Third-order nonlinear optical properties of CuS/reduced graphene oxide nanocomposites

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Abstract. CuS/Reduced graphene oxide (rGO) nanocomposites can be synthesized using the hydrothermal method. X-ray diffraction and transmission electron microscopy analyses demonstrated that CuS uniformly covered the surfaces of rGO. In this paper, the nonlinear optical (NLO) properties of the CuS/rGO composites with different graphene content were investigated by a Z-scan technique. The results show that while reverse saturable absorption (RSA) is prominent in pristine CuS, saturable absorption (SA) is dominant in pristine rGO. A transition from RSA to SA is seen when the graphene content is increased in the CuS/rGO nanocomposite. The measurements results show that the improvement of nonlinearity is related to the synergistic effect between two or more materials. The research content in this paper can establishes a foundation for further study of CuS/rGO nanocomposites application in NLO devices.

1 Introduction

Graphene and its derivatives have been widely concerned in basic research and industrial applications due to their two-dimensional atomic thin nanostructures and electrical conductivity. Recent studies shown that physical or chemical treatment for graphene by functional modification can improve the NLO properties [1,2]. Some studies also shown graphene hybrid nanostructure materials composed of semiconductor materials, such as graphene (G)/ZnO, G/MoS2, graphene oxide (GO)/ZnS, rGO/Bi2S3, rGO/CdSe, and rGO/α-MnS [3–8], have better NLO performance. As a self-doped P-type semiconductor material, CuS has a bandwidth between 1.2 eV and 2.0 eV. It has a promising future in the fields of solar cells, photoelectric switches and gas sensors. However, CuS is easy to agglomerate, which seriously affects its application. Therefore, graphene and its derivatives are considered as the ideal substrates for composite materials due to their unique layered structures, which maybe make up for the deficiency of CuS. But most studies of CuS are on its catalytic properties and pyroelectric effect [9,10].

In this paper, CuS/rGO nanocomposites were synthesized. Moreover, structural and morphological characterizations of CuS/rGO composite were performed and their third-order NLO properties were studied. The test results show that CuS/rGO nanocomposites have unique NLO properties, which is different from GO/ZnO, CdSe and so on. We studied the NLO properties of the compounds in depth, and found the co-existence of reverse saturable absorption (RSA) and saturable absorption (SA). In the end, a NLO absorption transition occurs in CuS/rGO nanocomposites. It is very important and useful to regulate the NLO properties by tuning amount of graphene. The wavelength in the visible range is selected because graphene exhibits better optical nonlinearity in this range than in the near-infrared regime [11], mid-infrared regime [12] and THz regime [13]. The rough surface caused by the defect and larger particle size of the samples will lead to certain scattering phenomenon. We choose picosecond pulse and lower energy for overcoming thermal scattering and surface scattering in all samples. Nonlinear material CS2 was used to calibrate Z-scan, the absorption and scattering effects of the samples can be ignored in the measured data. This study mainly explores the nonlinear absorption and refraction related to light intensity and reveals its intrinsic optical nonlinearity [14,15]. We focus on the evolution of third-order NLO properties in composites, as well as the relationship between optical nonlinearity and the amount of graphene.

2 Experimental procedures

2.1 Sample preparation

GO was prepared by the improved Hummers method [16]. The specific preparation method of CuS/rGO nanocomposites is as follows.

First, 9 mg of GO was added into 40 ml of ethylene glycol. Then, 169 mg of CuCl2·2H2O and 364 mg of C16H10(CH3)3NBr were added into the solution after the GO dispersed evenly. The solution was fully dissolved with a magnetic stirrer.

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Second, 76 mg of CH₄N₂S was added into 40 ml of ethylene glycol and dispersed evenly with a magnetic stirrer. The two solutions were mixed and stirred for 30 min. Then, the mixture was moved to a reactor and reacted at 180°C for 12 h. The reactant was centrifuged from the mixture and rinsed with anhydrous ethanol and deionized water.

Finally, CuS/rGO was obtained after drying at room temperature. In preparation of the first kind of solution, the simple substance of the CuS microspheres can be obtained without adding GO.

2.2 Instruments and characterization

The X-ray diffraction (XRD) of samples were measured by XRD (Bruker D8 Advance, Bruker Inc.). Transmission electron micrograph (TEM) images were measured by JEOL JEM-2100, JEOL Ltd. Inc. Scanning electron microscope (SEM) images were measured by Carl Zeiss Inc. FTIR spectra were obtained on Bruker Optics Vertex 70 (Bruker Inc.). Ultraviolet Visible absorption spectra were acquired on UV-Vis, Cary 5000, Agilent Inc. X-ray Photoelectron Spectroscopy (XPS) were obtained on ESCALAB 250Xi, Thermo Fisher Scientific Inc. The NLO properties were investigated by means of the Z-scan detecting system with a Nd:YAG mode-locked pulse laser (EKSPLA, PL2251) at 532 nm with 30 ps (FWHM) pulses and the repetition of 10 Hz. The beam waist radius used at focal point was 10.6 μm, with a single lens of f/1.4250 mm, the diameter of the laser beam is about 8 mm and the aperture linear transmittance was 36%.

