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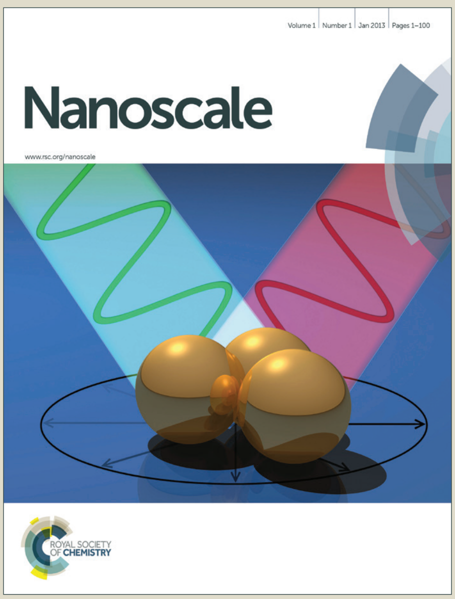

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Article

Frozen Matrix Hybrid Optical Nonlinear System Enhanced by Particle Lens

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In this work, a Graphene Oxide (GO) nano-sheets and SiO_2 micro-beads hybrid system based on frozen matrix was investigated for its enhanced optical nonlinear performance. Frozen matrix is a novel approach that hosts the optical nonlinear nano-particles, which combines the strengths from both liquid and solid phase systems for high performance photonic applications. The SiO_2 micro-beads were used to induce local field enhancement effect that improved the optical nonlinearity of GO nano-sheets. The nonlinear performance of the hybrid system is several orders larger than the existing GO nano-sheets liquid dispersion. In addition, this frozen matrix and local field enhancement effect are two facile and versatile methods that can be applied to many types of nano-particle dispersions.

Introduction

The progress in the optical technology has paved the way for many revolutionary technologies, such as all-optical switching, photonic computational devices, laser weapons and super-resolution optical imaging techniques, which significantly change many aspects of our daily life.[1-5] To satisfy the requirements of these advanced applications, there is a growing need for optical nonlinear materials with high performance and reliability.

For this purpose, optical nonlinear nano-materials dispersed inside the liquid and solid state matrix have been intensively studied,[6-10] which provide various platforms to host nano-materials of metals, semiconductors and organics. However, the primary limitation of the liquid matrix is its fluid nature, which blocks its way from research to real applications. In addition, the optical nonlinear nano-materials in liquid may precipitate after a long resting time or exceed a certain amount, which limits the life time of the applications and the concentration of the optical nonlinear nano-materials. Solid state matrix seems to be a good supplementary solution. However, the compatibility of the solid state matrix is not as good as the liquid one and the dispersion process for nonlinear nano-materials is often not as simple.

In this paper, a hybrid system is proposed to overcome the limitations by the utilization of frozen matrix with a low melting point. It preserves the advantages of the liquid system but also fulfils the requirement of solid state devices. Furthermore, this hybrid system has many unique features favourable for optical nonlinear devices. Comparing to the conventional solid state matrix commonly used for optical nonlinear systems, this low melting point frozen matrix is widely compatible to many types of nonlinear materials including metals, semiconductors and organics, especially for organic candidates such as Graphene Oxide (GO) that is vulnerable to high temperature.[11,12] Another superior feature of the frozen matrix is to prevent the aggregation of the dispersed particles. Previous researches report that the high concentration of optical nonlinear nano-materials can enhance the optical nonlinear performance.[13] However, an excessive concentration causes the system to be unstable and the materials aggregate after a period of time. In the frozen matrix, a stable system with high concentration can be fabricated. Furthermore, the frozen matrix also presents the capability to protect the nonlinear nano-material from excessive input laser energy. At a high laser fluence, the frozen matrix can melt and absorb the excess heat, protecting the hybrid system against possible damage. Then, the hybrid system recovers to its original state when the frozen matrix releases the heat to the surrounding and re-solidifies. This phase transition provides a self-healing capability and is helpful for the applications operating at a high laser power. To our best knowledge, it is the first time that the phase transition of the host matrix is exploited to improve the performance of the optical nonlinear nano-material dispersions.

Specifically, a frozen matrix hybrid system based on Graphene Oxide nano-sheets and particle lens (Fig. 1(a)) was fabricated

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and studied in this paper. This hybrid system makes good use of natural materials, such as water and SiO_2, to greatly enhance the GO optical nonlinearity and reliability. The overall nonlinear performance achieves a record that is several orders higher than the water and glass dispersions including Ag, Au, Cu and GO (a summary can be found in the supplementary materials), which is contributed from the combination of frozen matrix and particle lens.

