

Preparation and Microwave Absorbing Properties of Yolk Shell C@C Microspheres

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Abstract: As a typical dielectric loss medium, carbon material has always been the most attractive candidate material for microwave absorption because of its characteristic advantages. However, much less attention has been paid to the reasonable design of micro-structure to improve its performance. According to the transmission behavior and loss mechanism of electromagnetic wave, uniform yolk shell C@C microspheres as a new type of microwave absorbers were creatively prepared by "coating-coating-etching". Compared with solid carbon microspheres, the unique micro-structure endows better BET surface and pore volume to the yolk shell C@C microspheres. The microwave absorption performance was tested in the frequency range of 2GHz to 18GHz. As expected, the yolk shell C@C microspheres exhibit excellent reflection loss characteristics, with strong reflection loss (-41.84dB at 9.2GHz) and wide effective absorption bandwidth(7.9~10.2GHz). This good performance is so for indeed better than most pure carbon absorbers reported. The electromagnetic parameters show that the yolk shell structure is conducive to the matching of characteristic impedance and can obtain ideal microwave absorption ability.

Keywords: Microwave absorption, Carbon absorber, Yolk shell structure, Phenolic resin.

1. Introduction

The rapid development of science and technology has brought great convenience to all aspects of people's life and work, especially in electronic information technology. The wide application of electromagnetic wave in science and technology brings convenience to people, but also causes serious electromagnetic radiation and interference, bringing a series of social problems [1-4]. The development and application of absorbing materials are of great significance to reduce electromagnetic radiation pollution in daily life and pursue stealth in military.

Traditional absorbing materials have various shortcomings and are difficult to meet the requirements of "thin, light, wide and strong". New absorbing materials need to be researched and developed [5]. Carbon absorbing material has the advantages of light weight, high electrical conductivity, simple preparation technology [6-11], but a single carbon material of magnetic loss will appear impedance matching imbalances, and wave absorption performance is bad. However, the micro-structure of carbon material has good plasticity and stability, so the surface modification of carbon materials can be carried out [12]. Cheng et al. constructed a core-shell structure composite of Fe₃O₄ nanocrystals/mesoporous carbon hollow spheres (MCHS) based on impregnation and calcination methods. MCHS is characterized by good dielectric loss capacity and light weight, and Fe₃O₄ can generate magnetic loss and adjust impedance matching characteristics [13]. Wei et al. prepared C@NiCo₂O₄@Fe₃O₄ layered core-shell composite material. The sea urchin-like structure generated by NiCo₂O₄ and the inner core void generated by decomposition of carbon sphere are conducive to electromagnetic wave attenuation, and its minimum loss is -43dB at 13.4GHz, when the matching thickness is 3.4 mm.

In this study, the "coating - coating - etching" process was used to construct the yolk shell micro-structure by using the

phenolic preparation process, combined with the ethyl orthosilicate coating and hydrofluoric acid etching process. The unique micro-structure endows the yolk shell C@C microspheres with better BET surface and pore volume. The construction of yolk shell micro-structure can provide a new idea for designing and manufacturing carbon-based microwave absorber with improved performance.

2. Experimental

2.1. Material

Formaldehyde, tetraethyl silicate, hydrofluoric acid, ammonia, resorcinol, anhydrous ethanol. All chemicals are analytical grade and without any further treatment, and all experiments will use deionized water.

2.2. Construction of Yolk Shell Structure

In order to construct the yolk shell structure C@C microspheres, phenolic resin (PR) microspheres were selected as template. The formaldehyde and resorcinol were used as raw materials to prepare phenolic resin (PR) microspheres, and then silica was coated on the surface of phenolic resin microspheres with tetraethyl silicate as raw materials to form PR@SiO₂ spheres. The obtained products were washed and dried, and PR@SiO₂ microspheres were dispersed in a mixture of ethanol, deionized water and ammonia by ultrasound. Resorcinol and formaldehyde were added, and the mixed solution was stirred and polymerized for the second time (stirring time was 6h, 8h, 10h, respectively) to form a layer of phenolic resin shell. The PR@SiO₂@PR microspheres obtained by centrifugation and washed with deionized water and ethanol, then the precursor of yolk shell structure was obtained by vacuum drying.

The prepared PR@SiO₂@PR microspheres were pyrolyzed in N₂ atmosphere at different temperatures (650°C, 700°C, 750°C) for a certain time to obtain C@SiO₂@C microspheres. The SiO₂ layer was corroded by hydrofluoric acid, and yolk

shell C@C microspheres were obtained by centrifugal washing.

