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Research on the dielectric constant of graphene solution at the microwave frequency of 9.212GHz

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Abstract

In order to measure the graphene's dielectric constant, the microwave cavity perturbation method was employed. At the frequency of 9.212 GHz, graphene with three concentrations of 5 g ml^{-1}, 2.5 g ml^{-1} and 1.25 g ml^{-1} was studied respectively. For these three solutions, as inserted depth in the microwave resonator, concentration and capillary's diameter changed, the dielectric constant's real part and imaginary part were all measured, calculated and discussed. The results showed that the real part of the graphene's dielectric constant increased with the increase of the depth of the capillary into the resonator, decreased with the increase of the capillary diameter. The conductivity of graphene solution was measured which decreased with the increase of liquid concentration.

1. Introduction

It was well known that graphene was a famous two-dimensional carbon nano-material with hexagonal honeycomb lattice composed of carbon atoms and sp2 hybrid orbitals [1–3]. Graphene was first isolated from graphite by Novoselov and co-workers [4, 5]. It could also be understood as cut-out carbon nanotubes, paved to form atomic monolayer graphene. These atomic layers were unusually stable, highly elastic, strong, and highly conductive. Because the energy spectrum had the dispersion relation of cone shape on the six corners of the first Brillouin zone [6]. It was different from traditional crystalline materials. The graphene crystal had unique quantum properties: anomalous quantum Hall effect, weak localization, minimal conductance and so on [7–10]. It was of many advantageous and widely used in a lot of fields, such as laser Q-switched, sensors, electronic device, and so on [11–13].

The dielectric constant of materials was an important parameter to describe the electromagnetic properties of materials [14]. The measurement of the dielectric constant of materials was very significance for studying the microwave properties of materials and designing microwave devices, obtaining structural information of materials to promote the development of new materials, promoting modern cutting-edge technology, etc. The 9.2 GHz microwave frequency was often used as the working frequency of optical fiber transmission, microwave amplifier, band-pass filter, laser, medical treatment, etc. Therefore, it was of practical significance to study the dielectric properties of graphene at this frequency.

Dielectrics were often insulators. Examples included porcelain, mica, glass, plastics, and various metal oxides. Some liquids and gases could be used as good dielectric materials. The study of dielectric constant of graphene solution could provide reference for liquid energy storage and energy loss. At present, most of the researches on the dielectric constant of graphene were about its derivatives or composites[15–18]. Using graphene to improve the dielectric constant of other materials. They used instruments to study the dielectric constant of graphene materials at different frequencies. However, there was no report about the dielectric constant of graphene solution. There were several methods to measure the dielectric constant of solid and liquid, such as free space method, resonant cavity perturbation, bridge method, strip line method and so on [19–22].

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Resonant cavity method was one of the most accurate methods for measuring dielectric constant of various dielectric materials [23]. Therefore, this letter presented the dielectric constant measurement of graphene by microwave resonant cavity perturbation method in different capillaries, different concentrations, and different depths inserted into the resonance cavity, respectively, and summarized the changing law.

2. Principle of measurement

The dielectric constant had plural form, its real part was called the dielectric constant, and its imaginary part was the loss factor. ε' was the real part of the dielectric constant, also called the capacitance rate, which reflected the ability of matter to store electromagnetic energy or charge, and represented the energy absorption. ε' was the imaginary part of the dielectric constant, which related to the loss of the current formed by the free charge of the material and represented the energy loss.

The complex permittivity can be expressed by the following formula:

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon' - i\frac{\sigma}{\omega} \tag{1}$$

Where ε was complex permittivity of the medium, i is the imaginary unit sign, σ is the conductivity of the medium, and ω is the electromagnetic wave angular frequency. For this formula, it can be seen that the conductivity is proportional to the imaginary part of the dielectric constant. The larger the imaginary part of dielectric constant, the greater the conductivity. However, since this paper mainly discusses the real part of the dielectric constant of graphene, there is no discussion on the relationship between the conductivity and the imaginary part of the dielectric constant.

Moreover, the dielectric constant is also related to the chemical potential [24]. For graphene, when the chemical potential increases, the real part of the dielectric constant of graphene changes from positive to negative. And when the chemical potential reaches a certain value, the change trend of chemical potential also changes, from increasing to decreasing.

The electric potential produced by dielectric under the action of alternating electric field lags behind the electric field by a phase angle. And there are

$$tan\delta = \varepsilon''/\varepsilon' \tag{2}$$

Because the energy loss of dielectric is proportional to $tan\delta$, $tan\delta$ is also called loss factor or loss tangent.

The resonant cavity was a closed metal conductor cavity with the characteristics of energy storage, frequency selection and so on. The commonly used resonators were rectangular and cylindrical. The rectangular cavity could be divided into two types: through resonant cavity and reflective resonant cavity. This paper employed reflective resonant cavity perturbation method to measure the dielectric constant of graphene solutions. The sample was placed in the center position of the resonant cavity's where the electric filed was maximum and the magnetic field was minimum. If the volume of the sample was much smaller than the resonator, it could be concluded that the electromagnetic field of the rest of the sample remains unchanged except for the change of the electromagnetic field at which the sample was located. So according to the perturbation theory of resonator, the formulas of dielectric constant's real part ε' and imaginary part ε'' of could be derived as followed [25]:

$$\varepsilon' = \frac{(f_s - f_0)}{2f_0\frac{V_s}{V_0}} + 1 \tag{3}$$

$$\varepsilon'' = \frac{\frac{1}{Q_{LS}} - \frac{1}{Q_{L0}}}{4\frac{V_s}{V_0}} \tag{4}$$