GO is a promising nonlinear nano-material due to its outstanding optical properties originated from the hybridization of the sp^{2-} and sp^{3-} carbon atoms.[14-17] One of the most preeminent features of GO is that its physical and chemical properties can be manipulated via the reduction reactions to change the type and density of oxygen containing groups, which makes its optical nonlinearity tunable for different devices.[18-20] Meanwhile, the graphene based material is robust and chemically stable, which is crucial for the massive scale production.[17-20]

SiO_2 micro-beads play another important role in the system. Many optical nonlinear materials have greater nonlinearity at a higher light intensity.[6, 18, 20] Serving as the particle lens, SiO_2 micro-bead induces the focusing effect which can greatly enhance the local light intensity. As a result, SiO_2 micro-bead can improve the optical nonlinearity of the system. In our work, SiO_2 micro-bead can greatly enhance the local light intensity by more than 25 times. It is worth mentioning that this local field enhancement is not only limited to the GO. SiO_2 micro-beads are stable and highly comparable with other optical nonlinear nano-materials. Therefore, our new approach to enhance optical nonlinearity is universal, which has a big potential to be applied to other systems. Meanwhile, this method is simple and straightforward. It does not require any sophisticated processing approach or further treatment of the optical nonlinear materials. It only requires the dispersion of SiO_2 micro-beads with the nonlinear material and then an improved optical nonlinearity can be achieved.

This frozen matrix hybrid system can well address the challenges in high power laser devices, which is the key for many applications ranging from industry to military defence.[2, 21-24] Optical nonlinearity and resistance against optical damage are directly related to the functionality and reliability of these devices. Based on the frozen matrix and particle lens, a solid system with high resistance against optical damage and optical nonlinearity can be achieved, which is the key for components in the high precision laser processing techniques and laser weapon systems. With the improved material properties, these devices will have a higher stability, longer life time and superior functionality.

Results and Discussion

Material properties and sample fabrication

The modified Hummers method was adapted to synthesize the GO nano-sheets in de-ionized water (DI water).[25] The details can be found in the supplementary materials. The concentration of the GO was calculated to be 5 g/L. The GO product was characterized using a Raman spectroscope. As shown in Fig. 1(b), the curve contains the D-band peak (1339 cm^{-1}) and G-band peak (1585 cm^{-1}), corresponding to the oxygen containing groups in the GO products, which is consistent with the results published previously.[19] SiO_2 micro-bead dispersion inside DI water was purchased from Thermo Scientific. Fig. 1(c) shows the Scanning Electron Microscope (SEM) image of the SiO_2 micro-beads on a silicon substrate. Most of the SiO_2 micro-beads are in well-round shape and the diameter was measured to be 1000 nm.
The fabrication of the frozen matrix is shown in Fig. 1(d). A cell made of optical glass was used to make the frozen matrix. The cell is transparent at the wavelength from 400 to 1200 nm. The optical path for the cell is 1 mm. Liquid was injected into the cell carefully to avoid forming air bubbles. Then the cell was transferred into an enclosed cold environment cooled by the dry ice. Due to the small volume of the liquid, the freezing process completed in less than half a minute. Two types of samples were prepared, namely the GO sample and GO + SiO_2 micro-beads composite. The GO sample has the concentration of 4.54 g/L. For the GO + SiO_2 micro-bead composite, the GO concentration is the same and the number of micro-beads per unit weight (g^{-1}) is 8.2×10^9.

Finite-difference time-domain (FDTD) simulation

FDTD simulation was carried out (software: Lumerical) to study the focusing effect of the SiO_2 micro-beads at the wavelength of 800 nm. The results are shown in Fig. 2(a). A SiO_2 sphere (1000 nm diameter) was placed inside the frozen matrix with the incident light propagating along the –Z direction from the top plane. The refractive indices of silica and ice were taken into consideration in our simulation. As can be seen in the figure, the incident light is focused by the SiO_2 micro-bead due to the light refraction at the SiO_2-ice interface. The SiO_2 micro-bead serves as a particle lens, which causes the incident light to be focused in the region beneath the SiO_2 micro-bead (denoted in the red color in Fig. 2a). Consequently, the light intensity in this region is increased greatly. Based on the simulation results, it can be concluded that this localized focusing effect induced by the SiO_2 micro-bead enhances the intensity of the incident light intensity by more than 25 times at the central region of the focusing area. The focusing area was measured to be around 1.01 μm^3, which is around 1.9 times of the volume of the bead. The incident light intensity is closely related to the optical nonlinear performance of the GO materials and this local field enhancement can increase the optical nonlinear performance of the GO.[18]
FDTD simulations were also conducted to investigate the SiO_2 micro-bead of other diameters (500 nm and 2 μm). The

detailed results can be found in the supplementary materials. For the 500 nm SiO_2 micro-bead, its diameter is smaller than the wavelength of the incident light. Due to the diffraction of the light, the particle lens of this dimension has a diminished focusing effect. The local field enhancement is found to be less than 25% comparing to the 1000 nm SiO_2 micro-bead. On the other hand, the results for 2000 nm SiO_2 micro-bead demonstrated that the local light field in the central area was enhanced by more than 25 times. However, the micro-beads of the large dimension precipitate very fast inside water. It is very challenging to fabricate a frozen matrix with the 2 µm SiO_2 micro-beads well dispersed.