2.3. Characterization

The crystal phase of the C@C micro-spheres were characterized by X-ray diffraction (XRD). The morphology of the samples were tested by transmission electron microscope (TEM). The sample and paraffin were mixed at a certain mass ratio. The vector network analyzer is used to measure the electromagnetic parameters (ϵ' , ϵ'' , μ' , μ'') from 2-18 GHz, and the reflection loss (R) was calculated based on the relative complex permittivity and permeability measured by the transmission line theory[14-16], according to the following formula(1) and (2). The attenuation constant(α) and impedance (Z_{in}) are calculated according to the following formula(1) and (3).

$$|Z_{in}| = \left| \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \frac{2\pi f d \sqrt{\mu_r \epsilon_r}}{c} \right] \right| \quad (1)$$

$$R = 20 \lg \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (2)$$

$$\alpha = \frac{\pi f \sqrt{2\mu' \epsilon'}}{c} \sqrt{\frac{\epsilon'' \mu''}{\epsilon' \mu'} - 1 + \sqrt{\left(\frac{\epsilon'' \mu''}{\epsilon' \mu'}\right)^2 + \left(\frac{\epsilon''}{\epsilon'}\right)^2 + \left(\frac{\mu''}{\mu'}\right)^2}} \quad (3)$$

3. Results and Discussion

Fig.1 is TEM diagrams of the yolk shell C@C microsphere pyrolyzed at 700°C with 10h of secondary coating time. We can clearly observe the real microstructure of microspheres, where each particle can be divided into three parts, one can distinguish between core and shell, a national standard of egg yolk shell structure, suggesting that uniform yolk shell C@C microsphere was prepared successfully by "coated-coated-etching" process, following by carbonization and hydrofluoric acid etching. The obtained carbon material can keep spherical shape without any other impurities, indicating

that the yolk shell structure has good thermal stability and chemical stability.

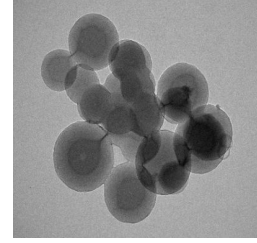


Figure 1. Morphology of the yolk shell C@C microsphere pyrolyzed at 700°C with 10h secondary coating time

According to the preliminary experimental results, both the carbonization temperature and the thickness or form of silica that has an impact on the performance of the final C@C microspheres, and the two degrees are similar. Therefore, we discussed the influence of the carbonization degree under different reaction time of silica respectively, in order to obtain a more accurate influence law.

Fig.2(a,b,c) are the curves of reflection loss rate corresponding to different thicknesses with frequency, when the reaction time of coated silica is 6h. The peak value of reflection loss rate of samples at all temperatures gradually moved to the low frequency as increasing of the thickness of absorbing sample of yolk shell C@C microspheres, in line with the theory of 1/4 wavelength. It can be seen from the figure that when the final carbonization temperature is 650 °C, the overall reflection loss rate is the best and the reflection loss rate is the lowest. The lowest reflection loss rate is -28 dB at 5.8 GHz and -26 dB at 14 GHz, and the effective absorption bandwidth is about 4 GHz. The effective absorption bandwidth of carbonized samples at 650 °C can cover 4-15 GHz with increasing thickness. When the carbonization temperature is 700 °C, the overall level is decreased compared with 650°C, but when the thickness is 1.5mm, the minimum reflection loss is similar to 650°C. However, when the final carbonization temperature was 750 °C, the overall reflection loss rate decreased significantly, and the sample thickness of yolk shell C@C microspheres did not reach -10 dB with the thickness of 3-5 mm.

