Preparation and UV-Visible Extinction Property of RGO/Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ Composite

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Abstract. A reduced graphene oxide (RGO)/copper-cobalt ferrite (CCF) composite (CCFR) was synthesized via solvothermal method and characterized by SEM. The transmission spectra of the material were measured in the UV-Vis region (240-800 nm), which can be used to calculate the mass extinction coefficient. The results show that CCFR sample was prepared successfully. Its mass extinction coefficient is in the range of 1.3~1.6 m$^2$/g in the UV-Vis region, which means it is an excellent optical extinction material. The experimental results and methods can provide references for the application of RGO and CCFR in the UV-Vis band.

1. Introduction

In 2004, Andre Geim, a scientist at the University of Manchester in the United Kingdom, used a special transparent adhesive tape to “stick” monoatomic graphite graphene from highly oriented pyrolytic graphite [1]. It is a hexagonal shape composed of carbon atoms. The crystal of honeycomb lattice structure is the thinnest material found in the world at present, and its thickness is only 0.335 nm. Graphene has excellent electromagnetic properties. Studies have shown that monolayer graphene has a 2.3% absorption rate in a wide optical range so that it is theoretically a good optical extinction material. Li [2] proved that the graphene smoke screen has a good extinction performance in the infrared band through the smoke box test. Ma [3] used the K-K relation and the T-matrix method to invert the graphene reflectance spectrum to obtain the extinction efficiency factor of graphene in the UV-NIR region. The results show that graphene has good extinction property in the 240-2600 nm band.

At present, the spectral interference properties of graphene-based composites are mainly concentrated in the microwave band, and research in the optical band is still lacking. Graphene has excellent dielectric properties, but it does not have magnetic properties so that it just has a single loss mechanism, and its attenuation performance in the microwave band needs to be improved. If the graphene and the ferrite are composited, the composite material will have both electrical loss and magnetic loss, which is beneficial to improving the attenuation performance of the electromagnetic wave.

The preparation methods of graphene/ferrite composites include solvothermal method, hydrothermal method, coprecipitation method, sol-gel method and gas phase diffusion method [4-8]. The application fields mainly include photocatalyst, electrode materials and absorbing materials, etc. [9-11]. In this
paper, a simple solvothermal method was used to compound the copper-cobalt ferrite (Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$) and RGO at a mass ratio of 7:3. RGO/copper-cobalt ferrite composite was successfully synthesized. The SEM was used to characterize the morphology and structure of the composites. The transmission spectra of RGO, CCF and CCFR in the UV-Vis band (240-800 nm) were tested. The corresponding mass extinction coefficients were calculated by using the Lambert-Beer law. The experimental results and methods can provide references for the applications of RGO and CCFR in the UV-Vis band.

2. Experimental

2.1. Materials and Apparatus

The RGO used in the experiment was purchased from Suzhou Carbon Technology Co., Ltd.; Hexahydrate ferric chloride (FeCl$_3$·6H$_2$O), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), and Copper chloride dihydrate (CuCl$_2$·2H$_2$O), ammonium acetate (NH$_4$Ac), polyvinylpyrrolidone (PVP), ethylene glycol (mass fraction 99%), and ethanol (mass fraction 95%), all of which were of analytical grade. The instruments and equipment used include analytical balances, thermostatic magnetic stirrers, vacuum drying ovens, centrifuges, scanning electron microscopes, and UV-Vis spectrophotometers.

2.2. Synthesis of CCFR

The RGO/copper-cobalt ferrite composite (CCFR) was synthesized by solvothermal method. The preparation process was as follows. Firstly, 0.388 g of RGO, 6 mmol of FeCl$_3$·6H$_2$O, 1.5 mmol of CoCl$_2$·6H$_2$O and CuCl$_2$·2H$_2$O, 5g of NH$_4$Ac, and 0.5g of PVP were respectively added to 60 ml of ethylene glycol, and the mixed solution was magnetically stirred for 2 h to form a uniform suspension. Secondly, the suspension was transferred to a PTFE inner liner with an inner volume of 100 ml stainless steel, and the autoclave was placed in a vacuum drying oven at 200° C. The reaction time was 20 h. In three steps, the product was processed: the high-pressure reactor was taken out and cooled to room temperature, and the resultant product was washed with alcohol 5 to 7 times, then dried in a vacuum drying box at 80° C., and then ground through an agate mortar to obtain product CCFR.

2.3. Characterization

The morphology analyses of samples were carried out on scanning microscopy (SEM, HITACHI S3400N). First, the conductive adhesive is glued on the sample plate. Then, the sample powder is dispersed in anhydrous ethanol, and a uniform suspension is formed by ultrasonic vibration. The suspension is then dropped on a single crystal silicon wafer through a disposable plastic pipette and allowed to stand until the suspension is dried. The silicon wafer can be adhered to the conductive adhesive for experimental observation.

2.4. Extinction coefficient

2.4.1. Experimental solvent

The sample was dispersed in several common transparent solvents such as water, ethanol, ethylene glycol, and acetone, and the dispersion effect of the solvent was judged by recording the suspension time of the sample in the solvent. The results show that due to the high density of ethylene glycol, the sample has a long suspension time and stable state in ethylene glycol, which has a significant effect on the dispersion of the sample. Therefore, ethylene glycol was used as a solvent in this experiment.