Where f_0 was the central frequency of vacant resonator, and f_s was the central frequency of samples put into the cavity. V_0 and V_S were the volume of the resonator and the measured sample respectively. The resonator's quality factors before and after the samples inserted into the cavity were Q_{L0} and Q_{LS} which could be determined by the following formula:

$$Q_{L0} = \frac{f_0}{|f_1 - f_2|} \tag{5}$$

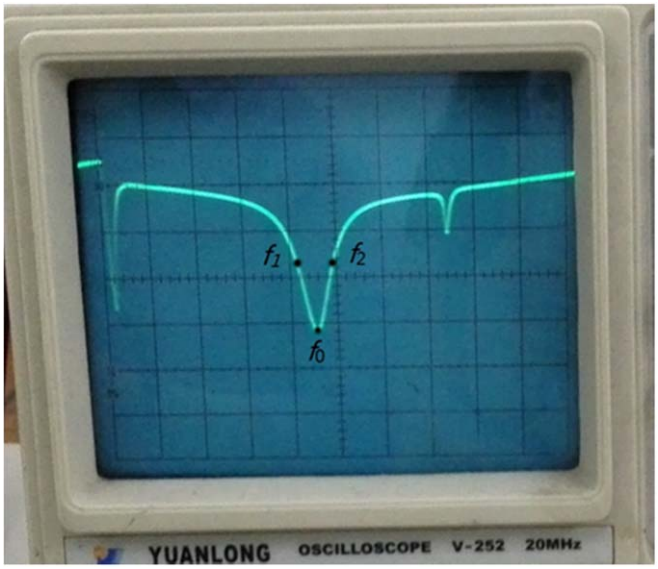


Figure 1. The reflection curve on the oscilloscope.

$$Q_{LS} = \frac{f_s}{|f'_1 - f'_2|} \tag{6}$$

Where f_1 and f_2 were the frequencies located at the half maximum of the reflection curve in the cavity, respectively, as presented in figure 1. Meanwhile, the frequencies of the half maximum of the reflection curve after inserting the sample were f_1' and f_2'. Frequency f was obtained from the wavelength λ of the corresponding position on the reflection curve by looking up the wavelength frequency scale contrast table. The V_s would change if the depth of the sample into the resonator was changed, so the dielectric constant real ε' was related to the V_s in addition to the f_s. Therefore, formula (1) used MATLAB software for three-dimension composition, as shown in figure 2. It could be seen from figure 2(a) that the overall trend of ε' changed with V_s and f_s. Figure 2(b) was the image when the ε' was intercepted, which could more clearly see the trend of change. The real part of ε' dielectric constant decreased when the V_s and the f_s increased.

3. Experimental facility

Figure 3 showed the structure of the experimental device. Gunn diode microwave source emitted microwave at the frequency of 9.212 GHz. The microwave passed through the isolator, the attenuator, the frequency meter, the microwave waveguide, the circulator, and then was introduced into the resonator, after reflected and imported into the isolator, finally, the resonant curve of the reflective resonator was displayed on the screen of the oscilloscope. A capillary with the measured sample, such as 5 g ml^{-1}, 2.5 g ml^{-1}, and 1.25 g ml^{-1} graphene solutions was placed into the rectangular resonant cavity. Changing the depth of capillary entering the resonant cavity by using height lifting frame. When the depth was changed, the reflected resonance curves on the oscilloscope would show corresponding changes, thus the dielectric constants of the samples measured at different depths could be calculated.

4. Characterization of graphene

4.1. Raman spectrum

The Raman spectra were measured by ATR6600 and Atr8300–633/532 respectively. Figure 4 showed the sample and the Raman spectra measured that under four different conditions. Figure 4(a) showed the results obtained by putting graphene solution into a glass sample bottle and testing it with ATR6600. It can be seen from the Raman spectrum that obvious characteristic signals could be seen at the wavelength of 1300 cm^{-1} and 1600 cm^{-1}, which was consistent with the characteristic peak of graphene mentioned in the reference [26]. Therefore, it can be judged that the sample used for experiments was graphene solution. Figures 4(b) and (c) showed the Raman spectra of graphene before and after drying by ATR8300–633. There was no significant

