Effect of Convection on the Distortion of Spatial Self-Phase Modulation Pattern in Graphene Dispersions

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Abstract. Effect of convection on the distortion of spatial self-phase modulation (SSPM) pattern in graphene dispersions has been investigated. When a Gaussian laser beam is transmitted through graphene dispersions, the interference pattern in the far-field first forms a series of circular rings, but the upper half of the rings collapses rapidly after a period of time, forming a stable distorted pattern. Experimental results show that thermal convection effect plays a dominant role for the distortion of the SSPM pattern. In the absence of convection in the beam cross section, the interference rings are circularly symmetric rings. In the presence of convection in the beam cross section, the interference rings exhibit circularly asymmetric rings. Theoretical analyses have then been given for the reason of the interference rings distortion. Convection can effectively change the spatial symmetry distribution of polarized graphene sheets and non-linear refractive index in the beam cross-section, thus making the interference rings distortion based on the spatial self phase modulation. It is concluded that the distortion of the interference pattern is originated from the thermal convections induced by laser heating.

1. Introduction

Graphene has attracted great attention due to its peculiar electronic structures and two-dimensional (2D) crystal properties since it first became experimentally accessible in 2004 [1], [2], [3], [4], [5]. It exhibits not only remarkable mechanical and thermal properties [6], but also unique electronic and photonic properties [3]. Owing to the strong inter-band $\pi$ - $\pi^*$ electron transitions, graphene has a large effective third-order nonlinear susceptibility $\chi^{(3)}$, which has been confirmed by Z-scan and four-wave mixing experiments [2]. The nonlinear optical effects of two-dimensional materials occur due to their light intensity dependent nonlinear refraction index. Spatial self-phase modulation (SSPM) is a third-order nonlinear optical effect. Light waves at different radial positions will interfere with each other and cause spatial self-phase modulation (SSPM) because the phase shifts in the radial direction are different for the nonuniform intensity distributions [3], [4].

When a Gaussian laser beam passes through a nonlinear optical medium, the refractive index is a function of the intensity distribution. In terms of the third order nonlinearity, the refractive index can be expressed as $n = n_0 + n_2 I$, where $n_0$ and $n_2$ are the linear and nonlinear refractive indexes, respectively, I is the laser intensity. Zhao J. M’s group reported SSPM of the graphene dispersion, and proposed a wind-chime model to explain the emergence of the electron coherence from the nonlocal graphene sheets [3], [4]. The wind-chime model claims that only those polarized and reoriented graphene sheets in the beam cross section make contributions to the SSPM image. However, the SSPM patterns are not stable, being distorted from symmetric patterns to asymmetric ones with the upper part squeezed in a short time. The distortion phenomena of the SSPM pattern have been reported in lots of nonlinear materials [7], [8], [9]. Ji et al. [7] reported the gravitation dependent of the SSPM in carbon nanotube suspensions and estimated the change in the nonlinear refraction due to gravity.
Wang G. Z. et al. [8] found it is the change of the nonlinear refractive index $n_2$, rather than $n_0$, dominating the distortion of the SSPM pattern in graphene dispersions. They show that the distortion originates mainly from the non-axis-symmetrical thermal convections of the graphene nanosheets induced by laser heating. However, it is still not very clear how the thermal convection affects the dynamic process of the SSPM pattern distortion.

In this work, the changes in the SSPM patterns of the samples with and without convection against time and laser intensity have been investigated. It is found that the distortion of the SSPM pattern actually originates from the convection in the cross section of the laser beam in the graphene dispersion. This study will provide a great help to understand the nonlinear optical properties of graphene and to explore its application in optical and optoelectronic fields.

2. Experiment

The graphene dispersion with a concentration of 0.15 mg/ml in N-methyl-2-pyrrolidone (NMP) was prepared by ultrasonic method. Graphene powder and NMP solvent were commercially available. Quartz cuvettes with different optical path lengths (thickness) were used to keep the graphene dispersions.

A graphene dispersed gel was prepared to study the SSPM patterns of the colloid state sample against time and laser intensity. Agar was used as a coagulant to prepare the gel. Agar is a polymer, its structure is full of micro-pores, and the size of the pores can be controlled by the gel concentration. We prepared an agar solution with a concentration of 0.05 mg/ml at 100 °C, dropped the agar solution (3-5 drops) into the graphene dispersion at temperature above 50 °C, sealed the cuvette containing the mixture of the graphene dispersion (0.15 mg/ml) and agar solution with a cap, then upside down the cuvette for several times. The agar and graphene dispersion were uniformly mixed. The newly prepared graphene-agar mixture was still in a liquid state. It takes about 1 hour for the mixture to solidify into gel at room temperature. The solidification time depends on the amount of the agar added.

