

Supporting Information

Protein-Derived Hybrid Carbon Nanospheres with Tunable Microwave Absorbing Performance in the X-band

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Materials

Type-B gelatin (derived from bovine skin) was commercially available and bought from Sigma-Aldrich, USA. Acetone and glutaraldehyde (GA) were provided by Sinopharm Reagent Co. Ltd. The modified epoxy resin and polyamide resin were bought from Ning-ping Chemical Co. Ltd. (Tianjin, China).

Synthesis process and mechanism of gelatin nanospheres

Synthesis process

In brief, 5 g gelatin powder was dissolved in 100 ml of deionized water. 100 ml of acetone was then poured into the gelatin solution. The mixture was cooled to room temperature until the precipitation process was entirely finished. The supernatant was discarded and the precipitate was re-dissolved in deionized water at 50 °C. Under magnetic stirring at 800 rpm, the pH of the solution was adjusted to 12 and 320 ml of acetone was injected. After that, 3 ml of GA (25% v/v aqueous solution) was added, the mixture was kept stirring overnight for crosslinking. The dry GNs powder were collected via centrifugation and lyophilization.

Synthesis mechanism

When solved in deionized water, the gelatin chains are sufficiently uncoiled and the addition of the desolvating agent caused a better controlled precipitation of the macromolecules. Under the stirring condition, the addition of the desolvating agent (acetone in this work) reduced the water available to keep the gelatin in solution, resulting in shrinkage of the hydrated gelatin chains. After the pH of gelatin solution is

adjusted to 2, which is far away from its isoelectric point, the nanospheres carry the most positive charges and remain stable due to the repulsion of similar charges. At a certain point, the hydration was too low and the protein chains precipitated as nanoparticles. After the addition of GA, the carboxyl on gelatin nanospheres can be crosslinked by the aldehyde of GA, the nano-spherical shape formed by the protein chains of gelatin can be fixed. The dry GNs was finally obtained after centrifugation and freeze-drying.

The mechanism of crosslinking by GA is illustrated in Figure S1. The excess addition of GA is to crosslinking the protein macromolecule by the reaction between the aldehyde group and amino group. After crosslinking, the spherical form of GNs can be fixed finally, or the protein macromolecule will always in a metastable state.

The preparation of gelatin-derived carbon nanospheres/epoxy resin composites (GCNs/resin)

The epoxy resin and polyamide resin were mixed with a mass ratio of 4:1 and then diluted by adding proper amount of acetone. A certain amount of GCNs were added to the foregoing mixture and dispersed homogeneously by alternative mechanical agitation and high-power ultrasonic agitation. The slurry was then left in 80 °C for 48 h until the curing process was complete. The GCNs/resin composites samples were denoted as GCNs-T-C (C represents the loading content (wt.%) of absorbent), including three content fractions of GCNs from 10 to 30 wt.%. (e. g. a sample that was made by 20 wt.% GCNs-750 was named as GCNs-750-20%).

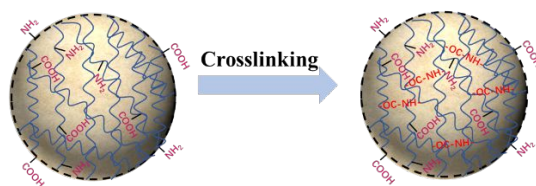


Figure S1. The mechanism of crosslinking by GA.

Characterization

The microstructure of the GCNs and GCNs/resin composites were identified by scanning electron microscopy (SEM; S-4700, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM; Talos F200X, 200kV, FEI, USA), both of them were equipped with energy dispersive spectrometer (EDS). Dynamic light scattering (DLS; Zetasizer Nano-ZS, Malvern Instruments Ltd, UK) was used to analyze the size of GCNs particles in water. Phase compositions of GCNs were characterized by Raman spectra with a He-Ne laser ($\lambda = 532$ nm) (RMS; Renishaw, UK), X-ray photoelectron spectra (XPS; K-Alpha, Thermo Scientific, Waltham, MA, USA) and X-ray diffraction (XRD; Rigaku-D/max-2400, Tokyo, Japan) radiation. The surface structures were characterized by Fourier Transform infrared spectroscopy (FT-IR; iN10MX, Nicolet, USA). The electrical conductivity of the GCNs/resin composites were measured using a four-point probe device (Model ET9000; Eastchanging, China).