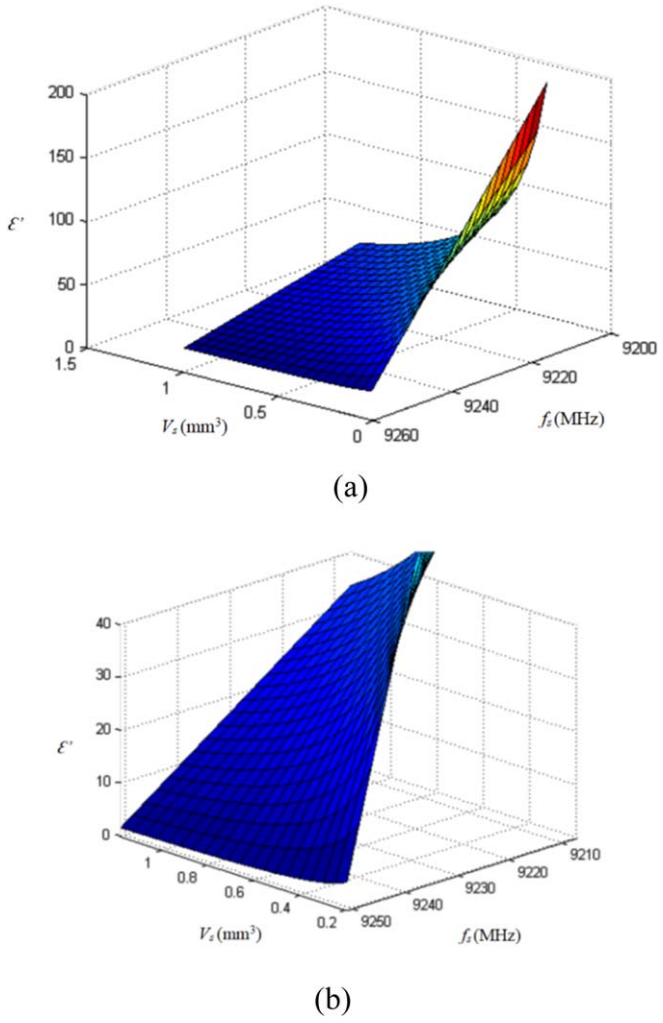


Figure 2. Diagram of the relationship between the real part of the dielectric constant ε' and the perturbation frequency and the volume of the measured medium: (a) ε' (0−100); (b) ε' (0–40).

difference between the results of the two images, and there were obvious characteristic signals in 1350 cm^{-1} and 1600 cm^{-1} bands. This showed that the sample is consistent with the characteristics of graphene, and the solid state or liquid state had little effect on the results. Figure 4(d) showed the result of testing dried graphene with ATR8300–532. It could be seen that there are obvious characteristic signals in 1343 cm^{-1} and 1600 cm^{-1} bands, which were also consistent with the characteristics of graphene.

4.2. Morphological characteristics

Atomic force microscopy(AFM) was used to obtain the surface morphology and image of graphene. The principle of AFM was that the force between atoms increases rapidly as the distance between atoms decreases to a certain extent.

The circular reflector (15 mm in diameter and 4 mm in thickness) in the laboratory was used and graphene solution was applied on it evenly. After standing for 15 h, the graphene solution was dried and tested by AFM. The obtained morphology was shown in figure 5(a), and the height image was shown in figure 5(b). In the graphene morphology, we drew a white line to determine the two points of the substrate and the sample surface to get its height. It could be seen from the height diagram that the surface height of graphene on the reflector was about 134 nm. This height was much thicker than graphene. This may be because our graphene was obtained by drying the solution. And it was difficult to ensure that the surface was clean, there was likely to be adsorption, resulting in the measured thickness was too large. The morphology of graphene solution had not found any cooperative units for the time being, so we had not measured the morphology of grahene solution, and we will continue to supplement it later. Moreover, we measured the dielectric constant of graphene solution, the solis morphology had little to do with this paper.

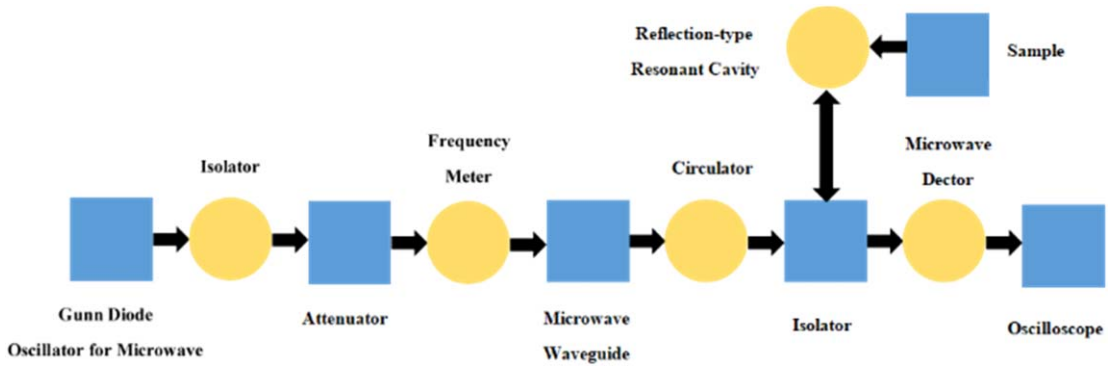


Figure 3. The structure of the experimental device.