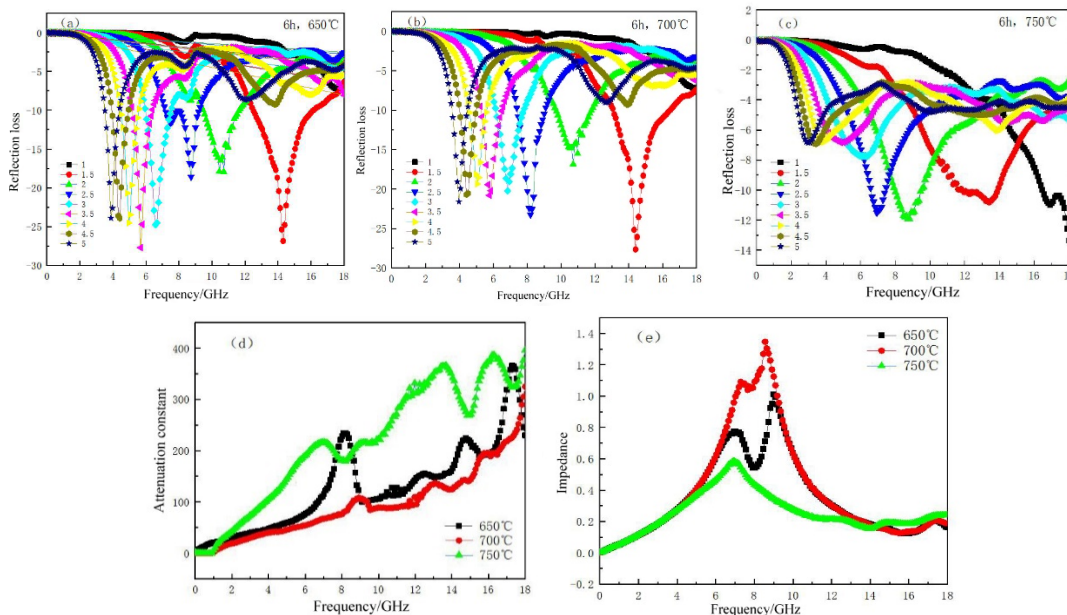


Figure 2. Microwave absorption performance diagram (the reaction time of coated silica is 6h)

(a,b,c: reflection loss rate at different temperature; d: Attenuation constant; e: Impedance)

As can be seen from Fig.2(d) and Fig.2(e), when the final carbonization temperature is 750 °C, the attenuation constant is the best, but the higher attenuation capacity is not conducive to impedance matching, resulting in the decline of

absorbing performance. In addition, the carbonization temperature of 650 °C is higher than that of 700 °C, and the impedance coefficient is closer to 1, the absorption performance is the best. It can be seen that only high attenuation and matching ability can achieve better absorption performance.

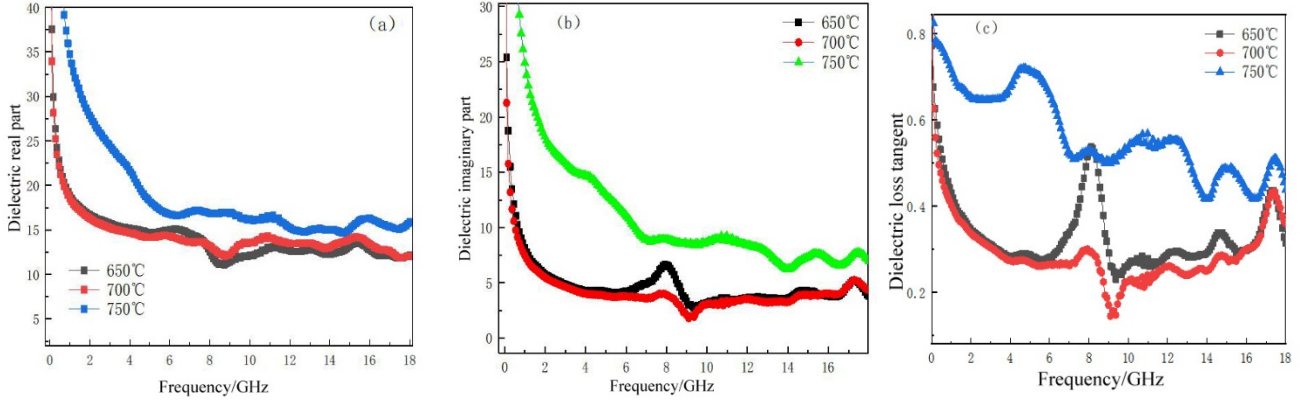


Figure 3. Dielectric loss diagram(the reaction time of coated silica is 6h)
(a: Dielectric real part; b: Dielectric imaginary part; c: Dielectric loss tangent)

As a pure carbon material, the yolk shell C@C microspheres has a negligible magnetic loss mechanism, so the incident electromagnetic wave attenuates with a single dielectric loss mechanism. As can be seen from Fig.3, the real and imaginary parts of the dielectric constant of the carbon microspheres increase with the increase of the carbonization temperature. The dielectric loss is the best when the carbonization

temperature is 750 °C, which corresponds to the larger attenuation constant shown in Fig2(d). This may be related to the increasing degree of graphitization of carbon materials by carbonization temperature. However, it can be seen from the impedance diagram in Fig. 2(e) that high temperature carbonization destroys impedance matching and leads to a decrease in absorbing performance.