Figure 1 shows the schematic diagram of setup to study the SSPM pattern of the graphene samples.

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Figure 1. Schematic diagram of setup to study the SSPM pattern of the graphene samples

3. Results and Discussion

First, the time dependence of the interference phenomenon of graphene dispersions was studied. Figure 2 shows a temporal evolution of the SSPM patterns with a 100 mW laser. It can be seen that the dynamic process contains two stages. At the initial period, the pattern quickly expanded from a bright spot into symmetrical concentric rings until it reached its maximum at about 0.5 s (Figures 2a-c). Then,
the upper part of the rings quickly collapsed, the pattern changed from a circular symmetry to an asymmetric one with a vertical distortion (Figures 2d and e). The distorted pattern maintained stable after about 1 s (Figure 2e).

Figure 2. The temporal evolution of the SSPM pattern with a 100 mW laser passing through the graphene dispersion horizontally

Figure 3. Changes in the SSPM patterns of the graphene dispersions with different incident laser powers (mW)

Then the intensity dependence of the interference effect was investigated. Figure 3 shows a typical change in the interference patterns with different laser powers incident on the graphene dispersions. It can be seen that the number of rings and the vertical asymmetry of the interference rings patterns increase monotonously with the incident laser intensity increasing from 8 mW to 100 mW.

A wind-chime model is proposed by Zhao J. M’s group to explain the emergence of electron coherence from the nonlocal graphene sheets [4]. Whenever the laser light is present, the electrons and holes in graphene would move in opposite directions, being antiparallel and parallel to the electric field, respectively. That results in a polarized graphene sheet. Initially there might be an angle between this polarization and electric field, which is associated with the interaction energy. Reorientation of the graphene sheets aligns them while minimizing the interaction energy. Alignment also comes from the interaction between the graphene sheets, which is due to the giant intrinsic charge mobility caused by the dis-localization of the π-electrons. The essential point is that the carriers within different sheets are perfectly in phase, namely being coherent in the light field, thus each sheet contributes constructively to the SSPM ring patterns. Each sheet contains an axis parallel to the external field, as if each sheet is “hung” by a vertical “thread.” This image mimics that of a wind chime, so called it as wind-chime model. The wind-chime model reveals that the origin of the SSPM ring pattern is the reorientation and alignment of the graphene sheets induced by the electromagnetic field. Reorientation time of the graphene sheets in the laser beam is in the order of about $10^{-1}$ s.

Since graphene possesses high thermal conductivity and optical absorption coefficient [5], laser energy is absorbed by the graphene sheets and then transferred to the liquid, which lead to an increase in the local temperature in the dispersion. Then conduction and convection take place and produce a spatial temperature distribution in the dispersion which can differ from the applied Gaussian laser intensity. When the sample is continuously irradiated by a high-power cw laser beam, the graphene sheets can be effectively heated and the temperature gradient along the vertical direction arises, resulting in a strong thermal convection in the beam cross section in the dispersion.

Figure 4 show that the absorption power of the graphene dispersions increases nearly linearly with the increase of the input laser power. This means the absorption rate of the graphene dispersions for the same sample is a constant, almost no dependence on the incident laser intensity. The absorption rates of two samples with concentrations of 0.5 mg/ml and 0.15 mg/ml are 75% and 45%, respectively. The absorption rate of the sample with higher concentration is greater than that of lower concentration. The greater the concentration, the more effective graphene layers in the laser path, and the more energy to be absorbed.

Figure 5 shows the maximum temperature difference $\Delta T_{\text{max}}$ in the graphene dispersions versus the incident laser power. The temperature of the dispersion is a maximum at the center line and decreases radially outward in the beam cross section. It can be seen that the maximum temperature difference between the center of the beam and the surrounding liquid gradually increases as the incident laser
power increases, and it reaches about 25 °C at a laser power of 150 mW. Convection velocity \( v_y \) is equal to its maximum value at the beam center, given by [9]

\[ v_y(0) = \frac{\alpha_T \Delta T_{\text{max}} \pi a^2}{16 \mu} \]  

(1)

where \( g \) is the gravity acceleration, \( \alpha_T \) the thermal expansion, \( \Delta T_{\text{max}} \) is the maximum temperature difference in the liquid, \( a \) is the radius of the laser beam and \( \mu \) the viscosity. From equation (1), one can see that the convection velocity in the vertical direction is proportional to the maximum temperature difference in the liquid. Then the spatial distribution of the change in refractive index which is given by:

\[ n(x, y, t) = n_0 + \frac{dn}{dT} \Delta T(x, y, t) \]  

(2)

where \( \frac{dn}{dT} \) is the thermo-optic coefficient of the medium.