Nonlinear Absorption Characterization

The nonlinear absorption performance of the samples was characterized at the wavelength of 800 nm using a femtosecond pulsed laser (Spectra-Physics, 100 fs pulse duration, 1 kHz repetition rate). The output fluence F_{out} versus the input fluence F_{in} for different samples were plotted in Fig. 2(b). The input laser fluence ranged from 2.3 to 5.5 µJ/cm^2. It was found that the SiO_2 micro-beads and the matrix did not demonstrate any nonlinear response in this laser fluence range (data can be found in appendix). The linear transmittances of the GO and GO + SiO_2 micro-beads composite were measured to be around 10.1%, which is plotted as the black solid line for a reference. For the GO sample, the nonlinear transmittance, which is calculated by the F_{out}/F_{in} ratio, greatly exceeds the linear transmission. It is further noticed that the slope of dF_{out}/dF_{in} increases as the incident laser fluence increases from 2.5 to 4.7 µJ/cm^2, which shows that the GO sample has enhanced optical nonlinearity at a high laser fluence. The transmittance reaches its maximum value at ~4.7 µJ/cm^2, which indicates that the absorption of GO is saturated. This nonlinear absorption curve demonstrates typical features of a saturable absorber and its trend agrees with the previous research on the physics of the saturable absorption of graphene material.[13] The moderation depth, which is defined to be the change between the saturated value and the linear transmittance, is calculated to be more than 180%. This saturable absorption of the GO is attributed to the ground state bleaching of the sp^2 domain. Specifically, the band gap of the sp^2 domain is only ~0.5 eV. Consequently, there is a high opportunity for electrons to be excited by photons, which results in the depletion of the valence band and the filling of the conduction bands.[10, 26] When the conduction band is saturated, the material does not further absorb photons. Thus the transmittance of the material increases. The GO + SiO_2 micro-beads composite shows the same saturable absorption features as the GO sample. Furthermore, the nonlinear transmittance (F_{out}/F_{in}) of the GO + SiO_2 micro-beads composite is higher from 2.3 to 5.5 µJ/cm^2. It suggests that in this range of laser fluence, the nonlinear performance of the GO + SiO_2 micro-beads composite is much better than the GO sample.

It is interesting to notice that when the incident laser fluence exceeds 4.2 µJ/cm^2, the transmittance of the GO sample turns to be similar to the transmittance of the GO + SiO_2 micro-beads composite. To study this phenomenon, dynamic thermal fusion theory was applied to study the physics behind.[27] The energy required to melt the frozen matrix was calculated. It was found that the incident laser fluence was sufficient high to rise the temperature of the matrix to its melting point. However, in our experiments, the sample was surrounded by dry ice to maintain a low temperature environment. Part of the incident laser energy was used to balance the cooling effect. The matrix stayed frozen when the incident laser fluence is low. When the incident laser energy exceeded the maximum cooling capacity, the matrix melted and behaved differently from its solid state. Based on this dynamics, the nonlinear absorption curve can be divided into three cases according to the incident laser fluence, which are illustrated by Fig. 3.

In Case I, when the heat generated is less than the cooling capacity, the matrix remains frozen. In this situation, the matrix is a homogenous dispersion of the particles. The optical effects include light scattering, absorption and transmission. The scattering effect is mainly attributed to two types of scattering centers, which are the defects in the frozen matrix and SiO_2 micro-beads. Comparing to the wavelength of 800 nm, the Graphene Oxide sheets are too small as the key scattering center. Considering the high transparency of the water and SiO_2 at the wavelength of 800 nm, the absorption is mostly due to the Graphene Oxide, which shows nonlinear behavior at different laser fluences. Consequently, incident light which is not scattered or absorbed can transmit through the sample.

The scattering, absorption, and transmission of the GO + SiO_2 micro-beads composite were also analyzed in different cases. In Case I, the sample remains frozen, which means the scattering does not change. The increase of the transmission is caused by the decrease in Graphene Oxide absorption, which is due to the saturable absorption.

In Case II, when the heat generated exceeds the maximum cooling capacity, the matrix partially melts and absorbs the excess heat. Comparing to the solid phase, the liquid phase matrix has less scattering, which was confirmed by comparing the linear transmittance of the samples in liquid and frozen state. The reason may be the liquid phase has fewer defects comparing to the frozen phase. As a result, the transmittance of the sample increases, which is due to the GO saturable absorption as well as the reduction of the scattering. The matrix returns to its frozen state after the laser irradiation and this process protects the GO from the optical damage. In Case III, when we further increase the incident laser fluence, the frozen matrix fully melts. The sample now has the least scattering and reaches its maximum transmittance.

