Preparation of nickel-coated graphene and evaluation of infrared interference performance

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Abstract—In this paper, reduced graphene oxide (RGO) was prepared by oxidation-reduction method, and then RGO/Ni composite was prepared by chemical plating method. The RGO and RGO/Ni samples were characterized by the methods of SEM, TEM, XPS, EDS, XRD, etc. The complex refractive index of the samples in 2~14 μm infrared wavebands was measured by ellipsometry method, and the infrared absorption characteristic was calculated by DDA method. Then, the infrared interference performance was tested by the method of Fourier transform spectrometer connected with smaller smoke box, and the dispersivity was also comprehensively evaluated by Carr index method. It is found that electroless nickel plating not only can ease the secondary agglomeration between the RGO layers, improve its dispersivity, but also change the electromagnetic properties of graphene surface and significantly improve its infrared absorption. From the infrared interference performance test, it can be seen that the average extinction coefficients of RGO smoke to 3~5 μm and 8~14 μm infrared is 2.56 m\(^2\)/g and 1.8 m\(^2\)/g, respectively. While the average infrared extinction coefficients of RGO/Ni in the corresponding wavebands is 2.9 m\(^2\)/g and 2.55 m\(^2\)/g, respectively. It further indicates that the surface modification of electroless nickel plating can greatly promote the infrared interference performance of RGO. In particular, the far-infrared extinction performance has been obviously improved.

1. Introduction
Smoke screen has been used in military for thousands of years. The earliest "smoke" mainly appeared in ancient wars as a means of concealment and communication. It was not until the explosion of World War I that the use of smoke screen was officially transformed into combat support operations. With the rapid development of photoelectric detection technology and the practical application of precision guided weapons, the requirements of battlefield survival for smoke protection ability are becoming higher and higher. Because infrared guidance has the advantages of high precision, strong anti-interference ability and good concealment, it has become one of the main guidance methods of many long-range precision strike weapons. At this time, the conventional smoke screen that can only resist visible light viewing equipment can no longer meet the needs of combat. At present, the development of new infrared interference smoke screen materials has become an important topic in the field of passive interference.

Graphene is a two-dimensional nano carbon material with single atom thickness. It has a special microstructure. Compared with traditional smoke screen materials, graphene not only has lower density, larger specific surface area, excellent conductivity and suspension performance, but also has the unique
properties of micron and nano materials. It has great application value in infrared interference. Theoretically, the extinction ability of smoke to infrared mainly depends on its attenuation performance and suspension performance. According to a few literature reports, the infrared extinction ability of graphene depends on its extinction mechanism dominated by absorption attenuation. Although graphene powder shows good near-infrared interference performance, its far-infrared interference performance needs to be further improved. Besides, the problem of poor dispersion caused by the easy agglomeration of graphene power has not been effectively solved \cite{1-3}. However, graphene's unique two-dimensional structure and huge specific surface area provide unlimited possibilities for the preparation of wide band composite infrared interference materials. Graphene is used as the base material to load electromagnetic wave loss components such as metal, ferrite and polymer. Each component can form complementary advantages, which can reduce the density of composites, maintain good suspension performance, expand the electromagnetic wave loss mechanism of new materials and improve the dispersion performance of materials. It is expected to obtain better infrared interference effect.

In this paper, graphene was prepared by redox method. Aiming at the problems of limited far-infrared interference performance and easy agglomeration, the surface of graphene was modified by electroless nickel plating, and the material was characterized. The infrared absorption characteristics of the material were calculated based on DDA method, and the infrared interference performance and dispersion performance of graphene before and after modification were experimentally studied. This study can provide more data basis and method reference for the follow-up application research of graphene in infrared interference.

2. Experiment

2.1. Chemical reagents and instruments

The chemical reagents used for preparation of RGO mainly include flake graphite, concentrated sulfuric acid, potassium permanganate, 30% hydrogen peroxide, absolute ethanol, etc. The chemical reagents used for preparation of RGO/Ni mainly include stannous chloride, palladium chloride, concentrated hydrochloric acid, nickel sulfate, sodium hypophosphite, sodium citrate, ammonium chloride, ammonia, etc. The chemical reagents used in the experiments are analytical pure, and the water used is deionized water.