If the thermal refractive index change is practically independent of the propagation coordinate (thin sample approximation), the phase shift can be determined by [10]

\[ \Delta \psi(x, y, t) = \frac{2\pi}{\lambda} l \left[ n(x, y, t) - n(0, 0, t) \right] \]  

(3)

where \( \lambda \) is the laser wavelength, \( l \) is the sample length. Equation (3) indicates that the phase shift changes with time and convection velocity in the vertical direction after the laser propagating through the nonlinear medium.

Above results indicate that the convection in the beam cross-section produces a spatial temperature distribution in the liquid which can differ significantly from the applied Gaussian laser intensity. The asymmetric change in temperature distribution will cause the spatial asymmetric distribution of the refractive index, further lead to the asymmetric distribution of the phase shift, resulting the distortion of the SSPM pattern. Therefore, the distortion of the SSPM pattern can be induced only when the convection occurs in the beam cross-section.

Since the convection makes the interference pattern distorted, if there is no convection in the graphene dispersion, the interference pattern should not be distorted. We know that thermal effect in liquid medium in contrast to that in solid or gel material can be accompanied by the appearance of convection currents due to local laser heating of the liquid. When a laser beam propagates in a solid or
gel medium, absorption of radiation and thermal conduction will be the only significant transport mechanism, no convection present in the solid or gel medium.

Figures 6 and 7 shows changes in the SSPM patterns of the graphene dispersed gel samples with a horizontally incident laser at different time and powers, respectively. It was found that the SSPM patterns of the gel sample kept circular symmetry and no distortion occurred with either time or the input laser power. The outermost diameter of the SSPM pattern gradually increased with the increase of the time and the laser power, too. The SSPM patterns of the gel sample took about 3 seconds to reach the maximum (Figure 6d), while this process in liquid sample is about 0.5 s. This probably due to the relatively large viscosity of the gel, and the greater resistance to re-orientation of the graphene sheets in the gel. On one hand, the graphene sheets in the sample were polarized and re-oriented by the laser electric field. On the other hand, the re-orientation of the graphene sheets was resisted by the surrounding liquid or gel during their rotation process. The graphene sheets in the agar meshes of the gel can't form convection, but they can be slightly rotated by the electric field of the laser in their own position. Thus, the reorientation process takes longer time than that in liquid sample. This result proves not only that the SSPM pattern comes from electron coherence from the nonlocal polarized and reoriented graphene sheets, which is in good agreement with the wind chime model [3], [4], but also the convection is the dominant factor for the SSPM pattern distortion of the graphene dispersion.

In the absence of convection in the beam cross section for the gel sample, because of the Gaussian distribution of the laser intensity, the temperature and irradiance fields in the sample are radially symmetric about the axis of the beam, the temperature dependent refractive index profile of the sample is circular and symmetrical, too. Thus the SSPM pattern is stable and circularly symmetric, as shown in Figures 6 and 7.

In the presence of an upward convection in the beam cross section, the rising heated graphene sheets are replaced by cool parts, causing changes in the distribution of the temperature and polarized graphene sheets. The graphene sheets in the bottom portion of the beam are those flowing into the beam from the external laser beam by convection process. They are cool and non-polarized. The non-polarized graphene sheets are in random orientation, and have no contribution to the SSPM. After a period of time, they will be polarized and reoriented by the electronic field when they approach the area near the beam center. The upper portion of the beam is not affected by the convection currents as severely as the lower portion, most of graphene sheets in the upper half of the beam are polarized and aligned along the external electric field because they have been in the beam for enough time to be polarized and reoriented (the polarized time is about 0.1 s). The distribution of the polarized and aligned graphene sheets becomes asymmetric due to the influence of thermal convection in the beam section, resulting in asymmetrical distribution of the non-linear refractive index, further leading to the distortion of the SSPM patterns.

In a word, the convection in the beam cross section can effectively change the spatial symmetry distribution of the polarized graphene sheets and the non-linear refractive index of the graphene dispersion, which ultimately leads to the distortion of the SSPM pattern.
The distortion extent and region of the SSPM patterns in the liquid graphene dispersion depend on the velocity and direction of convection in the graphene dispersions. These results will be discussed in detail in another article.

4. Conclusion
In this paper, it was found that the distortion of the SSPM patterns of the graphene dispersion is originated from the convection in the beam cross section. In the absence of the convection in the beam cross section, the SSPM patterns exhibit circular symmetry, no distortion appears with time and the incident laser power. However, the distorted SSPM patterns are obtained when the convection presents in the beam cross section. The convection in the beam cross section produces a spatial temperature distribution in the dispersion which can differ significantly from the applied Gaussian laser intensity. The asymmetric change in temperature distribution will cause the spatial asymmetric distribution of the polarized graphene sheets and the non-linear refractive index, further lead to the asymmetric distribution of the phase shift, resulting in the distortion of the SSPM pattern.

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6. References
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