

Electronic Supplementary Information

Synthesis of nitrogen-doped reduced graphene oxide/cobalt-zinc ferrites composite aerogels with superior compression recovery and electromagnetic wave absorption performance

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Experimental section

Materials

Graphite oxide was provided by Suzhou TANFENG Graphene Tech Co., Ltd (Suzhou, China). Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), zinc chloride (ZnCl_2), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate (NaAc), ethylenediamine (EDA), ethylene glycol (EG), polyethylene glycol (PEG, $M_w = 6000 \text{ g} \cdot \text{mol}^{-1}$) and anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$) were commercially available from Adamas-beta®. All the chemical reagents were analytical grade and used without further purification. Deionized water was produced in the laboratory (electrical resistivity $\sim 18.2 \text{ M}\Omega \cdot \text{cm}$).

Preparation of cobalt-zinc ferrite ($\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) microspheres

$\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microspheres were prepared by a simple solvothermal route. Firstly, 1.08 g (4 mmol) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.24 g (1 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.21 g (1 mmol) ZnCl_2 were completely dissolved into 60 mL of EG by vigorous stirring. Then, 5.4 g of NaAc and 1.5 g PEG were fully dissolved into the mixture solution under vigorous stirring, respectively. Next, the homogeneous solution was poured into a Teflon-lined stainless-steel autoclave and reacted at 200 °C for 8 h. Afterward, the obtained products were collected by magnetic separation, and then purified by repeated washing with deionized water and anhydrous ethanol for several times, and dried at 55 °C for 24 h in a vacuum oven.

Preparation of nitrogen-doped reduced graphene oxide/cobalt-zinc ferrite (NRGO/ $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) composite aerogels

NRGO/ $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composite aerogels were synthesized by a facile hydrothermal method. Typically, aqueous graphene oxide (GO) dispersions (3.0 mg/mL) were firstly

obtained by ultrasonication of 90 mg of graphite oxide in 30 mL of deionized water for 1 h and further vigorously stirring for 30 min. Then, 30 mg of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders were completely dispersed into aqueous GO dispersions by ultrasonication for 30 min and vigorous stirring for another 30 min, respectively. Next, a certain amount of EDA was injected into the mixture dispersions and vigorously stirred for 30 min. Afterward, the reaction mixtures were poured into a Teflon-lined stainless-steel autoclave and reacted at 120 °C for 12 h. Finally, the as-prepared NRGO/ $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composite hydrogels were dialyzed in a 10% (v/v) $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ solution for 48 h and then lyophilized at -50 °C for 48 h to obtain NRGO/ $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composite aerogels.

Characterization

Crystalline phase structure was characterized by X-ray diffraction (XRD, LabX XRD-6000, Japan) with Cu-K α radiation ($\lambda = 0.154$ nm) in the scattering range (2θ) of 10–80° with a scanning rate of 2 °/min. Fourier transform infrared (FT-IR) spectra were recorded in the wavenumber range of 500–4000 cm^{-1} using a Nicolet 380 spectrometer (ThermoFisher Scientific, USA). Raman spectra were acquired at room temperature by using a laser confocal Raman spectrometer (Renishaw-2000, UK) in the range of 250–2500 cm^{-1} with an excitation wavelength of 532 nm. Surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA). The micromorphology was observed with a field emission scanning electron microscopy (FESEM, Hitachi-Su8020, Japan) equipped with the energy dispersive X-ray spectrum (EDS) device, and field emission transmission electron microscopy (FETEM, FEI-TF20, USA).

Electromagnetic parameters including the relative complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) were measured by a vector network analyzer (VNA,

AV3629D, China) using the coaxial-line method in the frequency range of 2.0–18.0 GHz. Before being tested, the as-prepared composite aerogels were homogeneously mixed with paraffin wax (which was transparent to the electromagnetic waves) in different filler contents (10.0 wt.%, 15.0 wt.% and 20.0 wt.%) and then pressed into toroidal-shaped ring with outer diameter of 7.0 mm, inner diameter of 3.04 mm and thickness of 2.0 mm. The electrical conductivity was measured by a four-point probe method (Suzhoujingge electronics Co., Ltd, ST2722-SZ, China).