The instruments used in the experiments mainly include model Sl-234 electronic balance, model Hh-2 electric heating constant temperature water bath pot, model SHB-III circulating water multipurpose vacuum pump, model KQ-250DB numerical control ultrasonic cleaner, model LC-LX-L60D desktop centrifuge, model 101-2BS electrothermal blowing, model FD-1A-80 freeze dryer, model SK-B08123K vacuum/inert atmosphere tube furnace.

2.2. Experimental methods

Graphene (RGO) was prepared by improved Hummers method and thermal reduction method. The surface of RGO was modified by electroless nickel plating method. Electroless nickel plating process mainly includes sensitization/activation, degumming, electroless plating. The sensitization/activation process adopts colloidal palladium activation process, which can obtain sufficient Pd$^+$ catalytic active center on the surface of RGO. Degumming can remove the protective layer of alkaline stannide on the surface of RGO and maintain high catalytic activity. Colloidal palladium solution and conditions are shown in Tab.1, and the degumming solution and conditions are shown in Tab.2. The sodium hypophosphite alkaline system is used for electroless plating experiment. The loading capacity of RGO powder is 2/L, the composition of electroless nickel plating solution and conditions are shown in Tab.3.

| SnCl$_2$$\cdot$2H$_2$O(g/L) | PdCl$_2$(g/L) | HCl(mL/L) | T(℃) | Time(min) |
|---------------------------|--------------|-----------|------|-----------|
| 50                        | 0.5          | 300       | 45   | 20        |

Tab.1 Compositions of the colloid-palladium solution and operating conditions
2.3. Characterization of samples

The characterization instruments mainly include SEM (model QUANTA FEG450, FEI), TEM (model Talos F200X, Thermo Scientific), AFM (model Multimode V, Bruker), XPS (model ESCALAB 250Xi, Thermo Scientific), Lab Ram ARAMIS (model Thermo Fisher DXR, Thermo Scientific), XRD (model D8, Bruker), EDS (model X-Max, Oxford) and Laser particle size analyzer (model BT-9300H, Bettersize). The SEM-AFM instruments were used for characterizing the micromorphology of samples, the XPS-XRD instruments were used for characterizing the structural characteristics of samples, the EDS instrument was used for characterizing the element composition of samples and the Laser particle size analyzer was used for characterizing the particle size distribution of samples.

2.4. Measurement of complex refractive index

The real part and imaginary part of the complex refractive index in the mid-far infrared bands of RGO and RGO/Ni samples were measured by ellipsometry [4]. The instrument used was IR-VASE Mark II variable temperature infrared elliptical polarization spectrometer (J. A. Wallam company).

Since the imaginary part of the complex refractive index of one material is closely related to its absorption, the relationship between the imaginary part and the absorption coefficient is shown as Eq. (1) [5]. According to Eq. (1), the absorption coefficients of RGO and RGO/Ni samples in infrared bands can be calculated. Concurrently, the infrared extinction characteristics of RGO and RGO/Ni particles can be calculated by DDSCAT 7.3 program based on DDA method [4,6-8]. The values of particles size used in calculations were taken from the characterization results of each sample.

\[
A(\lambda) = 4\pi k / \lambda
\]

where \( k \) is the imaginary part of the complex refractive index, \( A(\lambda) \) is the absorption coefficient.

2.5. Infrared interference performance test

Fourier transform spectrometer (model WQF-530, Rayleigh) and smaller smoke box (length \( \times \) width \( \times \) height is 16 cm \( \times \) 13 cm \( \times \) 14 cm, volume is about 0.0015 m\(^3\) and optical path is 0.16 m) were used to test the infrared interference of RGO and RGO/Ni samples. The layout images of the test system are shown in Fig.1.