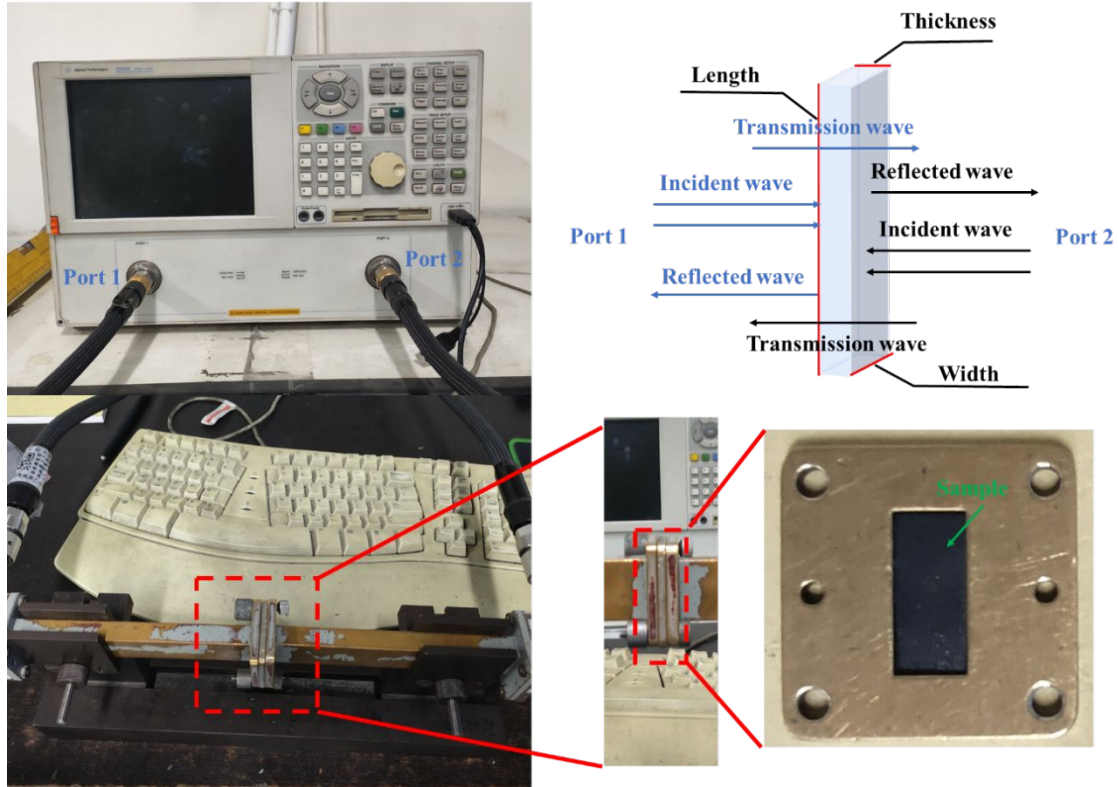


Figure S2. Optical photographs and mechanism of waveguide testing method.

The transmission/reflection (TR) method has been the most widely used method to measure the electromagnetic parameters of materials in the microwave absorbing field. Electromagnetic parameters of the material are obtained by inversion of the S parameters measured during the experiment. The rectangular waveguide method is used in this work. Newton-Simpson iteration method have been integrated into vector network analyzer for the inversion of electromagnetic parameters of non-magnetic materials. The main formula needed for the inversion in room temperature is as follows:

$$S_{21}S_{12} - S_{11}S_{22} = \exp [(-2\gamma_0)(L_{air} - L)] \frac{z^2 - \Gamma^2}{1 - z^2\Gamma^2} \dots \dots \dots \text{Equation S1}$$

where S11-S22 are the S parameters measured, Γ , z , γ and γ_0 represent the reflection coefficient, transmission coefficient and propagation coefficient of electromagnetic wave in air, respectively¹.