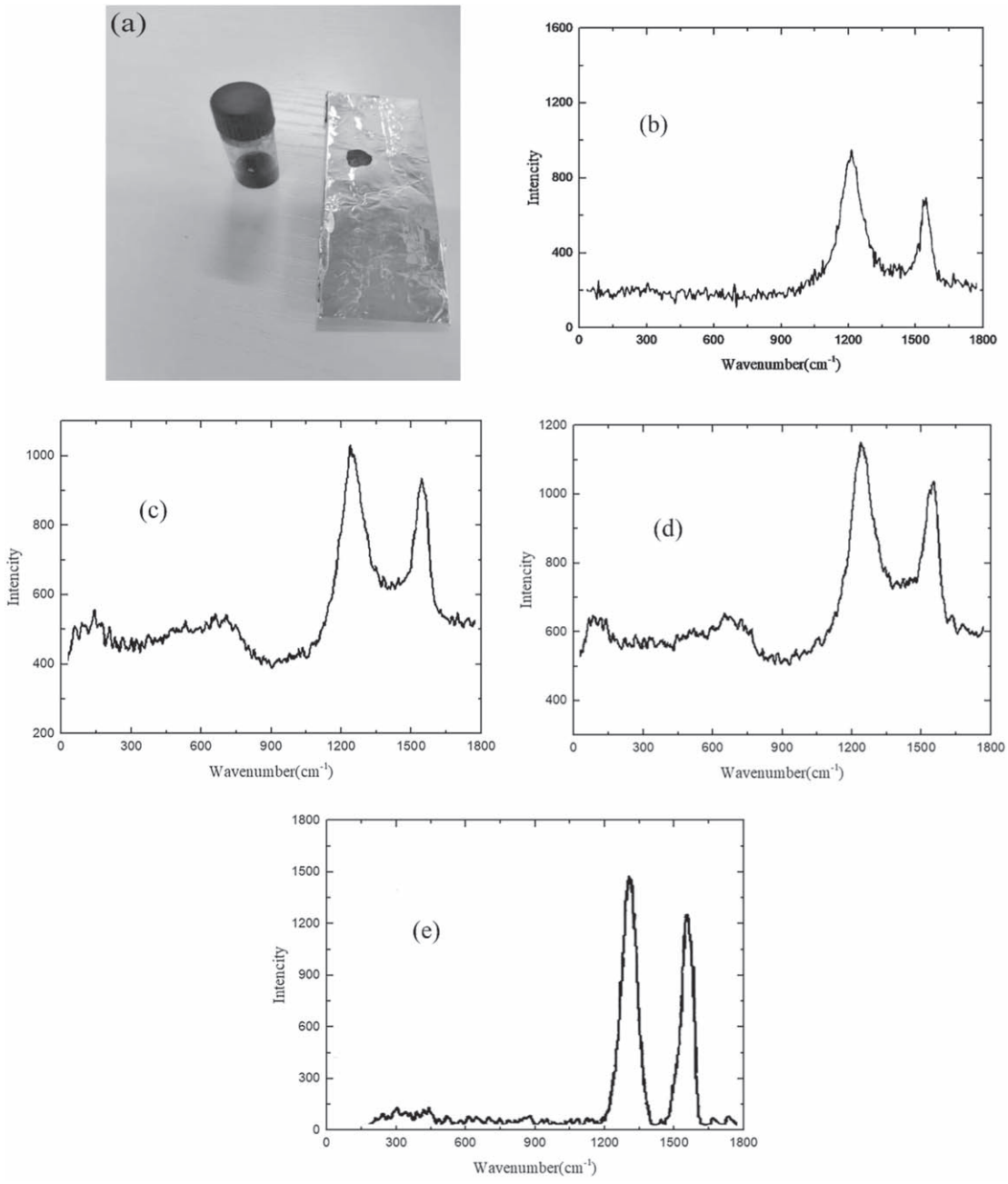


Figure 4. (a) Sample picture; (b) determination of graphene solution by ATR6600; (c) ATR8300–633 test of graphene solution before drying; (d) ATR8300–633 test of dried graphene; (e) ATR8300–532 test of dried graphene.

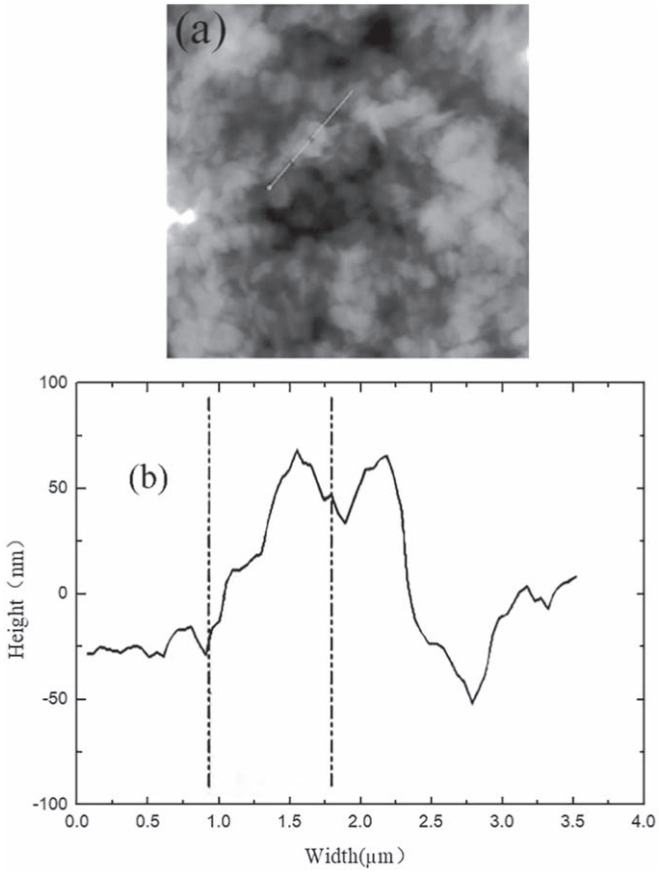


Figure 5. (a) Morphology (10 μm × 10 μm) of graphene on circular reflector; (b) height image of graphene on circular reflector.

4.3. Conductivity characteristics

The conductivity of different concentrations of graphene solution was also measured, and the relationship between conductivity and concentration was obtained.

Firstly, 1 ml of 5 g ml^{-1} graphene solution was diluted to 5 ml. Then 0.3 ml, 0.6 ml, 0.9 ml, and 1.2 ml from 5 ml solution were taken to prepare 4 ml solution. The four solutions of 0.075 g ml^{-1}, 0.15 g ml^{-1}, 0.225 g ml^{-1} and 0.3 g ml^{-1} were numbered from 1 to 4, as shown in figure 6(a). The conductivity of the four concentrations of graphene solution at 25 °C was tested, and the relationship between conductivity and solution concentra-tion was obtained, as shown in figure 6(b). It can be directly seen from the figure that the conductivity decreased with the increase of graphene solution concentration.