![Fig.1 The physical images of smoke box and infrared interference test system](image_url)
Test methods: (1) use Fourier spectrometer to quickly scan and collect the background transmission of blank smoke box. (2) Weigh a certain quality of sample into the smaller smoke box, turn on the fan for mixing, use the regulator to adjust the speed to make the sample disperse quickly in the smoke box, and start to scan the transmission of the sample quickly after the smoke screen is stable for 30s. After each test, store the data and empty the smoke screen in the smoke box. (3) Calculate the extinction coefficient of smoke screen to infrared according to Lambert Beer law\(^9\), and the calculation formula is shown in Eq. (2).

\[
T_s = \exp(-\alpha \cdot C \cdot L)
\]  \(\text{(2)}\)

where \(T_s\) is the infrared transmission (\%), \(\alpha\) is the infrared extinction coefficient (\(m^2/g\)), \(C\) is the mass concentration of smoke screen (\(g/m^3\)), \(L\) is the optical path of smoke box (\(m\)). Due to the smaller size of the smoke box, it is difficult to obtain the real-time concentration of the smoke screen. Therefore, we use the average mass concentration of the smoke screen instead of the real-time concentration in the calculation. The average mass concentration is equal to the ratio of the mass of the added test sample to the volume of the smoke box. In order to reduce the errors of extinction coefficient calculated by single concentration, the average extinction coefficient of smoke screen is calculated by testing different mass concentrations and corresponding transmissions. The calculation formula is shown in Eq. (3), which can be transformed from Eq. (2).

\[
-\ln T = \alpha \cdot CL
\]  \(\text{(3)}\)

As shown in Eq. (3), where \(\ln T\) is the natural logarithm of the average infrared transmission, \(CL\) is the area density of the smoke screen (\(g/m^2\)). By carrying out a linear quasi cooperative diagram between \(-\ln T\) and \(CL\), we can obtain the slope, which is the average infrared extinction coefficient of the smoke screen.

2.6. Dispersion performance test

The evaluation parameters measured by powder comprehensive characteristic instrument (\textit{model BT-1000, Bettersize}) include angle of repose (\(\theta_r\)), collapse angle (\(\theta_f\)), difference angle (\(\theta_d\)), plate angle (\(\theta_s\)), compression (\(C_p\)), dispersion (\(D_s\)) and homogeneity (\(M_f\)), etc. Then, the Carr index method\(^{10}\) was used to find out the corresponding index to each parameter, and the dispersibility of the samples was comprehensively evaluated through the flowability index (\(F_w\)) and floodability index (\(F_d\)). The calculation formulas of \(F_w\) and \(F_d\) are shown in Eq. (4) and Eq. (5).

\[
F_w = \theta_r\text{(index)} + C_p\text{(index)} + \theta_s\text{(index)} + M_f\text{(index)}
\]  \(\text{(4)}\)

\[
F_d = F_w\text{(index)} + \theta_f\text{(index)} + D_s\text{(index)}
\]  \(\text{(5)}\)

3. Results and discussion

3.1. Characterization analysis

3.1.1. Characterization results of RGO

The micromorphology characteristics of RGO is shown in Fig.2, the structural characteristics of RGO is shown in Fig.3, the particle size distribution of RGO is shown in Fig.4.
Fig. 2 SEM(a), TEM(b), AFM(c) of RGO

Fig. 3 XPS(a), Raman (b) of RGO

Fig. 4 DLS of RGO
As shown in Fig.2, there is stacking and agglomeration between RGO particle lamellae. The lamellar size is micron, ranging from several microns to more than ten microns; The particle lamellae are folded and have different degrees of bending, which is due to the large specific surface area and high surface energy of RGO. The particle lamellae will maintain its own thermodynamic stability through bending; RGO particles have a thin layer structure and the edge of the lamella is tilted. Combined with the height curve and phase image, it is analyzed that the thickness of most particle lamellae in RGO samples is about 5nm.