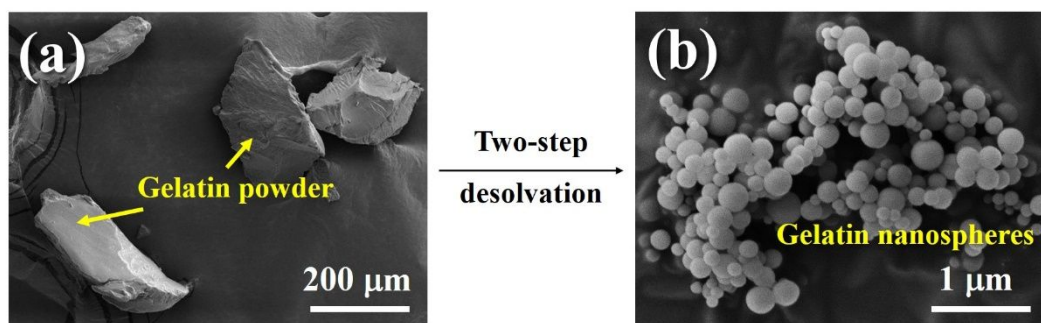


Figure S3. The SEM images of (a) raw gelatin powders, (b) gelatin nanospheres.

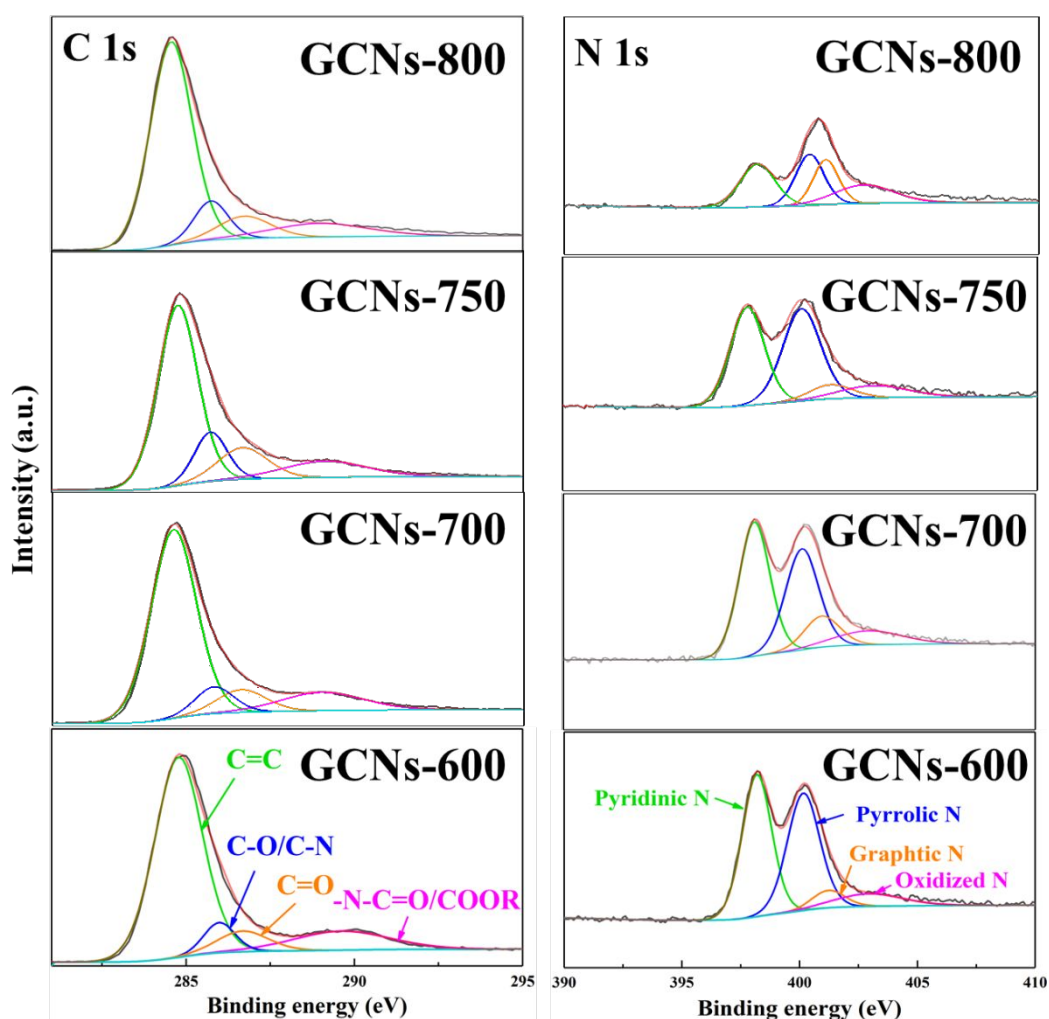


Figure S4. XPS spectra for the C 1s and N 1s of GCNs-600, GCNs-700, GCNs-750, GCNs-800

For C 1s, all the spectra can be divided into four components: C=C, C-O/C-N, C=O and -N-C=O/O=C-OR at ~ 284.8 , ~ 285.9 , ~ 286.7 and ~ 288.9 eV, respectively, manifesting the successful N, O doping in the materials. The peak fluctuation can be ascribed to the coexistence of dissociation of old functional groups and the polymerization of new functional groups during the carbonization process.

The N 1s spectrum existed as a combination of four forms in all samples, centering at 398.2, 400.0, 401.1 and 403.6 eV, corresponding to of pyridine N, pyrrole nitrogen,

graphite nitrogen and oxidized N. With the increasing carbonization temperature, the intensity of pyridinic N obviously decreases probably because of its instability. The incorporation of pyridinic N and pyrrolic N can raise the conductivity because of the