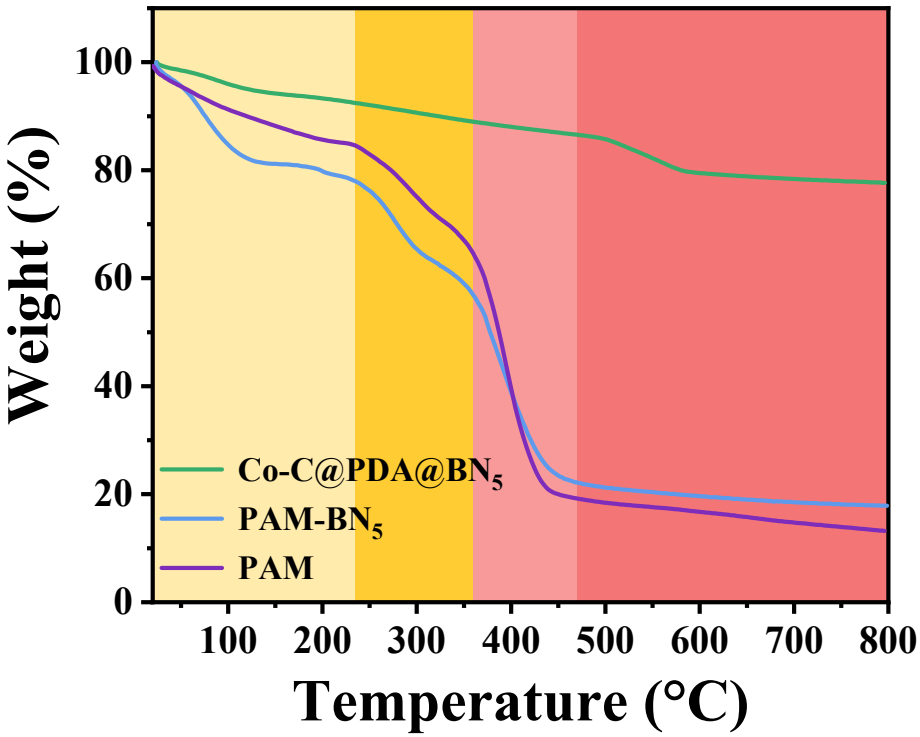

Fig. S3 TG curves of Co-C@PDA@BN_5, PAM, and PAM-BN_5