Based on the features of the thermal dynamics, it can be concluded that when the incident laser fluence is lower than 4.2 µJ/cm^2, the sample is in Case I. The transition from Case I to Case II happens at 4.2 µJ/cm^2. In Case II, the frozen matrix melts and the SiO_2 micro-beads in the GO + SiO_2 micro-beads composite begins to precipitate inside the liquid. Without the localized light enhancement from the SiO_2 micro-beads, the saturable absorption becomes similar to the GO sample.

Furthermore, the frozen matrix is in Case III when the incident laser fluence is higher than 4.7 μJ/cm^2 and the two samples have similar maximum transmittance. Meanwhile, the precipitation of the SiO_2 micro-beads in water was studied and the conclusion supports the dynamics mentioned previously (the details can be found in the appendix).

Open Aperture Z-scan characterization

From the above analysis, the optical nonlinearity of the hybrid composite in Case I was measured because the samples are frozen and stay in the solid state, in which the particles are well dispersed. Based on the input-output plot, the open aperture Z-scan characterization scheme was applied at the incident laser fluence of 3.4 μJ/cm^2, which is lower than the transition threshold between Case I and Case II. The same laser setup for the nonlinear transmission characterization was used to produce incident laser at 800 nm. The results are presented in Fig. 4. In our experiments, neither the frozen matrix nor the SiO_2 micro-beads shows any nonlinear absorption performance (The results can be found in the supplementary materials). For the GO sample, the peak in the open aperture Z-scan curve indicates a strong saturable absorption, which corresponds to the saturable absorption nonlinearity measured in the nonlinear transmission analysis. The peak normalized transmittance at the focal point (Z = 0 mm) is 1.19, which is similar to the data published in a recent GO study.[20] Comparing to the GO sample, the GO + SiO_2 micro-beads composite demonstrates an enhanced saturated absorption performance. In the identical laser condition, the peak normalized transmittance for the GO + SiO_2 micro-beads composite is 1.52, which indicates a big nonlinearity enhancement.

To test its self-healing capability, the GO sample was irradiated at a high laser fluence of 5.0 μJ/cm^2 which results in fully melting of the matrix. After the laser exposure, the matrix would re-solidify by dry ice cooling. A Z-scan was conducted in the identical condition described previously (laser fluence of 3.4 μJ/cm^2). It was found that the peak transmittance was almost the same as that before the laser exposure, which indicates that the frozen system can successfully recover from a fully melting phase. This phase transition process can absorb the excessive energy of the laser.

To get a better understanding on the nonlinear behaviors of the samples, the nonlinear absorption coefficient β was calculated by fitting the theoretical saturable absorption model with the experimental data.[28] The length of the light path and the linear absorption were taken into accounts to calculate the nonlinear absorption coefficient. The nonlinear absorption coefficient of GO sample is -0.65×10^4 cm/GW while the nonlinear absorption coefficient of GO + SiO_2 micro-beads composite is -1.31×10^4 cm/GW. The negative value corresponds to the saturable absorption feature. Comparing to the GO sample, the GO + SiO_2 micro-beads composite demonstrates an 101.5% enhancement on the nonlinear absorption coefficient. In the previous research, the nonlinear absorption coefficient of GO water dispersion was reported to be 2.5×10^{-2} cm/GW.[10] Comparing to it, our hybrid system demonstrated a much better optical nonlinearity.

This better nonlinear absorption performance is attributed to the following reasons. Firstly, the local field enhancement effect induced by the SiO_2 micro-beads plays an important role. As shown in the simulation, the local field is greatly enhanced in the region beneath the SiO_2 micro-bead. The GO dispersed in this region is exposed to a laser fluence more than 25 times stronger compared to the incident light. Based on the input-output characterization, it can be concluded that the GO sheets exhibit enhanced nonlinear absorption at a high laser fluence. Thus, the GO sheets in the local field enhanced region have enhanced nonlinear absorption response. In the GO + SiO_2 micro-beads composite, the GO is well mixed with the SiO_2 micro-beads and benefits from this local field enhancement effect. As a result, the GO + SiO_2 micro-beads composite has better nonlinear absorption than the GO sample. Secondly, the high concentration of the GO inside the frozen matrix also contributes to the huge nonlinear absorption response. The increase of the GO results in a larger number of the sp^{2-} domains which is the key for the nonlinear absorption. The GO and SiO_2 micro-beads tend to aggregate in high concentration liquid systems. In the frozen matrix, both particles are fixed in certain positions, which solve the aggregation problem. Therefore, very high concentration and high optical nonlinearity can be achieved by a frozen matrix hybrid system.

Conclusions

In summary, we designed a novel frozen matrix solid state system which demonstrates greatly enhanced optical nonlinear performance. This hybrid system was characterized for its nonlinear absorption performance by the open aperture Z-scan measurement. FDTD simulation has been conducted to explain the enhanced optical nonlinear performance of the hybrid system. The local field enhancement induced by the focusing effect of the SiO_2 micro-beads can greatly improve the optical nonlinearity of GO. The nonlinear absorption coefficient is much better than the GO dispersion reported previously. This frozen matrix and local field enhancement effect are two facile and versatile approaches which can be applied to other types of liquid based optical nonlinear systems. Our research demonstrates a new route to instigate explorations of different new materials as the matrix and particle lens for a better solid state optical nonlinear system.