The electromagnetic wave (EMW) absorption performance of absorbers was evaluated by the reflection loss (RL), which could be calculated by the following equations according to the transmission line theory:¹⁻³

$$RL(\text{dB}) = 20 \lg \left| \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0} \right| \quad (\text{S1})$$

$$Z_{\text{in}} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[j \left(\frac{2\pi f d}{c} \right) \sqrt{\mu_r \varepsilon_r} \right] \quad (\text{S2})$$

Herein Z_{in} is the input impedance of absorber, Z_0 is the impedance of free space, ε_r is the relative complex permittivity, μ_r is the relative complex permeability, d is the thickness of the absorber, c is the velocity of light in free space and f is the frequency. Generally, the EMW absorbers with $RL \leq -10.0$ dB were considered to be suitable for practical applications.¹⁻³

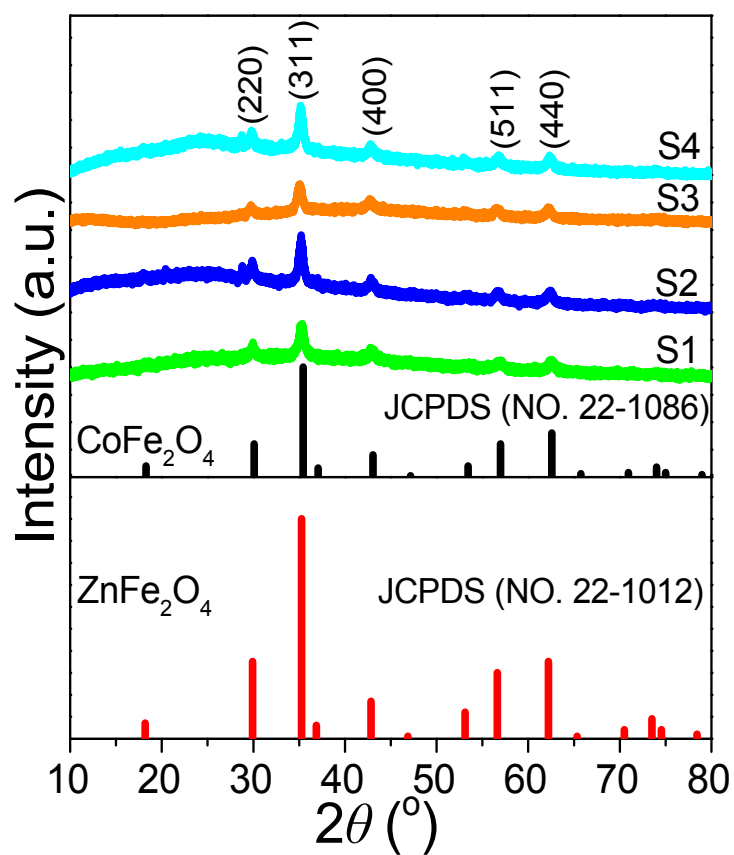


Fig. S1 XRD patterns of the samples of S1–S4.

Table S1 Typical physical parameters of the samples of S1–S4.

Samples	Bottom radius (cm)	Height (cm)	Volume (cm^3)	Weight (g)	Density ($\text{g}\cdot\text{cm}^{-3}$)
S1	0.90	2.30	5.85	0.0856	0.0146
S2	1.00	2.10	6.59	0.0863	0.0131
S3	0.95	2.50	7.08	0.0859	0.0121
S4	1.00	2.30	7.22	0.0898	0.0124



Fig. S2 Typical digital images of S3 before, during and after the compression test.