nature of their electron donors. The existence of these four N doping forms can also lead to the non-coincidence of charge centers, forming a dipole under the effect of electromagnetic fields and consuming electromagnetic energy through dipole polarization.

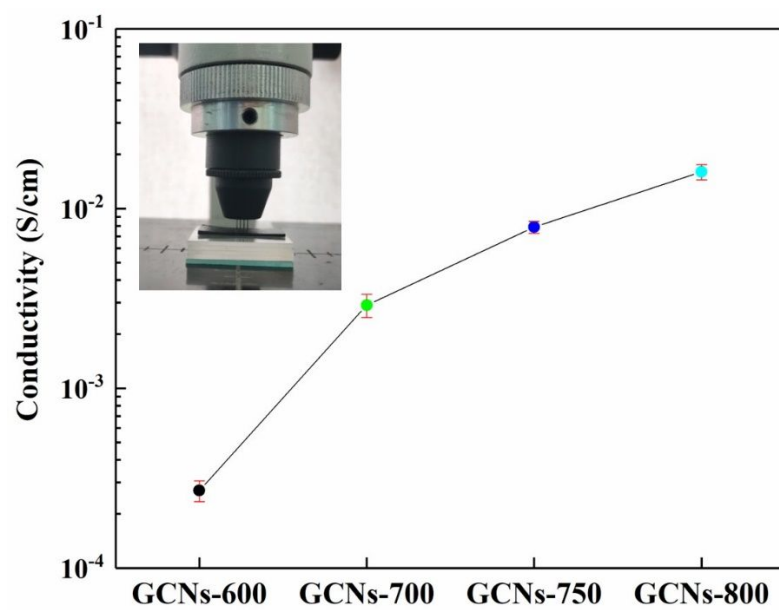


Figure S5. The conductivity of GCNs-T-20% composites as a function of carbonization temperature.

$$\left(\varepsilon' - \frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 - (\varepsilon'')^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 \quad \text{Equation S2}$$

where, ε_s represents the static permittivity, ε_∞ represents the relative dielectric permittivity at high-frequency limit. The curves of ε' and ε'' will form a semicircle if the polarization relaxation exist, the semicircles represent the appearance of relaxation process (Figure S6). The semicircles are getting less obvious with the increasing carbonization temperature, which may be caused by the reduced amount of N, O dopants. This proves the existence of dipolar polarization in this study.