4.4. Dielectric constant measurement

Before measuring the dielectric constant of the sample, the frequency characteristic of hollow cavity and hollow capillary were measured. Table 1 shown the resonant frequency f0 of hollow cavity. Then the resonant frequency f0' of capillaries with diameters of 0.5 mm and 0.9 mm were measured. Which were shown in the table 2 and table 3. Because in the wavelength frequency scale contrast table, a frequency corresponded to a certain range of wavelengths. Sometimes when the wavelength values were different, the frequency was the same.

The original concentration of 5 g ml^{-1} of graphene solution was configured with water into 2.5 g ml^{-1} and 1.25 g ml^{-1} solutions. A total of six capillaries were tested with different concentrations of graphene solution in capillaries with diameters of 0.5 mm and 0.9 mm, respectively. Measuring the dielectric constant by placing the capillary in a height lifting frame. The graphene's dielectric constant results were based on the frequency of the corresponding hollow capillary. The experimental data was shown in the figures 7–9. Three figures described the relationship between the real part of dielectric constant of graphene with the inserted depth. For the three concentrations of graphene solutions, the real part of the dielectric contain increased with the increase of the depth of the capillary into the resonator. At 0.5 mm diameter, the largest change in the real part of the dielectric constant with increasing depth was the concentration of 2.5 g ml^{-1} graphene, increased by 31.97. At 0.9 mm diameter, the largest change in the real part of the dielectric constant with increasing depth was the

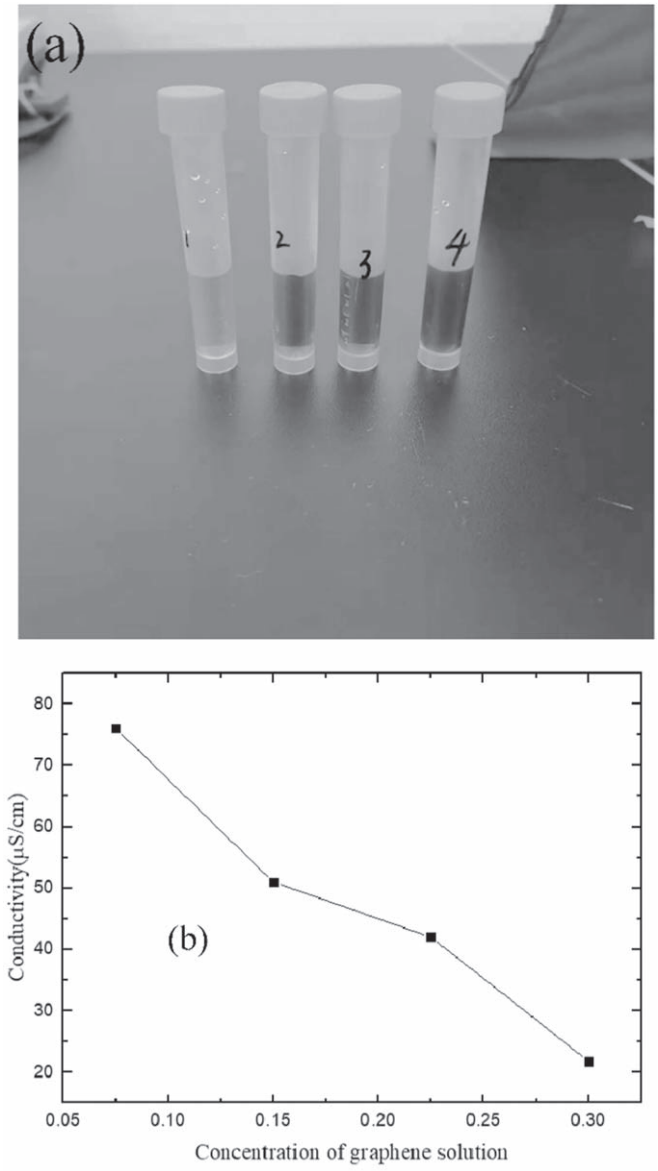


Figure 6. (a) Four graphene solutions with different concentrations; (b) the relationship between conductivity and concentration.

concentration of 1.25 g ml^{-1} graphene, increased by 14.44. It could be seen from the comparison that the real part of the 5 g ml^{-1} graphene dielectric constant at 0.5 mm diameter's capillary fluctuated the most with the increase of depth. In addition, the real part of the dielectric constant of the 0.5 mm's capillary was larger than the corresponding 0.9 mm.

Figures 10 and 11 described the relationship between the real part of dielectric constant of graphene with the concentration at the diameter of 0.5 mm and 0.9 mm capillary, respectively. It could be seen from figure 10 that the real part of graphene's dielectric constant changed obviously with the change of concentration. And the real part of the dielectric constant with the concentration of 2.5 g ml^{-1} was almost the largest in every depth. However, in figure 11, the real part of graphene dielectric constant was relatively gentle with the change of concentration

5. Results and discussion

Figures 12–14 described the relationship between the imaginary of dielectric constant of graphene with the inserted dept. We could know that the imaginary part of graphene's dielectric constant increased with the increase of depth, which was consistent with the real part of dielectric constant in 0.9 mm diameter's capillary. The imaginary part of the dielectric constant of three concentrations of graphene at the depth of 2 mm in 0.5 mm diameter's capillary had a minimum value. Then as the depth increased, the value increased. Liking the real part,

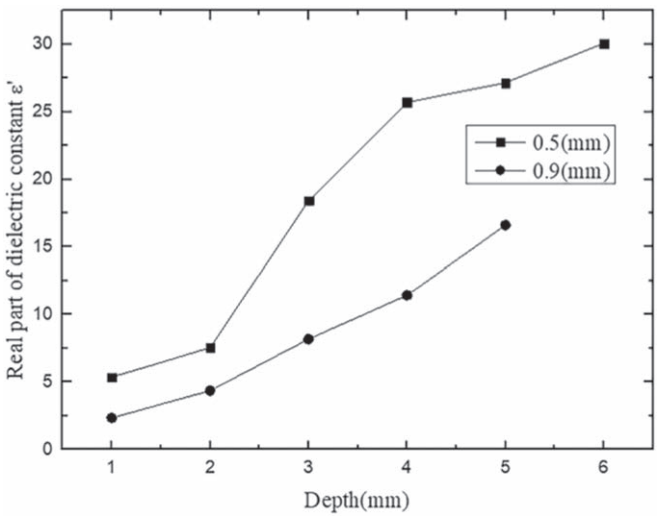


Figure 7. The real part of graphene's dielectric constant (5 g ml^{-1}) Versus inserted depth.