As shown in Fig.3, the XPS full spectrum of RGO contains obvious C1s peak (284.6 EV) and O1s peak (533.8 EV). The C1s peak comes from C-C (284.6 EV), C-O (286.4 EV) and C = O (288.5 EV). In the C1s high-resolution spectrum, the peak shapes of C-O and C = O are not obvious, and the key position of C is mainly C-C bond, indicating that the oxygen content in the sample is not high. After calculation, the contents of C and O are 93.82% and 6.18% respectively, in which a small amount of oxygen is introduced during the reaction, indicating that the reduction degree of graphene sample is sufficient, but not thorough enough. There are obvious G and D peaks in the Raman spectrum of the sample. The G peak near 1590 cm$^{-1}$ is caused by the E$_{2g}$ stretching vibration of C-C, and the D peak near 1350 cm$^{-1}$ is the embodiment of the disorder degree of graphene. The high intensity of D peak indicates that there are many structural defects due to the oxidation of graphite in the reaction process. After fitting, it is calculated that the intensity ratio (I$_D$/I$_G$) of D peak to G peak is 1.61, indicating that the thermal reduction degree of graphene is not good enough, and there are still some oxygen-containing functional groups that have not been reduced.

As shown in Fig.4, the equivalent volume particle size distribution of RGO sample shows typical lognormal distribution characteristics, indicating that the sample is well dispersed in ethanol medium, in which the agglomeration is not obvious. The D$_{50}$ of RGO sample is about 10.4 μm and the D$_{90}$ is about 21 μm, indicating that there are more particles with small size in the samples.

### 3.1.2 Characterization results of RGO/Ni

The micromorphology characteristics of RGO/Ni is shown in Fig.5, the structural characteristics and element composition of RGO/Ni is shown in Fig.6, the particle size distribution of RGO/Ni is shown in Fig.7

![Fig.5 SEM(a), TEM(b), SEAD(c), AFM(d) of RGO/Ni](image)
As shown in Fig.5, there are many nickel nanoparticles coated on the upper and lower surfaces of RGO. Most particles exist in a single form, with a little local aggregation. The agglomeration phenomenon between RGO/Ni particles is reduced and the dispersion is improved. This is because the large surface area, bending and surface folds of graphene effectively prevent the aggregation of nickel nanoparticles, at the same time, the loading of nickel nanoparticles also prevents the secondary agglomeration of RGO layers. The distribution and size of nickel nanoparticles coated on the surface of RGO thin layers are relatively uniform. The shape of nickel nanoparticles is approximately flat sphere, and its average diameter is about 50 nm; The electron diffraction patterns of RGO/Ni samples show a wide and bright halo ring and multiple weak halo rings, indicating that the nickel nanoparticles loaded on the surface of RGO have a certain microcrystalline structure; In the AFM diagram of the sample, the thickness of RGO layer within the regions of A to B and C to D is about 5.6 nm and 3.5 nm respectively, and the thickness of metal nickel coating within the region of E to F is about 11 nm. It can be calculated that the average thickness of RGO/Ni layer is about 16 nm.

As shown in Fig.6, the main elements contained in RGO/Ni sample are carbon and nickel, in addition to a small amount of oxygen and a small amount of phosphorus, it further shows that metal nickel has been successfully deposited on the surface of RGO. The existence of oxygen indicates that the oxygen-containing groups have not been completely removed during the preparation of RGO, while the existence of phosphorus may be due to the free electrons produced by the dehydrogenation side reaction of hypophosphite ion. The nickel coating is composed of metal nickel and a small amount of phosphorus. In the XRD spectra of the sample, the peak near 25°(2θ) is the amorphous diffraction peak of RGO. In
addition, a broadened diffraction peak appears at 44.5°(2θ), which corresponds to the (111) crystal plane of nickel. The broadening of the peak shape indicates that the crystallinity of metallic nickel in the coating is low and tends to transition to amorphous state, which is basically consistent with the analysis results of electron diffraction pattern above.