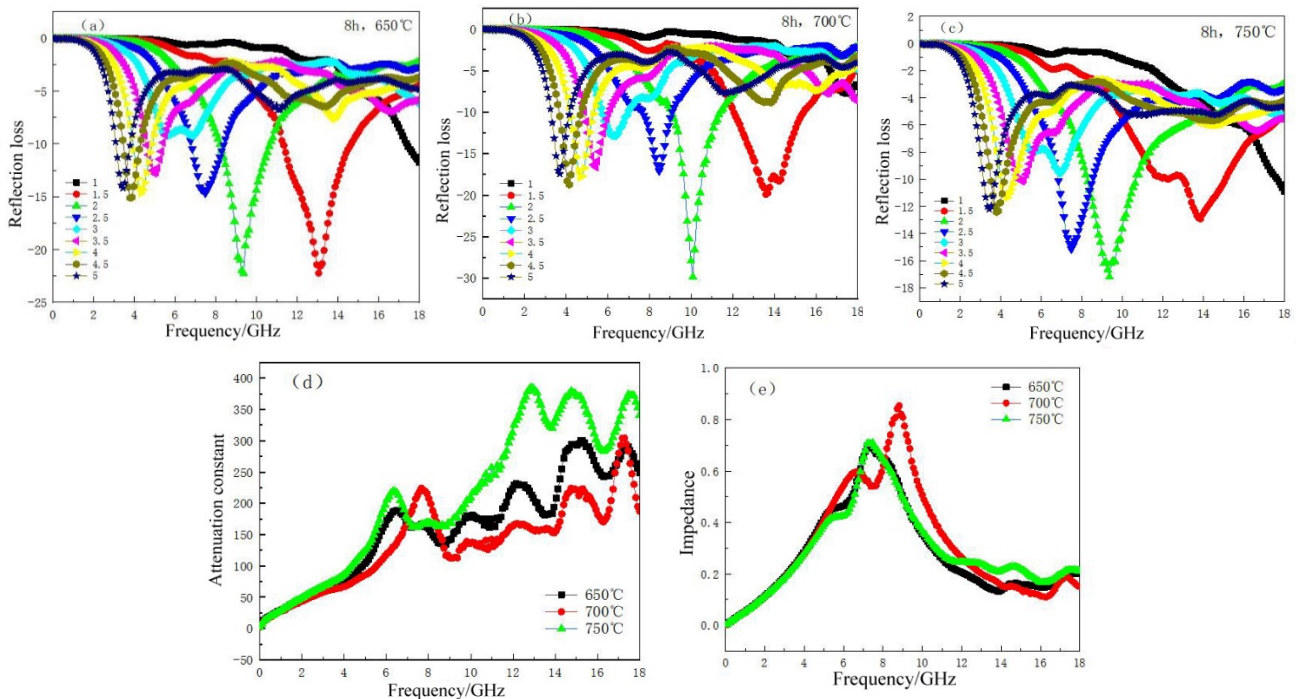


Figure 4. Microwave absorption performance diagram (the reaction time of coated silica is 8h)

(a,b,c: reflection loss rate at different temperature; d: Attenuation constant; e: Impedance)

Fig.4(a, b, c) are the reflection loss rates of different thicknesses as a function of frequency when the reaction time of coated silica is 8 h. It can be seen from the figure that the overall reflection loss rate is the best when the reaction time

of coated silica is 8 h and the final carbonization temperature is 700 °C. When the absorption sample thickness of C@C microspheres is 2 mm, the lowest reflection loss rate reaches -29.84 dB. The minimum reflection loss at 650°C is less than 700°C, but they were not different largely. The absorption performance at 750°C is still poor.

It can be seen from Fig. 4(d,e) that the dielectric property at stirring time of 8h is similar to that of 6h, and the attenuation constant is the best at carbonization temperature of 750 °C, but the impedance coefficient is obviously inferior to that at 700°C. The absorption performance is the best when

the final carbonization temperature is 700 °C. This may be related to the change of thickness and morphology during the formation of silica. The morphology of carbon material formed on this basis takes silica as template, so its influence cannot be ignored.

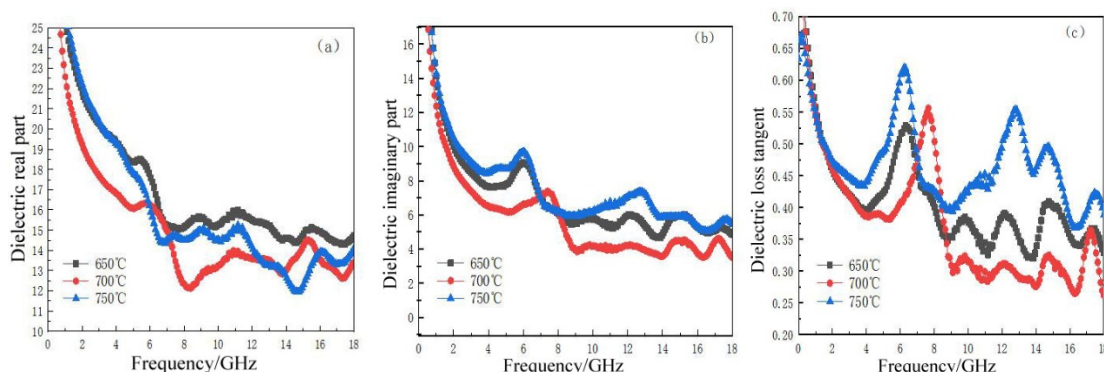


Figure 5. Dielectric loss diagram(the reaction time of coated silica is 8h)
(a: Dielectric real part; b: Dielectric imaginary part; c: Dielectric loss tangent)