Table 1. The frequency of hollow cavity.

f_1 (MHz)	f_0(MHz)	f_2 (MHz)
9245	9252	9258

Table 2. The frequency of hollow capillary (0.5 mm).

Depth(mm)	f_1' (MHz)	f_0'(MHz)	f_2'(MHz)
1	9245	9252	9258
2	9244	9251	9258
3	9244	9251	9257
4	9243	9249	9256
5	9241	9247	9253
6	9245	9252	9258

Table 3. The frequency of hollow capillary (0.9 mm).

Depth(mm)	f_1' (MHz)	f_0'(MHz)	f_2'(MHz)
1	9245	9252	9258
2	9243	9250	9257
3	9241	9248	9254
4	9239	9246	9252
5	9237	9244	9250

the imaginary part of dielectric constant in the 0.5 mm diameter's capillary was larger than the corresponding 0.9 mm, and varied greatly with the depth.

Figures 15–17 described the relationship between loss tangent and depth. It was obvious from the figure that the change of loss tangent of 5 g ml^{-1} is obvious. The other two change gently and the loss tangent of the two capillary tubes was similar. In addition, each concentration of 0.5 mm capillary would change significantly at the depth of 2 mm. The loss tangent decreased suddenly.

The real part of the measured dielectric constant of water was shown in table 4. It could be seen from the table that when the capillary diameter was 0.5 mm, the real part of the dielectric constant of water was larger than that of graphene solution of three concentrations. And the concentration of graphene solution decreased with the increased of the added water. Therefore, for the smallest 1.25 g ml^{-1} of graphene solution, its real part of the dielectric constant was the smallest of the three concentrations. When the capillary diameter was 0.9 mm, the real part of the dielectric constant of water was in the middle of the three concentrations of graphene solution, so the real part of the dielectric constant of 5 g ml^{-1} graphene solution was the largest.

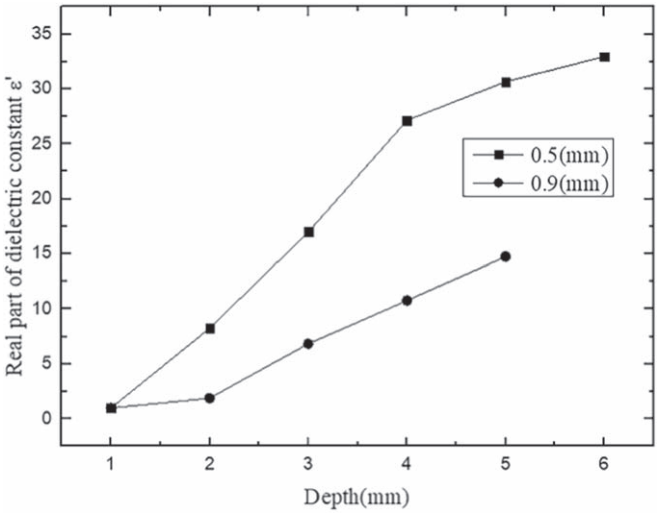


Figure 8. The real part of graphene's dielectric constant (2.5 g ml^{-1}) Versus inserted depth.

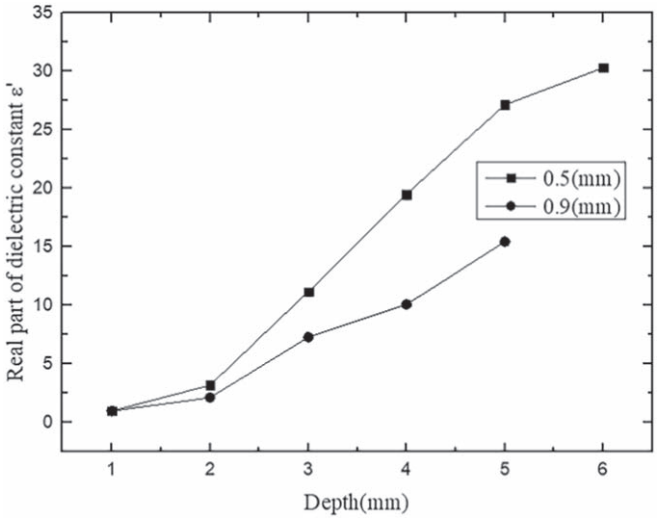


Figure 9. The real part of graphene's dielectric constant (1.25 g ml^{-1}) Versus inserted depth.