As shown in Fig.7, the equivalent volume particle size distribution of RGO/Ni sample also shows the characteristics of typical lognormal distribution. The D50 is about 11.7 μm, the D90 is about 24.3 μm. It shows that the deposition of nano-nickel particles increases the thickness of the particle layers, while the equivalent volume of RGO/Ni particles also increases.

3.2. Calculation and analysis of infrared absorption characteristics
The complex refractive index curves, the absorption coefficient curves, infrared extinction curves of RGO and RGO/Ni are shown in Fig.8 to Fig.10 respectively.

![Complex refractive index curve of RGO(a) and RGO/Ni(b)](image)

![Absorption coefficient curve of RGO(a) and RGO/Ni(b)](image)

![Infrared extinction curve of RGO(a) and RGO/Ni(b)](image)
As shown in Fig. 8, the real part ($n$) of RGO does not change significantly with the wavelength, and its value is basically stable near 2.5. The imaginary part ($k$) of RGO, the real part ($n$) and imaginary part ($k$) of RGO/Ni gradually increase with wavelength, with the values in the range of 0.5-1.8, 2.4-3.8, 2-2.9, respectively.

As shown in Fig. 9, the absorption coefficient of RGO sample basically decreases with the wavelength, and the absorption coefficient is the largest in the near-infrared band, which indicates that the absorption of RGO in the near-infrared band is strong, while its absorption in the mid-far infrared band is relatively weak. In the same infrared band, the absorption coefficient of RGO/Ni is greatly improved compared with RGO, indicating that the modification of electroless nickel plating effectively improves its infrared absorption capacity, especially the increase of the far-infrared absorption capacity is obvious.

The infrared extinction curves of RGO circular sheet particles with diameter of 5μm, thickness of 5 nm and RGO/Ni circular sheet particles with diameter of 5μm, thickness of 16 nm is shown in Fig. 10. From the comparison, it can be seen that the extinction, absorption and scattering efficiency factors ($Q_{ext}$, $Q_{abs}$, $Q_{sca}$) of RGO/Ni particles are greater than those of RGO particles, indicating that the modification of electroless nickel plating can greatly improve the infrared extinction of RGO, especially the increase of the infrared absorption capacity is obvious.

3.3. Results of infrared interference performance test

The transmission and average extinction coefficient of RGO smoke in 3–5 μm, 8–14 μm infrared bands are shown in Fig. 11 and Fig. 12. The results of RGO/Ni smoke in the same bands are shown in Fig. 13 and Fig. 14.
The extinction coefficient of smoke particles is an important parameter to characterize its shielding ability. The larger the extinction coefficient, the better the extinction effect and the stronger the interference ability. As shown in Fig.11 and Fig.12, it is calculated that the average extinction coefficient of RGO smoke screen to 3–5 μm and 8–14 μm infrared is 2.56 m²/g and 1.8 m²/g respectively, both of which are higher than the extinction coefficient of traditional infrared interference materials, such as copper powder and graphite [1], indicating that RGO smoke has good near-mid infrared interference performance, and its far-infrared interference performance needs to be further improved.

As shown in Fig.13 and Fig.14, the average extinction coefficient of RGO/Ni smoke screen to 3–5 μm and 8–14 μm infrared is 2.9 m²/g and 2.55 m²/g respectively. The results show that nickel plated graphene has excellent infrared extinction performance, and its infrared interference performance is greatly improved than that before modification, especially the far-infrared interference increases obviously.

3.4. Results of dispersion performance test
The result of dispersibility between RGO and RGO/Ni samples was shown in Tab.4. The dispersibility of one material is related to its floodability. As shown in Tab.4, it can be seen that the dispersion of RGO sample is far less than 50%, indicating that the splash tendency of RGO powders is very general, and its dispersion and floatability maybe also not good enough. Meanwhile, it can be seen that $F_w$ and $F_d$ of RGO powders is 57 and 52 respectively. Although the flowability of RGO is better than its floodability, but its dispersibility is still far from the relevant national military standards of flake graphite infrared interference smoke agent. After electroless nickel plating, the dispersion of RGO/Ni powders is 33.6%, and its $F_w$ and $F_d$ is 61 and 62 respectively. The evaluation results show that electroless nickel plating
can improve the dispersion of RGO powders, prolong the floating time of smoke particles, and increase the effective shielding time of smoke screen to infrared.