As can be seen from Fig.5, the difference of dielectric constants at the three carbonization temperatures is not large, and appears the phenomenon of cross fluctuation. Compared with the stirring time of 6 h, the dielectric parameters decrease overall, which is related to the morphology of silica, and its influence will be discussed in the following article. When the final carbonization temperature was 750 °C, the dielectric loss was the best. However, according to the impedance diagram in Fig. 4(e), high carbonization temperature destroyed

impedance matching and led to the decline of absorption performance, which was consistent with that of the stirring time of 6 h, indicating that the effect of heat treatment temperature was still dominant compared with that of silica. There is little difference between the dielectric loss capacity at 650 °C and 700 °C, but the impedance match is better at 700 °C (Fig. 5(e)), so the absorbing performance is better at 700 °C.

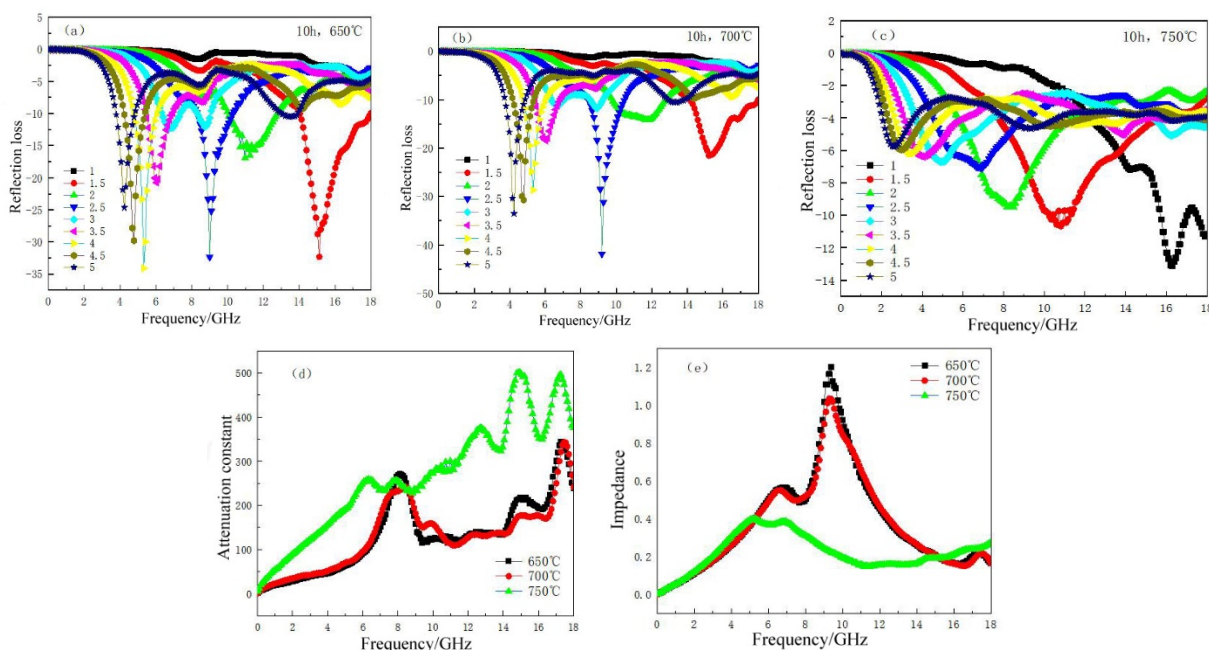


Figure 6. Microwave absorption performance diagram(the reaction time of coated silica is 10h)

(a,b,c: Reflection loss rate at different temperature; d: Attenuation constant; e: Impedance)

Fig. 6(a, b, c) are the curves of reflection loss rate corresponding to different thicknesses as a function of frequency when the reaction time of coated silica is 10 h. It can be seen from the figure that when the reaction time of coated silica is 10 h, the overall wave-absorbing performance of yolk shell C@C microspheres is similar to that of 8h, which increases first and then decreases with the increase of final

carbonization temperature.