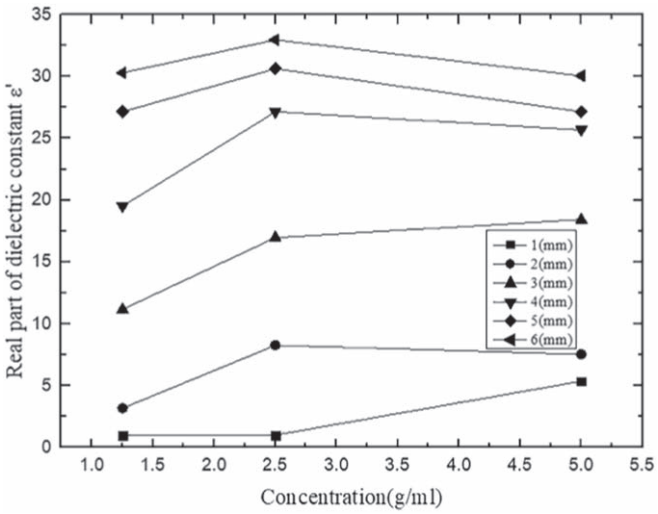


Figure 10. The real part of graphene's dielectric constant (0.5 mm) Versus Concentration.

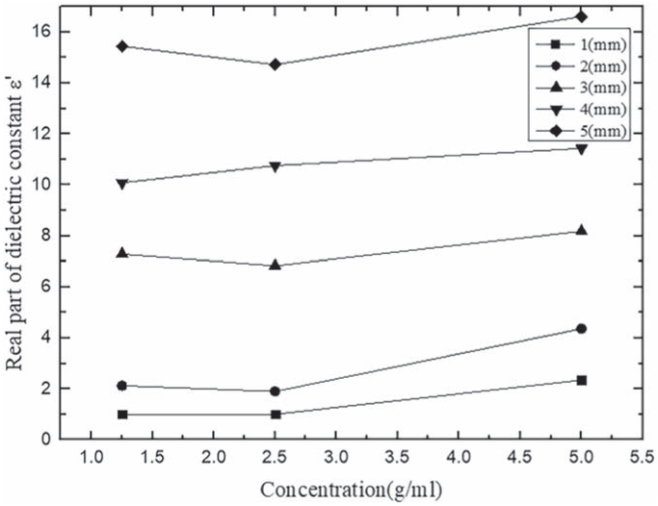


Figure 11. The real part of graphene's dielectric constant (0.9 mm) Versus concentration.

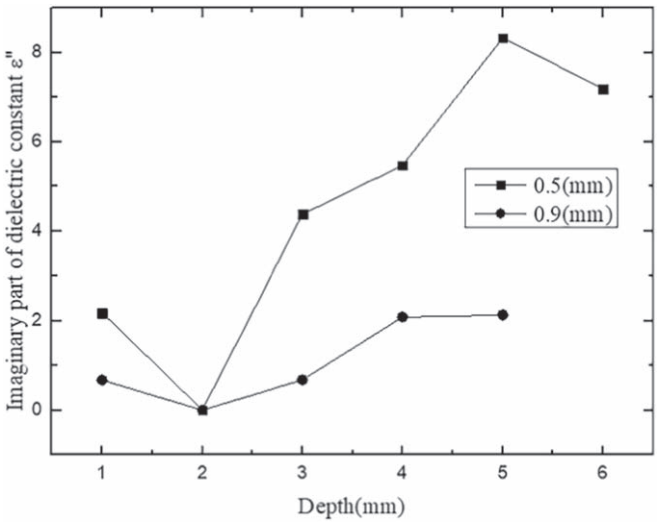


Figure 12. The imaginary part of graphene's dielectric constant (5 g ml^{-1}) Versus inserted depth.

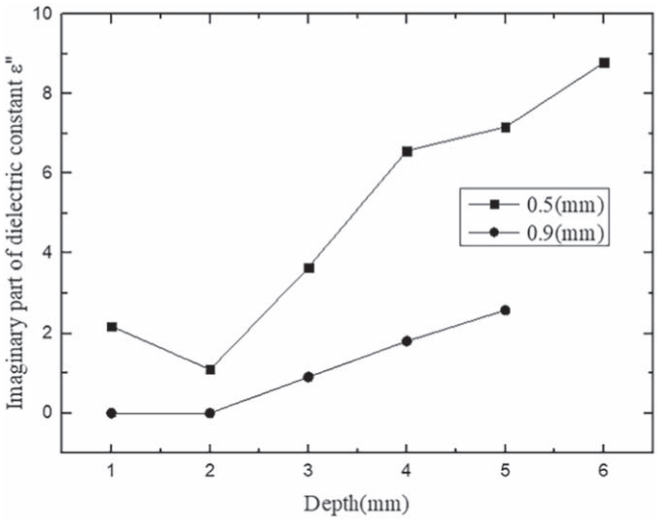


Figure 13. The imaginary part of graphene's dielectric constant (2.5 g ml^{-1}) Versus inserted depth.

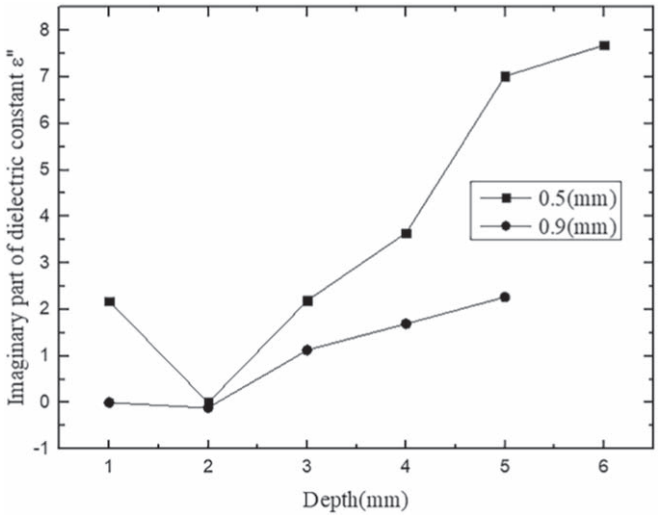


Figure 14. The imaginary part of graphene's dielectric constant (1.25 g ml^{-1}) Versus inserted depth.