| Evaluation parameters | RGO measured value | index | RGO/Ni measured value | index |
|-----------------------|-------------------|-------|-----------------------|-------|
| $\theta_r$            | 53.3°             | 12    | 45.3°                 | 15    |
| $C_p$                 | 31.8%             | 10    | 33.5%                 | 7     |
| $\theta_s$            | 68.2°             | 12    | 51.6°                 | 16    |
| $M_f$                 | 2.74              | 23    | 2.67                  | 23    |
| $F_w$                 | 57                | 24    | 61                    | 25    |
| $\theta_f$            | 48.5°             | 12    | 41.3°                 | 15    |
| $\theta_d$            | 4.8°              | 4     | 4°                    | 3     |
| $D_s$                 | 17.6%             | 12    | 33.6%                 | 19    |
| $F_d$                 | 52                | 52    | 62                    | 62    |

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

1. The characterization results show that the distribution and size of nano-nickel particles on RGO surface are uniform, which prevents the secondary stacking of RGO layers. The shape of nano-nickel particles is approximately flat sphere, and its average diameter is about 50 nm. The nickel nanoparticles deposited on the surface of RGO have a certain microcrystalline structure, and the content of phosphorus in the nickel coating is very low.

2. The analysis results of infrared absorption characteristics show that the modification of electroless nickel plating changes the electromagnetic characteristics of the surface of RGO and effectively improves the infrared absorption ability, especially the far-infrared absorption ability.

3. The results obtained from the tests show that electroless nickel plating on the surface of RGO can improve its dispersibility and far-infrared interference properties, which can be used as a reference for the expansion of modification methods of RGO.

References

[1] Liu Qinghai, Liu Haifeng, Dai Xiaodong, et al. Infrared interfering performance of graphene smoke screen[J]. Infrared Technology, 2019, 41(11): 1071-1076. (in Chinese)

[2] CHEN Hao, GAO Xinbao, XU Xingchun, et al. Middle and Far Infrared Interference Properties of CNT/graphene/carbon Composites Smoke Screen[J]. Chinese Journal of Energetic Materials, 2019, 27(3): 249-254. (in Chinese)

[3] Zheng Enshuang, Lei Chaoshuai, Li Jian, et al. The preparation of super lightweight magnetic Fe3O4/graphene/carbon aerogels and their use in electromagnetic interference shielding[J]. New Carbon Materials, 2020, 35(6): 707-715. (in Chinese)

[4] Li Kai, Wang Xuanuy, Gao Yanqing, et al. Complex refractive index and extinction performance of graphene in infrared bands[J]. Infrared and Laser Engineering, 2021, 50(4): 20200246. (in Chinese)

[5] Fan Jieping, Liu Huimin, Tian Qiang. The imaginary part of dielectric function and the absorption coefficient[J]. College Physics, 2009, 28(3): 24-25. (in Chinese)

[6] Draine B T, Flatau P J. Discrete-dipole approximation for periodic targets: theory and tests[J]. J. Opt. Soc. Am. A, 2008, 25: 2593-2703.

[7] Flatau P J, Draine B T. Fast near field calculations in the discrete dipole approximation for regular rectilinear grids[J]. Optics Express, 2012, 20: 1247-1252.

[8] Draine B T, Flatau P J. DDSCAT 7.3(CP)[EB/OL]. http://code.google.com/p/ddscat/.

[9] Wang Xuanuy. Technical basis of pyrotechnics [M]. Beijing: Tsinghua University Press, 2017. (in Chinese)

[10] Cui Ling, Sasabe Shuji, Shimizu Kenji, et al. Development and application for measuring method of powder flowability and floodability[J]. China Powder Science and Technology, 2012, (1): 72-77. (in Chinese)