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Supplementary

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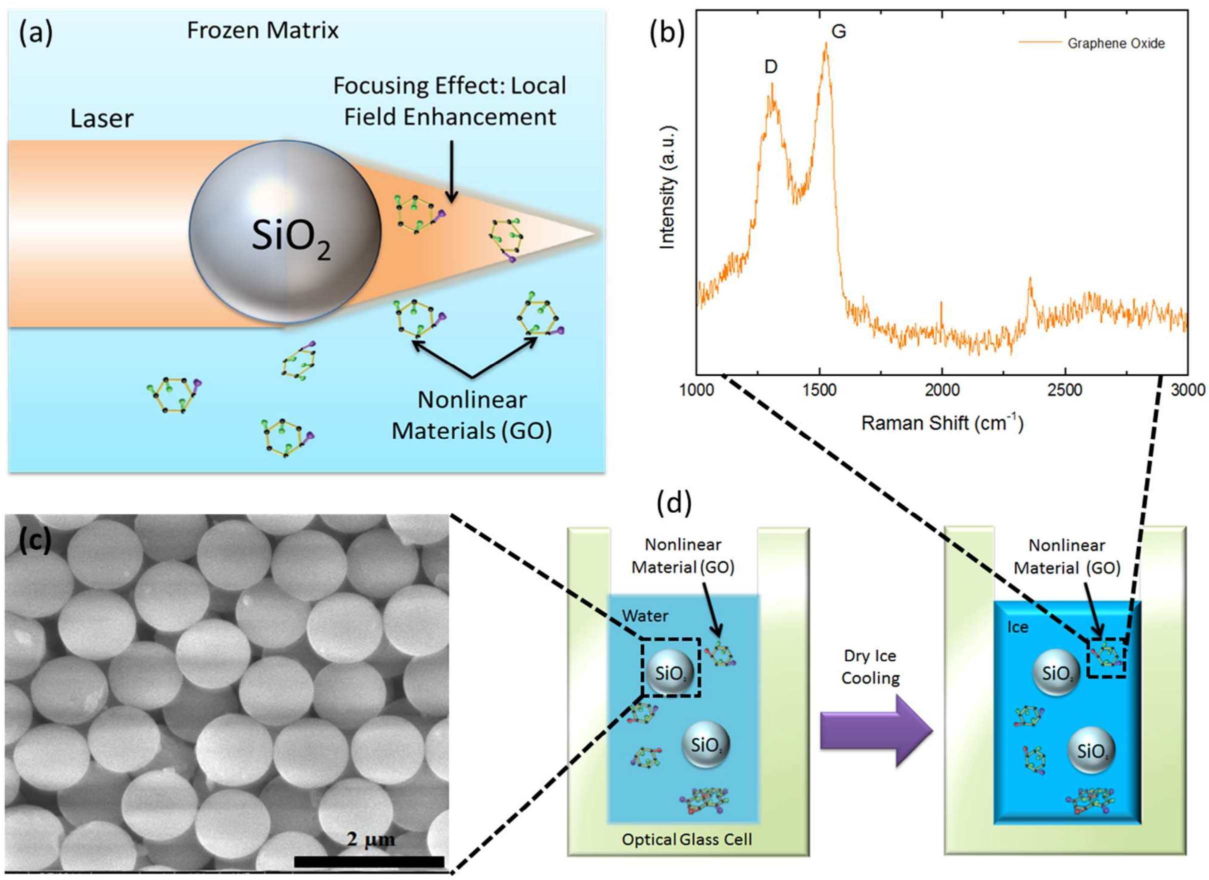

Fig. 1 (a) Schematic diagram of the local field enhancement effect in the hybrid dispersion: Graphene Oxide nano-sheets in the light focusing area experience an enhanced light field and demonstrate higher optical nonlinearity; (b) Raman spectra of the Graphene Oxide, with the D-band peak (1339 cm^{-1}) and G-band peak (1585 cm^{-1}), corresponding to the oxygen containing groups in the GO products; (c) SEM image of the particle lens (SiO_2 micro-beads with the diameter of 1000 nm); (d) Fabrication process of the hybrid dispersion: Frozen matrix is cooled by dry ice in an enclosed environment and the particles are fixed at certain positions.