2.4.2. UV-Visible transmission spectrum measurements

First, the UV-Vis transmission spectrum of ethylene glycol was taken as the baseline to eliminate the influence of the solvent on the experiment. Weigh 20mg of the sample to be dissolved in 80mL of ethylene glycol, and after 5 minutes of ultrasonic dispersion, a uniform suspension with a concentration of 0.2g/L was prepared. The transmission spectrum of samples were measured at 20°C in the ranges of 240-800nm.
2.4.3. Extinction coefficient calculation. After obtaining the transmission spectrum of the sample, according to the Lambert-Beer law, the extinction coefficient \( \alpha \) and the transmittance \( T \) of the sample have the following relationship at a certain concentration and light path:

\[
\alpha = -\frac{\ln (T)}{b \cdot c}
\]

(1)

Where \( b \) is the concentration of the substance and \( c \) is the thickness of the cuvette. The mass extinction coefficient of the sample is calculated by Eq.1. In order to reduce the experimental error, five experiments were performed for each sample, and the final experimental data were weighted and averaged from the five experimental results.

3. Results and discussion

3.1. Characterization of CCFR

![SEM images of (1) RGO; (2) CCFR.](image)

RGO can be seen in Fig. 1(1) and CCFR can be seen in Fig. 1(2). Inside the RGO sheet, the size of the CCF particles are about several tens of nanometers, which are uniformly distributed on the surface of the RGO sheet. There are obvious clusters of CCF particles at the wrinkles and edges of the sheets,
and the size of the CCF nanoclusters is several hundred nanometers. The reason is that defects, such as wrinkles and edges, destroy the stable energy level structure of the RGO and its electronic transport characteristics, which may prompted the formation of vacant electrons or enhanced energy level vibration. Therefore, the adsorption ability of RGO for CCF nanoparticles were enhanced.

3.2. UV-Visible extinction properties

![Fig. 2 UV-vis transmission spectrum of RGO](image)

![Fig. 3 UV-vis transmission spectrum of CCF](image)
Fig. 4 UV-vis transmission spectrum of CCFR

In the UV-Vis band, the absorption peak of the spectrum is mainly caused by the transition of valence electrons in the molecule. The valence electrons of the molecules are divided into three types: $\sigma$ bond electrons, $\pi$ bond electrons, and unbonded lone pair electrons (n electrons). After absorbing energy, these valence electrons will transition from the ground state to the excited state. RGO is a two-dimensional carbon material composed of carbon atoms in the form of $sp^2$ hybrid orbital hexagonal honeycomb lattice, each carbon atom corresponding to four valence electrons, of which three through $sp^2$ hybridization to carbon-carbon single bond, and the other exists in the form of n electrons which form large bonds in the p orbital. According to Fig. 2, the transmission spectrum of graphene shows a distinct absorption peak at 270 nm, which is due to the transition of n electrons to the $\pi^*$ bond electron. As can be seen in Fig. 3, the transmission spectrum of the copper-cobalt ferrite has a distinct absorption band between 650-700 nm. The spectral characteristics of the RGO and CCF are all reflected in the transmission spectrum of CCFR. It is also demonstrated from the perspective of the spectrum that the graphene/copper-cobalt ferrite composite material was successfully prepared in this experiment.
Fig. 5 UV-Vis extinction coefficient of RGO

Fig. 6 UV-Vis extinction coefficient of CCF
The mass extinction coefficient of the material can be calculated from the transmission spectrum by Eq.1. From Fig. 5 to Fig. 7, it can be seen that the extinction coefficient of RGO in the band of 240-800 nm is in the range of 2.68~3.82 m$^2$/g, which reaches a maximum around 270nm. The average extinction coefficient of RGO reaches 2.99 m$^2$/g. The extinction coefficient of CCF in the 240-800 nm band is in the range of 0.77~0.93 m$^2$/g, and the average extinction coefficient is 0.88 m$^2$/g. The extinction coefficient of CCFR in the band of 240-800nm is in the range of 1.32~1.55 m$^2$/g, and the average extinction coefficient is 1.44 m$^2$/g. It can be seen that the extinction property of RGO in the UV-Vis region is superior and the addition of RGO makes the extinction coefficient of CCFR significantly improved compared with that of CCF, which effectively compensates for the insufficiency of the ferrite. The composite material has an excellent extinction property the UV-Vis band.

4. Conclusion
The RGO/copper-cobalt ferrite composite was successfully synthesized by solvothermal method. Copper-cobalt ferrite nanoparticles were uniformly distributed on the surface of the RGO sheets. The extinction performance of RGO in the UV-Vis region is significant that the extinction coefficient of RGO in the band of 240-800nm is more than 2.68 m$^2$/g. The average extinction coefficient of CCFR in the UV-Vis band is 1.44 m$^2$/g. The experimental results and methods can provide references for the application of RGO and CCFR in the UV-Vis band.

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