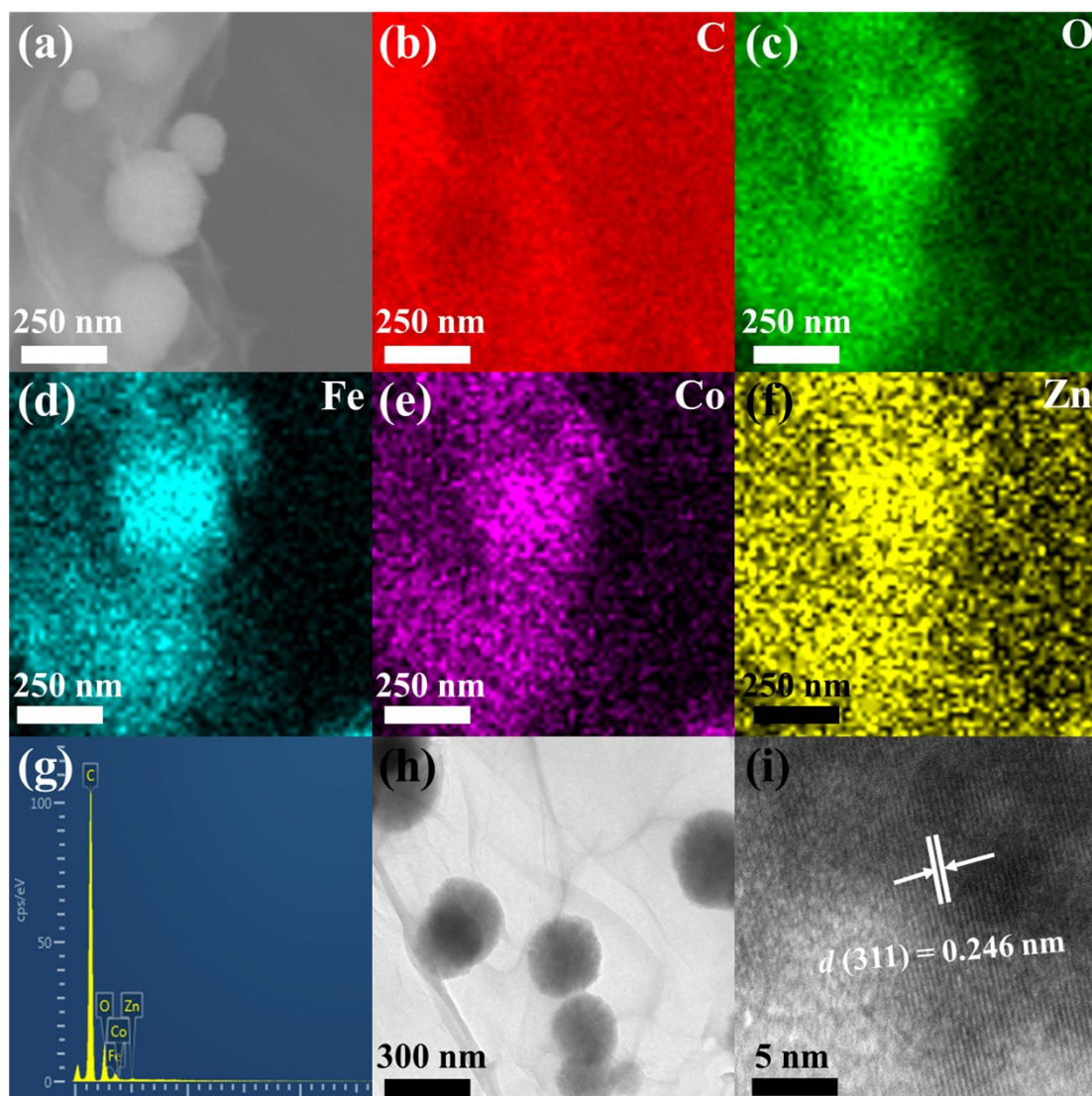


Fig. S3 SEM image: (a); EDS mapping images: C (b), O (c), Fe (d), Co (e) and Zn (f); EDS pattern: (g); Low-resolution TEM image: (h); High-resolution TEM image: (i) of S1.