The overall absorption performance is better. The lowest reflection loss rate is -34 dB at 5.3 GHz and -32.31 dB at 15.12 GHz, and the effective absorption bandwidth is 3.8 GHz. With the change of thickness, the effective absorption bandwidth of carbonized samples at 650 °C can cover 3.7-14.1 GHz. However, when the final carbonization temperature is 700 °C, the reflection loss rate is lower when the absorption sample thickness of yolk shell C@C is 2.5 mm

and 5 mm, especially when the absorption sample thickness of yolk shell C@C is 2.5 mm, the lowest reflection loss rate can reach -41.84 dB, and the performance is the best. When the final carbonization temperature is 750 °C, the overall level of reflection loss rate decreases obviously.

As can be seen from Fig. 6(d,e), when the final carbonization temperature is 750 °C, the attenuation constant is the best, but the highest impedance is only 0.4, resulting in

a decrease in absorption performance. The final carbonization temperature of 650 °C is slightly higher than that of 700 °C, and the impedance coefficient is closer to 1. Therefore, when the reaction time of coated silica is 10 h and the final carbonization temperature is 700 °C, the absorption performance is the best, followed by 650 °C, and the worst at 750 °C.

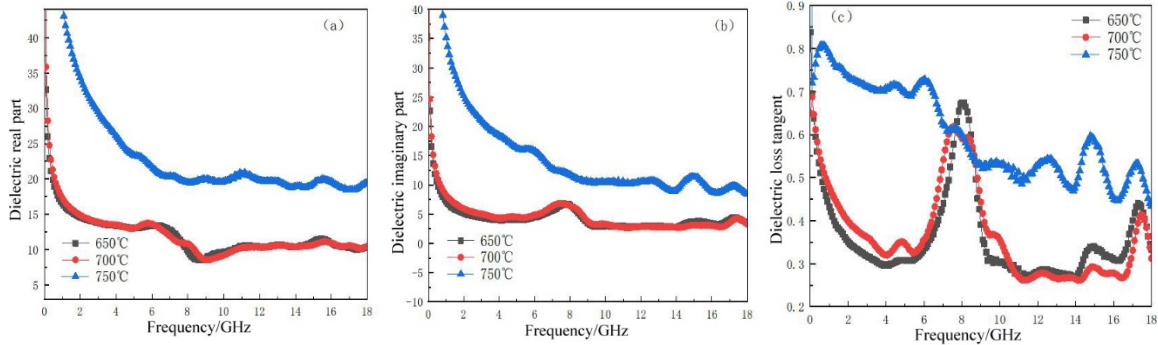


Figure 7. Dielectric loss diagram(the reaction time of coated silica is 10h)

(a: Dielectric real part; b: Dielectric imaginary part; c: Dielectric loss tangent)

As can be seen from the dielectric tangent value in Fig. 7, as for 6h and 8h, when the stirring time is 10 h and the carbonization temperature is 750 °C, the impedance mismatch is caused by the high dielectric property, and good absorbing performance cannot be obtained. The dielectric loss at 650 °C is similar to that at 700 °C.

Through the above analysis we can see that when the stirring time at the same time, the temperature had a great influence on the sample, in addition to the close minimum reflection loss of 6 h at 650°C and 700°C, regardless of the stirring time, wave absorption performance gets better and then worse with increasing temperature, this is because when the temperatures in a certain range, graphitization degree increase, is advantageous to the conductivity of carbon material loss, which is beneficial to the absorbing performance. When the temperature is too high, the dielectric

property is too high, which leads to the impedance mismatch of the material, and thus the absorbing property decreases. Both temperature and stirring time will affect the absorption performance of the sample. From the above analysis, it can be concluded that 700°C is the best carbonization temperature. Therefore, the influence of different stirring time at the carbonization temperature of 700°C on the performance of yolk shell C@C microspheres is further analyzed.

Fig.8 shows the influence of different stirring time on the absorption performance (carbonization temperature is 700°C). It can be seen from the reflection loss rates in Fig.8 that when the final carbonization temperature is 700 °C, the overall reflection loss rate is lower and better when the reaction time of coated silica is 10 h. There are three absorption samples with different thickness can reach below -30 dB. When the absorbing sample thickness is 2.5 mm, the lowest reflection loss rate is -41.84dB.