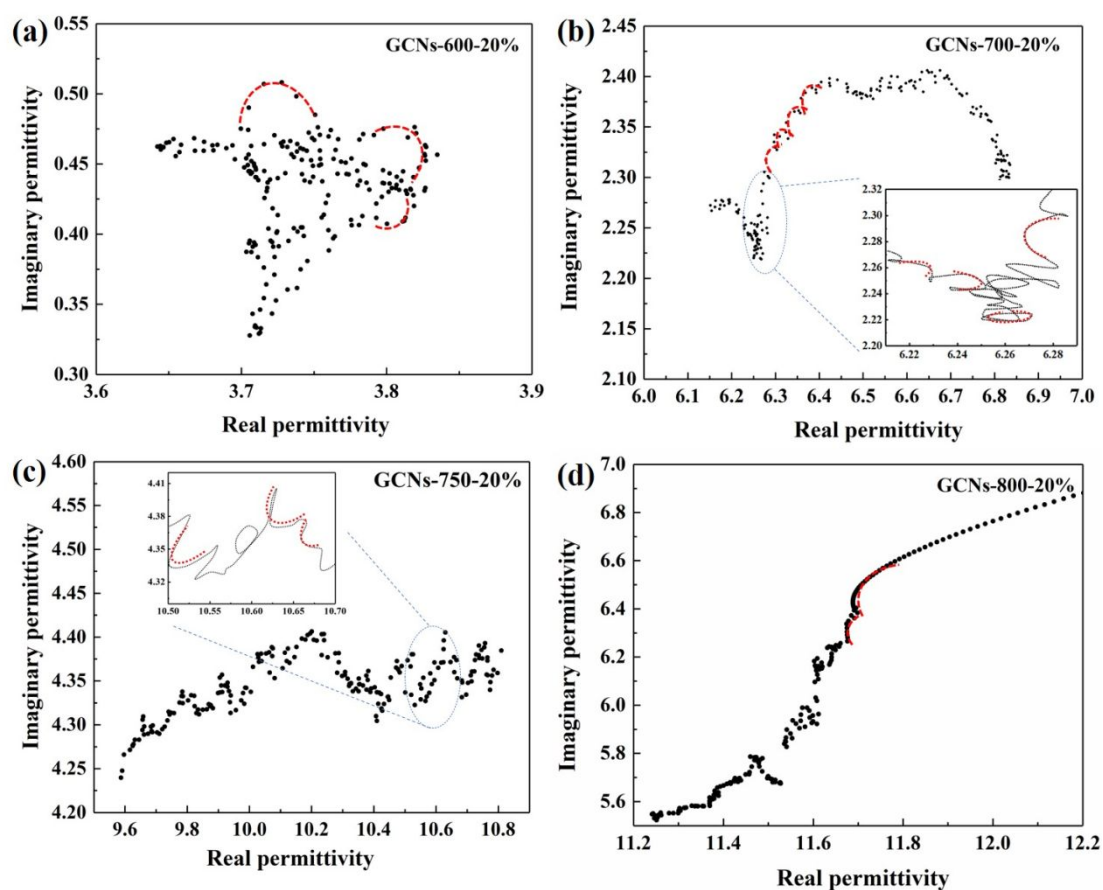


Figure S6. The Cole-Cole plots of GCNs-T-20% composites.
((a)T=600, (b) T=700, (c) T=750, (d) T=800)

References

- (1) Jia, H.; Zhou, W.; Nan, H.; Dong, J.; Qing, Y.; Luo, F.; Zhu, D. Enhanced high temperature dielectric polarization of barium titanate/magnesium aluminum spinel composites and their potential in microwave absorption. *J. Eur. Ceram. Soc.* **2020**, *40*, 728-734.