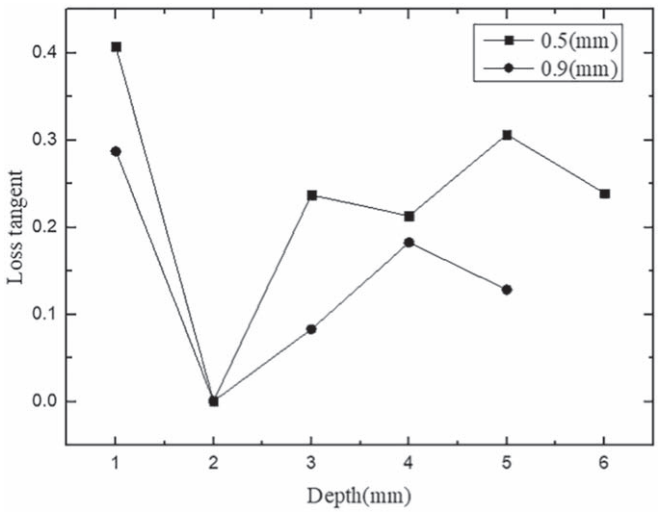


Figure 15. Relationship between loss tangent (5 g ml^{-1}) and depth.

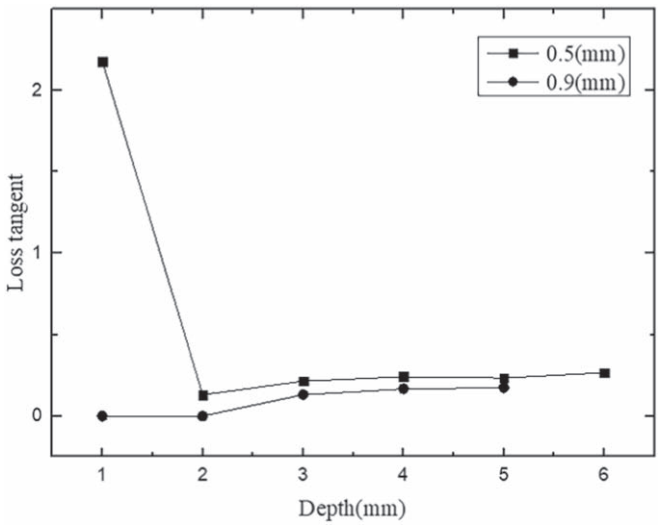


Figure 16. Relationship between loss tangent (2.5 g ml^{-1}) and depth.

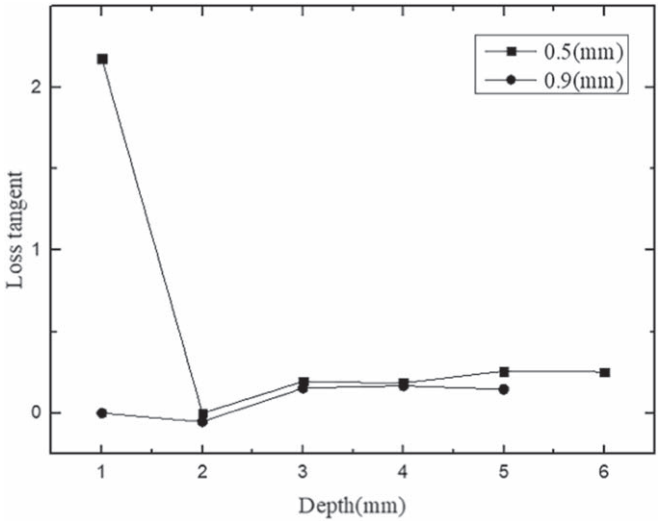


Figure 17. Relationship between loss tangent(1.25 g ml^{-1}) and depth.

Table 4. Real part of dielectric constant of water.

depth	0.5 mm capillary ε'	0.9 mm capillary ε'
2 mm	13.3348862	5.254953489
3 mm	26.15349343	8.315534068
4 mm	33.28837859	9.733851898
5 mm	43.95442724	19.99052925

It could be found that with the increase of the depth of the sample into the cavity (that is, the increase of V_S), the resonant frequency f_S decreased, and the real part ε' of the calculated dielectric constant also increased. This was consistent with the trend of the simulation formula in figure 2.

6. Conclusion

In this paper, the dielectric constants of graphene solution at different concentrations and the diameters of capillary as well as at different depths inserted into the cavity were studied by microwave resonant cavity perturbation method. The curves of dielectric constant varying with diameter, concentration and depth of cavity were obtained. It could be seen that the real part of the graphene's dielectric constain increased with the increase of the depth, decreased with the increase of the capillary's diameter, and fluctuated with the increase of the concentration. Meanwhile, the change of imaginary part of dielectric constant could also be seen. Because water was used as dispersant to dispose graphene solution, the graphene solution might be non-uniform, which may result in some inaccuracy in the experiment. But we considered the effect of hollow capillary on measuring the dielectric constant of graphene at the time of calculation. At present, only experimental tests were carried out in the subject, but no theoretical research was carried out. Next, in-depth research will be carried out. The results in this experiment would provide a reference for the further subsequent research on the graphene merits and its application in future.

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We would like to thank Jian Cui and the persons of OPTOSKY Optoelectronics Co. Ltd who provided the help for the Raman spectrums measurement.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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