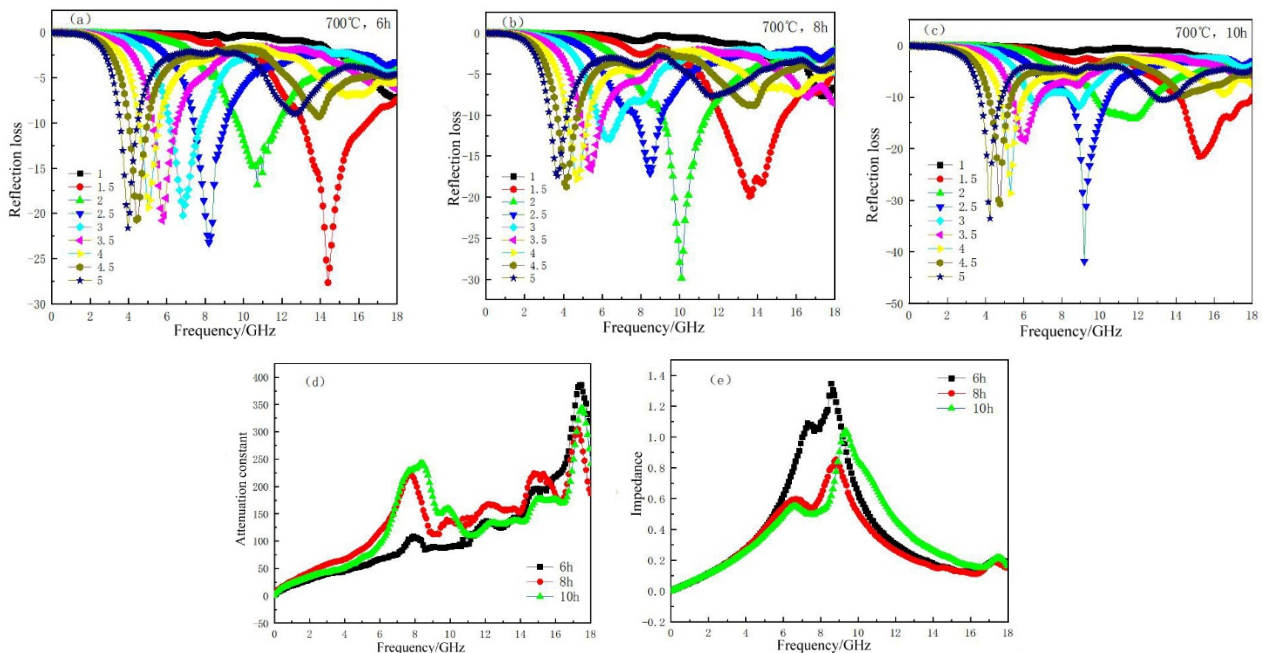


Figure 8. Absorption performance diagram (carbonization temperature is 700°C)

(a,b,c: reflection loss rate at different silica reaction time; d: Attenuation constant; e: Impedance)

When the final carbonization temperature is 700 °C, there is little difference in the attenuation constant between the coated silica reaction time of 8 h and 10 h(Fig. 8(d)). However, when the coated silica reaction time is 10 h, the impedance

coefficient is closer to 1, so the overall absorption performance is better(Fig. 8(e)). As a whole, the absorption performance of yolk shell C@C microspheres is better with the increase of the coated silica reaction time.

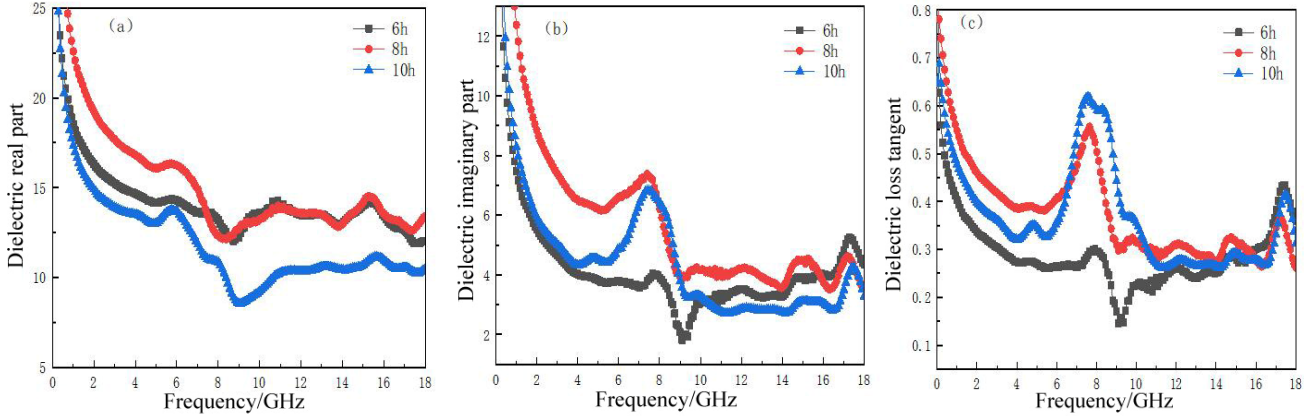


Figure 9. Dielectric loss diagram at different silica reaction time (carbonization temperature is 700°C)