3 Results and discussion

XRD patterns, TEM image and SEM images of all samples are shown in Figure 1. The peaks of characteristic diffraction at 2θ = 27.686°, 29.288°, 31.793°, 32.825°, 47.945°, 52.730°, 59.344°, corresponding to (101), (102), (103), (006), (110), (108), (116) planes of CuS (Fig. 1A).

The spectrum analysis shows that the CuS prepared in this paper has a hexagonal phase structure (PDF 99-0037). Compared with CuS, the diffraction curve of CuS/rGO has an additional diffraction peak package. This peak corresponds to the characteristic of rGO, which proves the CuS/rGO is successfully prepared. The rGO exists in a layered structure, the surface is smooth and clean without any attached particle. Additionally, there are many CuS

![XRD patterns of CuS and CuS/rGO (A), TEM (B), SEM (C) images of CuS, SEM images of the CuS/rGO (D).](image)
particles attached to the layered structure of reduced graphene oxide (Figs. 1B and 1C). Therefore, the CuS microparticles can be uniformly attached to the rGO through the compound reaction. In Figure 1D, the SEM image shows that the combination of CuS and rGO can effectively reduce the stacking of CuS elements. Therefore, we observe that the physical structure of the composite has also been greatly improved compared to the structure of the elemental material. The influence of CuS on the NLO properties of composites is highlighted due to the reduction of agglomeration in CuS.

The characteristic peaks of GO at 3394 cm\(^{-1}\), 1734 cm\(^{-1}\), 1624 cm\(^{-1}\), 1400 cm\(^{-1}\), 1223 cm\(^{-1}\), and 1054 cm\(^{-1}\) correspond to the telescopic vibration peaks of chemical bonds such as O\(\equiv\)H, C=O, C\(\backsimeq\)O\(\equiv\)H, C\(\equiv\)H, C\(\equiv\)O (Fig. 2A). The vibration peaks of CuS are relatively few. The characteristic peak at 619 cm\(^{-1}\) are generated by stretching vibration of Cu and S. The characteristic peaks at other positions are due to the adsorption of CuS during the preparation process. The characteristic peaks of oxygen-containing functional groups of CuS/rGO have disappeared, which also shows that GO is reduced. In Figure 2B, a redshift phenomenon appears in absorption peak of CuS/rGO compared with the absorption peak of CuS. It shows that the band gap of CuS/rGO is narrower than CuS, because CuS is chemically combines with some special sites on the rGO. The absorption peak of CuS/rGO is higher than CuS. Because, the absorption peak of CuS/rGO is not only derived from the electrons on the surface of the CuS crystal, but also from the electronic migration. Due to the fact that rGO serves as both a carrier and a photoelectron acceptor in the composite. The rGO was used as the substrate material can transfer the electrons generated on the surface of CuS, thus greatly increasing the rate of carrier generation. The energy band gap spectra of CuS and CuS/rGO is obtained from the Kubelka-Munk formula based on the UV−vis absorption Fig. 2.

Fourier transform infrared spectrum (A), UV-vis absorption spectra of CuS and CuS/rGO (B), energy band gap spectra of CuS (C) and CuS/rGO (D).
The energy band gap of CuS/rGO is 0.98 eV, which is smaller than the 1.55 eV of CuS. This proves that the semiconductor composite can adjust the band gap, which provides the possibility of adjusting the band gap of the material for practical applications in the future.

**Figure 3A** illustrates the “open-aperture” (OA) Z-scan curves of rGO, CuS and CuS/rGO composites samples. **Figure 3B** shows the typical “close-aperture” (CA)/OA Z-scan curves of rGO, CuS and CuS/rGO nanocomposites samples with a concentration of $0.2 \times 10^{-3}$ g/ml at the input single-pulse intensity of 9.4 GW/cm$^2$. The CuS/rGO nanocomposites samples were designed as S1, S2 and S3 with the different content of graphene: 5%, 10%, 20%, respectively. The normalized transmission curve of CuS shows a valley at the focus, suggesting that RSA dominates the NLO behavior in pristine CuS. As for CuS/rGO nanocomposites, as the graphene content increases through S1 to S3, the depth of the valley decreases. Two small symmetric peaks appear for S3 showing the presence of SA, and for pristine rGO only a single peak is seen, signifying the dominance of SA. This transition from the RSA to SA behavior is attributed to the synergistic effect related to the structure and energy gap of the composites [17,18]. The net absorption coefficient in the presence of SA and RSA is given by:

$$\alpha(I) = \alpha_0/[1 + (I/I_s)] + \beta_{\text{eff}}I$$  \hspace{1cm} (1)

where $\alpha_0$ is the linear absorption coefficient, $I_s$ is the saturation intensity related to the SA response, and $\beta$ is the RSA coefficient. The OA Z-scan curves are well fitted by this formula, confirming NLO process is RSA and SA in samples.