Fig. 1

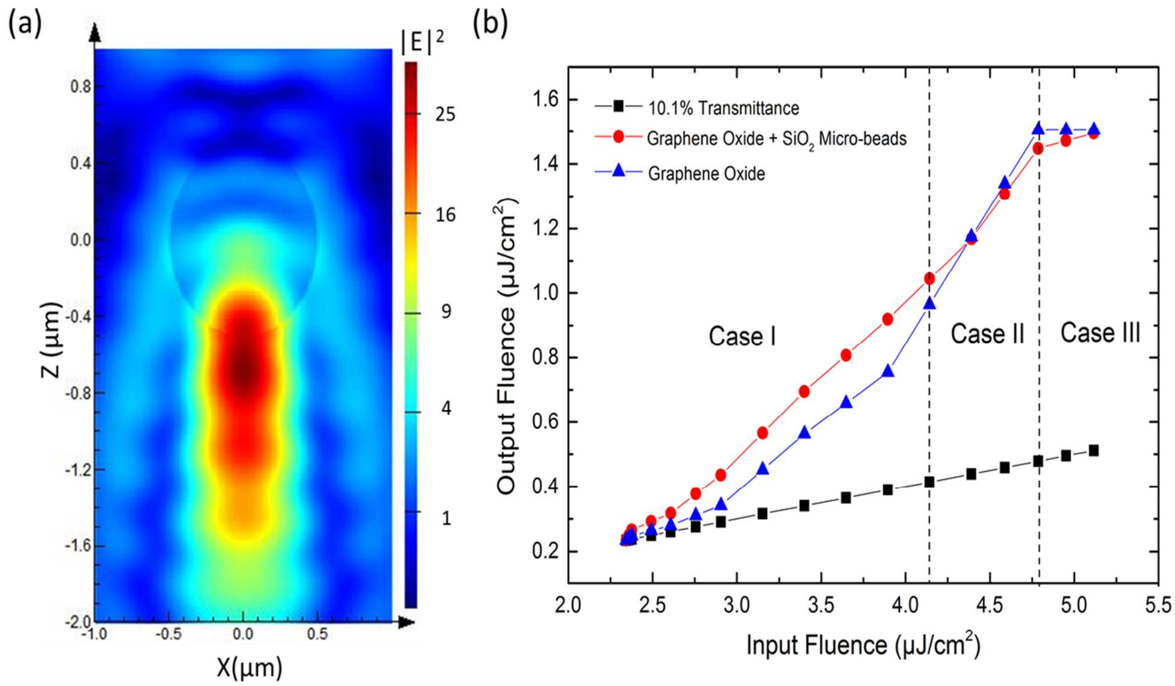

Fig 2. (a) FDTD simulation results of the particle lens in ice at the 800 nm wavelength: red color denotes that the light intensity is enhanced by more than 25 times at the central region of the focusing area; (b) Nonlinear absorption characterization at different laser fluences for GO (blue curve) and GO + SiO_2 (red curve) with the reference of 10.1% transmittance.

Fig. 2

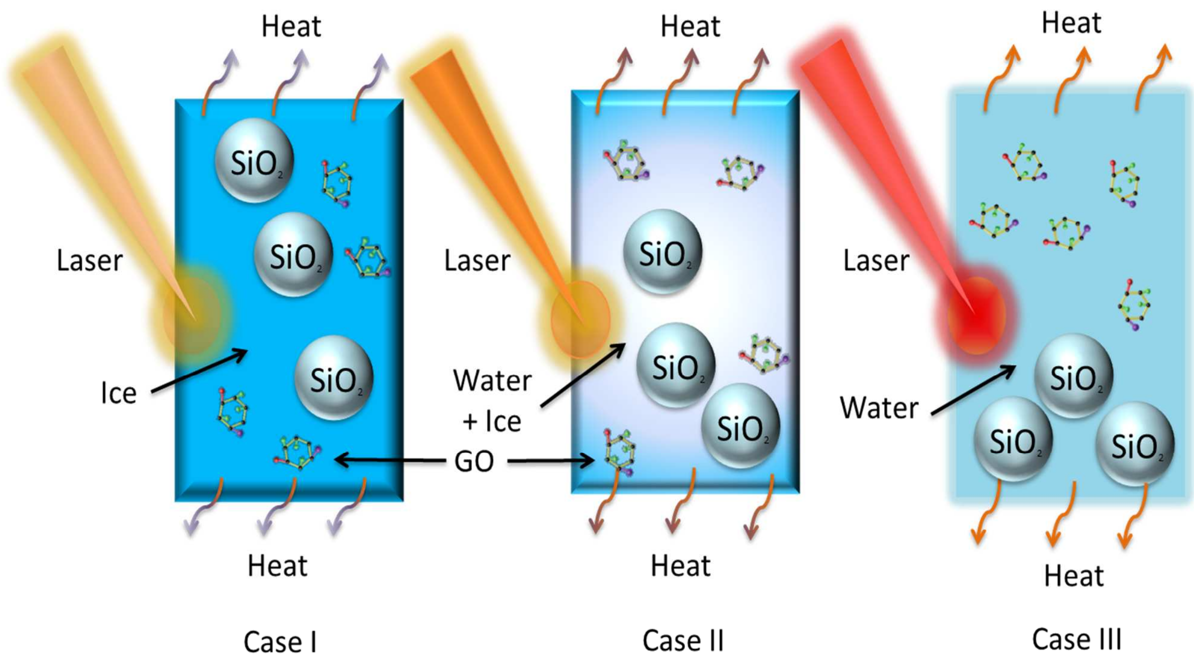

Fig. 3 Schematic diagram of the dynamic process of the GO + SiO_2 samples at different laser fluences: Case I. the laser fluence is low and matrix is fully frozen. Case II. the laser fluence is moderate and matrix is half melt. Case III the laser fluence is high and matrix is fully melt.