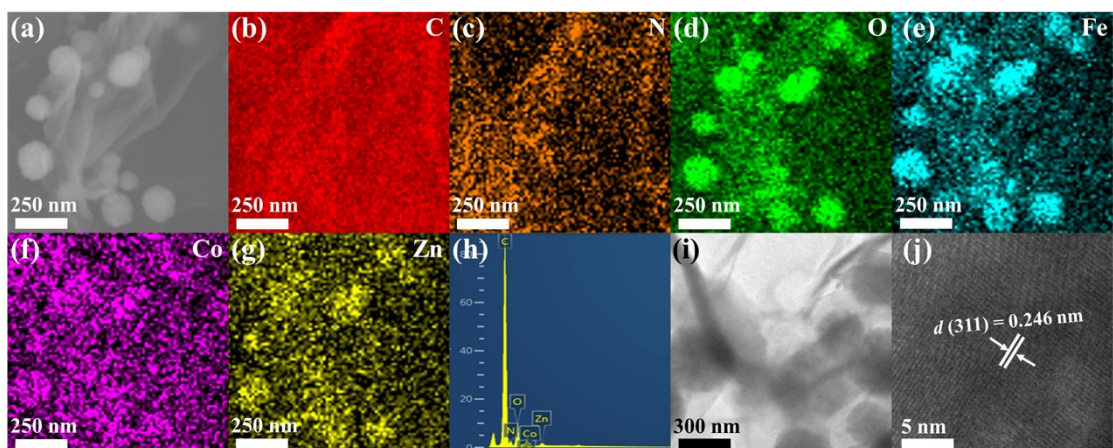


Fig. S4 SEM image: (a); EDS mapping images: C (b), N (c), O (d), Fe (e), Co (f) and Zn (g); EDS pattern: (h); Low-resolution TEM image: (i); High-resolution TEM image: (j) of S2.

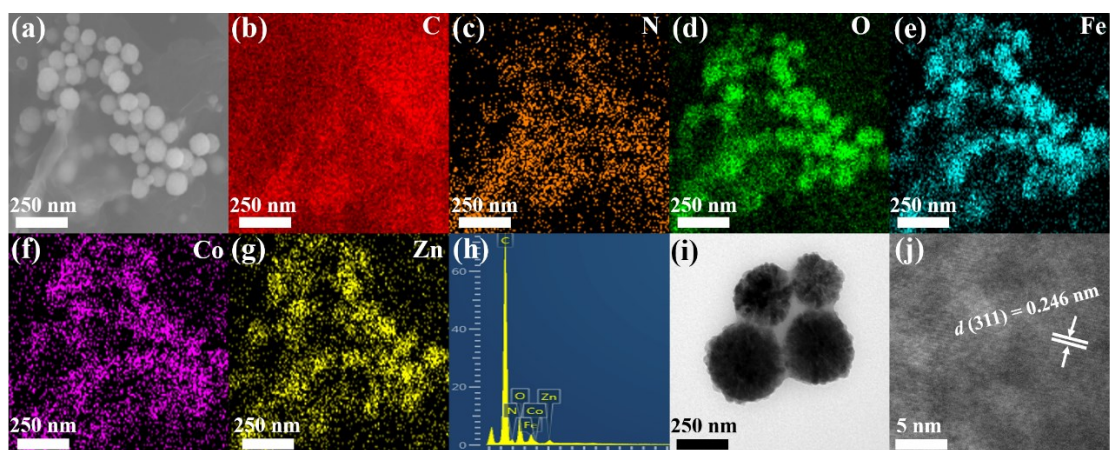


Fig. S5 SEM image: (a); EDS mapping images: C (b), N (c), O (d), Fe (e), Co (f) and Zn (g); EDS pattern: (h); Low-resolution TEM image: (i); High-resolution TEM image: (j) of S4.