The typical “closed-aperture” Z-scan traces divided by OA Z-scan (CA/OA) for all samples are depicted in **Figure 3B**. The CA/OA Z-scan results in a typical valley-peak Z-scan trace, which indicates a self-focusing medium.

The nonlinear refractive index $n_2$ of the sample can be obtained from peak–valley difference $\Delta T_{p-V}$ of transmittance curve:

$$n_2 = \frac{2.941 \times 10^6 \lambda \omega_0 n_0\Delta T_{p-V}}{E L_{\text{eff}}(1 - S)^{0.25}}$$ \hspace{1cm} (2)

where $S$ is linear transmittance, $\omega_0$ is beam waist radius, and $n_0$ is linear refractive index, which $\tau$ is pulse width.

The real and imaginary part of the third-order nonlinear susceptibility is given by:

$$\text{Re} \chi^{(3)} = \frac{cn_0^2\nu}{120\pi^2}$$  \hspace{1cm} (3)

$$\text{Im} \chi^{(3)} = \frac{\lambda cn_0^2\beta}{480\pi^2}.$$ \hspace{1cm} (4)

The third-order nonlinear susceptibility of sample can be expressed as:

$$\chi^{(3)} = \left[ (\text{Re} \chi^{(3)})^2 + (\text{Im} \chi^{(3)})^2 \right]^{1/2}.$$ \hspace{1cm} (5)

The third-order nonlinear parameters of samples are calculated and shown in Table 1.

The third-order nonlinear susceptibility of CuS is close to the imaginary part of the third-order susceptibility, the nonlinear absorption of CuS dominates the third-order NLO properties. In the case of 532 nm (2.33 eV) wavelength as the excitation wave, free carrier absorption and excited state absorption are the main mechanisms affecting the non-linear absorption of CuS microspheres. The RSA result from the excited state absorption (ESA) process. ESA is the dominant factor with sequential absorption of photons, whereas with simultaneous absorption RSA dominates the NLO absorption behavior. It is also observed that with the
increase of amount of rGO, the valley gets deeper and the shoulder peak becomes lower, which indicates that the NLO absorption process would experience a final transition in composites, RSA gradually dominated the NLO absorption behavior of the composites. The reason for this mechanism is related to the structure and energy gap of graphene. When the shoulder peak is negligible compared to the valley, the overall performance of NLO absorption in composites can be regarded as RSA effectively. The values of $\text{Re} \chi^{(3)}$, $\text{Im} \chi^{(3)}$ and $\chi^{(3)}$ are tiny decreased with a further increase in graphene. Therefore, the nonlinear absorption transform of composite may be due to the combined effect of multiple mechanisms. The measurements results show that the improvement of nonlinearity is related to the synergistic effect between two or more materials [19,20]. The composite process of materials reduces the agglomeration of CuS and the surface area of rGO increases. It can be deduced that there is a correlation between the synergy effect and the electron transfer in composites. Moreover, the direction and rate of electron transfer will have an effect on the synergy effect. Therefore, the $\text{Im} \chi^{(3)}$ trend of composites provides the excellent controllable properties of NLO for potential optical applications by tuning the amount of graphene.

4 Conclusions

In summary, high quality CuS microspheres and CuS/rGO nanocomposites were synthesized by the solvothermal method. The different measurement results show that the morphology of CuS is flower-like microspheres with uniform particle size and it can be uniformly attached to the layered structure of rGO. The origin and relationship between the all samples and their NLO properties under a single-pulse laser are investigated. Results show that RSA is prominent in CuS while SA dominates rGO. The NLO susceptibility was found to decrease to $3.652 \times 10^{-13} \text{esu}$ with a further increase of graphene, which results from the connection of small sp² clusters due to the increase in rGO. Such nonlinearity can be attributed to the local field effect arising from surface oxygen-containing groups and the transfer from the sp³ matrix to sp² domains and sp² clusters [21,22]. Furthermore, CuS/rGO composites show SA when the sample is away from the beam focus (moderate intensities), and RSA close to the focal position (high intensities). So, it is a useful way to tune the optical nonlinearity of CuS/rGO nanoparticles by controlling the amount of graphene. Understanding the effect of the amount of graphene on the unique NLO properties of CuS/rGO nanocomposites is very helpful for potential applications in areas of special NLO applications.

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Author contribution statement

Yu Hao and Lan Yang performed the experiments and wrote the manuscript. Jinze Li and Ruonan Xing did partial data collection and analysis. Yu Hao and Yuzong Gu discussed and revised the manuscript. Yuzong Gu directed and funded this work.

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