Fig. 3

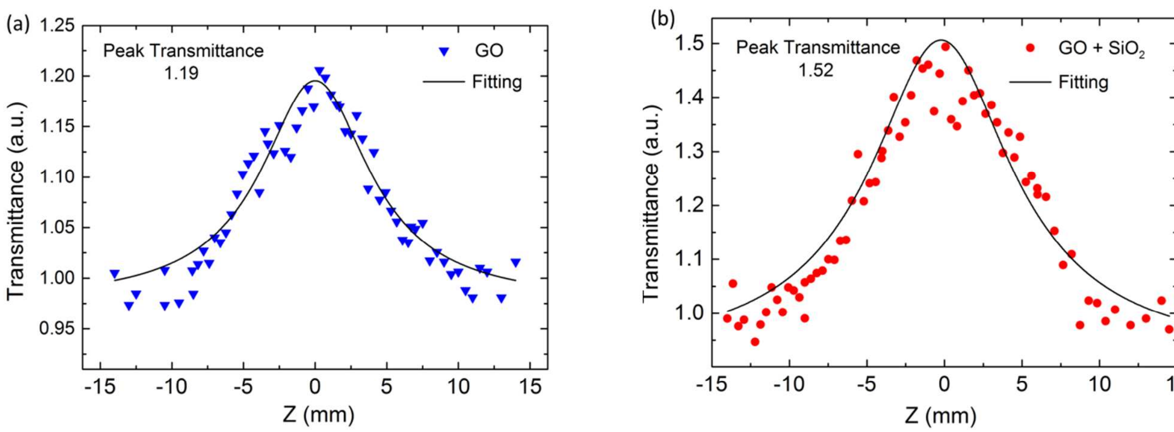

Fig. 4 Open aperture Z-scan characterization results of the (a) GO sample and (b) GO + SiO_2 micro-beads composite with the fitting for saturable absorption nonlinearity.

Fig. 4

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Supplementary

Frozen Matrix Hybrid Optical Nonlinear System Enhanced by Particle Lens

Lianwei Chen,[a] Xiaorui Zheng,[b] Zheren Du,[a] Baohua Jia,[b] Min Gu*[b] and Minghui Hong*[a]

Table S1: Summary of Nonlinear Coefficients

Material Type	Wavelength of Z-scan	Dispersion Matrix	Nonlinear Coefficients	Reference
Au	532 nm	Glass	-7.0 cm/GW	S. L. Qu, Y. W. Zhang, H. J. Li, J. R. Qiu, C. S. Zhu, *Opt. Mater.*, 2006, **28**, 259-265
Silver	795 nm	Water	8 cm/GW	R. A. Ganeev, M. Baba, A. I. Ryasnyansky, M. Suzuki, H. Kuroda, *Opt. Commun.*, 2004, **240**, 437-448
Silver	532 nm	Glass	19.3 cm/GW	S. L. Qu, Y. W. Zhang, H. J. Li, J. R. Qiu, C. S. Zhu, *Opt. Mater.*, 2006, **28**, 259-265
Cu	800 nm	Water	-2.36×10^{-3} cm/GW	G. H. Fan, S. T. Ren, S. L. Qu, Q. Wang, R. X. Gao, M. Han, *Opt. Commun.*, 2014, **330**, 122-130
Cu	800 nm	Alcohol	-3.74×10^{-3} cm/GW	G. H. Fan, S. T. Ren, S. L. Qu, Q. Wang, R. X. Gao, M. Han, *Opt. Commun.*, 2014, **330**, 122-130
Graphene Oxide	800 nm	Water	-2.5×10^{-2} cm/GW	X. L. Zhang, Z. B. Liu, X. C. Li, Q. Ma, X. D. Chen, J. G. Tian, Y. F. Xu, Y. S. Chen, *Opt. Expr.*, 2013, **21**, 7511-7520.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Graphene Oxide Synthesis

Firstly, $NaNO_3$ and graphite were mixed inside the concentrated H_2SO_4 solution. By vigorous stirring, $KMnO_4$ was added into the suspension followed by the addition of H_2O_2 to trigger the chemical reduction reaction. The mixture was kept at 90 °C. When the reaction was completed, the product was washed and dried. After the purification, the GO sheets were obtained and dispersed inside DI water.