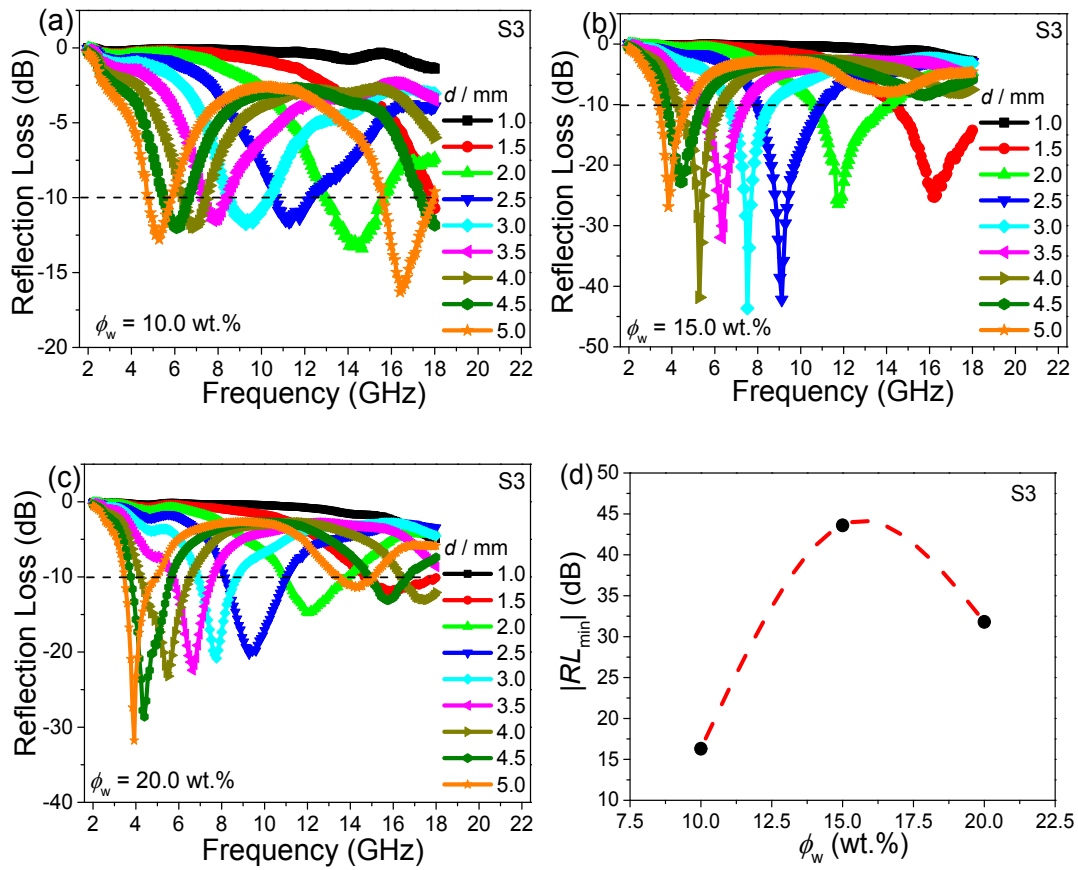


Fig. S6 $RL \sim f$ curves: 10.0 wt.% (a), 15.0 wt.% (b) and 20.0 wt.% (c); $|RL_{\min}| \sim \phi_w$ curve of S3 (d).

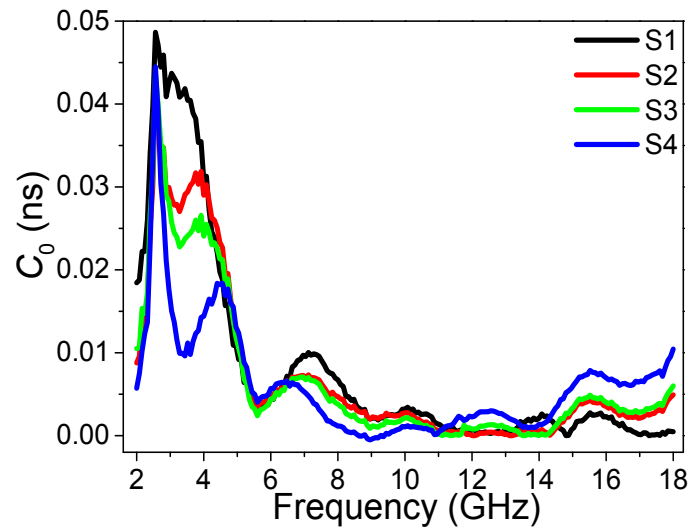


Fig. S7 $C_0 \sim f$ curves of the samples of S1–S4.

Notes and references

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