(a: Dielectric real part; b: Dielectric imaginary part; c: Dielectric loss tangent)

It can be seen from Figure 9 that the real and imaginary dielectric part reach the highest, when the reaction time of coated silica is 8 h, but this may be related to the promotion effect of high carbonization temperature, thin interlayer and transitional carbon shell on dielectric properties, which reflects the dual effect of carbonization temperature and silica morphology. On the whole, the dielectric loss capacity at 8 h is advantageous in a wide frequency range. However, the impedance diagram in Fig.8(e) shows that the impedance

coefficient is the worst when the reaction time of coated silica is 8 h, so the absorption performance is poor. The dielectric loss is slightly lower when the reaction time of coated silica is 10 h than that of 6 h. However, the impedance matching is better when the reaction time of coated silica is 10 h, so the absorption performance is better when the reaction time of coated silica is 10 h. As a whole, the absorption performance of yolk shell C@C microspheres is better with the increase of the coated silica reaction time.

In order to further analyze the absorbing mechanism, debye theory is used to discuss the internal polarization.

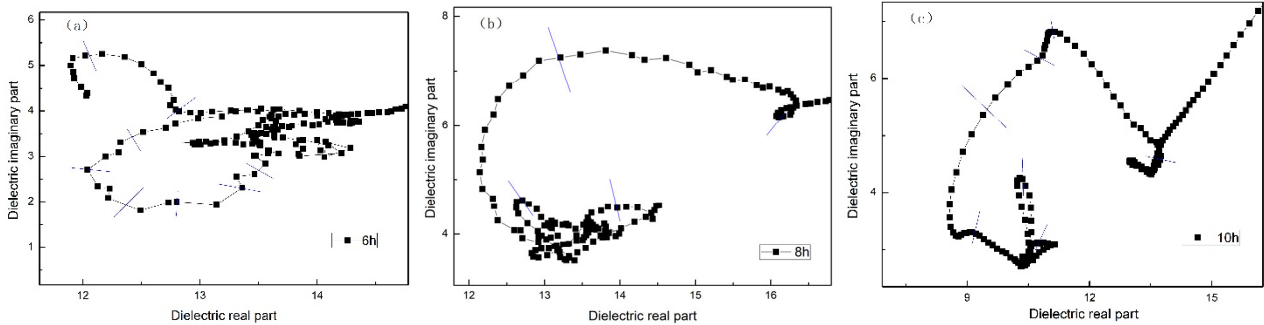


Figure 10. Cole Cole ring of electric loss

(a: 6h; b: 8h; c: 10h)

In Fig.10(a), it can be seen that there are 8 relaxation rings at 6 h. It can be seen from the other two figures that there are only 4 obvious relaxation rings for 8 h and 7 for 10 h. The number of dielectric relaxation ring represents explanatory material interface polarization effect[15]. When silica coated time is short, silicon dioxide in PR covering the surface of the ball more uneven, the late etching the formation of the shell layer more uneven, more interface, interface polarization effect is stronger. However, although the interface polarization effect is strong, the dielectric loss capacity of the composite is not very high, which may be related to the influence of carbonization temperature on the resistance loss capacity of the composite. Generally, the higher the carbonization temperature is, the greater the resistance loss is. Therefore, although the interface polarization effect is not

strong at 10 h, the resistance loss capacity brought by the relatively dense carbon shell is improved, which can also be seen in the long straight tail of the Cole-Cole ring in Fig.10.

In conclusion, the reaction time coated with silica at lower temperature has a great influence on the absorption performance of yolk shell C@C microspheres. However, when the final carbonization temperature is 750 °C, the effect of the reaction time coated with silica on the absorption performance of yolk shell C@C microspheres is small, and when the carbonization temperature is 750 °C, the overall absorption performance is poor, because the carbonization temperature greatly improves the resistance loss at this time, so that the effect of silica morphology is insignificant. The high temperature carbonization temperature is too high, resulting in the destruction of impedance matching, so the absorption performance decreases. When the carbonization

temperature is not too high, the carbonization temperature and the reaction time of coated silica affect and restrict each other, and jointly determine the absorption performance of yolk shell C@C microspheres.

4. Conclusion

In summary, yolk shell C@C microsphere absorbing material with multi-layer shell structure was synthesized by a relatively simple synthesis method. The sample quality was light and cheap. When the carbonization temperature is 700 °C and the reaction time is 10h, the reflection loss (-41.84 dB at 9.2GHz) and the ultra-wide response bandwidth (7.9-10.2 GHz) can be achieved, which has very excellent performance in pure carbon materials. The construction of carbon coated carbon shell structure opens up new ideas in the multilayer and porous design of absorbing materials in the future.

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