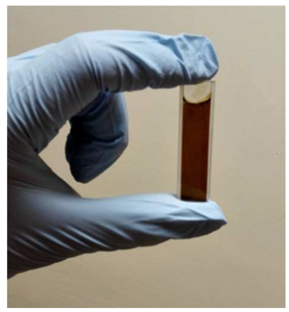

Fig. S1. Optical image of the Graphene Oxide dispersion

FDTD Simulation

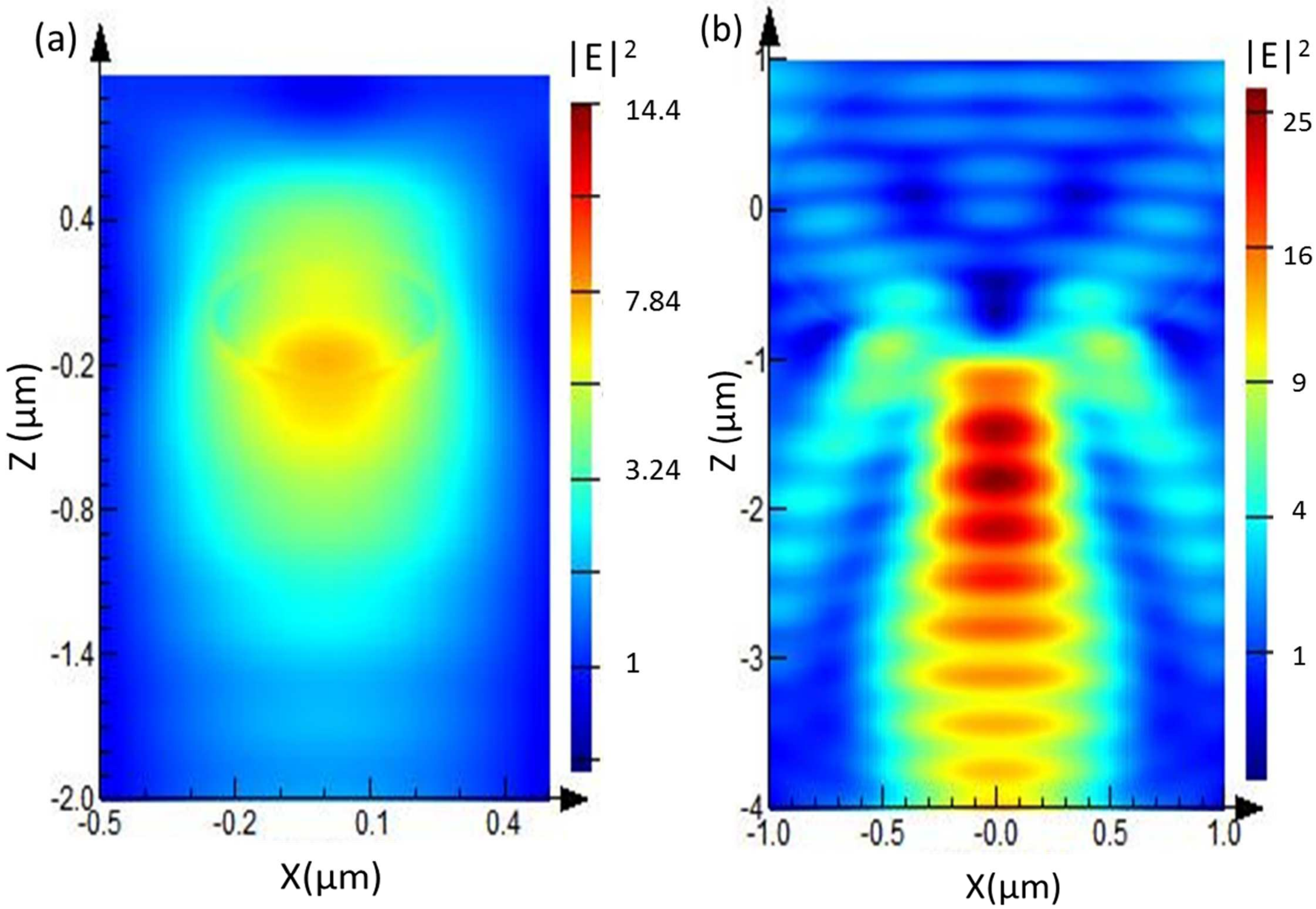

Fig. S2. FDTD simulation results for SiO_2 micro-bead with (a) 500 nm and (b) 2μm diameters in frozen matrix (ice)

SiO_2 Micro-bead Precipitation Study

SiO_2 micro-bead dispersion in water was injected into a glass cell. The cell was aligned vertically. The time was counted for the SiO_2 micro-bead to fully precipitate to the bottom. The precipitation speed can be calculated (precipitation distance of the cell divided by the time of precipitation). It was found the precipitation speed of the SiO_2 micro-bead is ~83.3 μm/s. In the nonlinear absorption characterization, the laser spot on the sample is ~34 μm (diameter). The size of the melting area is comparable to the size of the laser spot. As a result, once the matrix was melt, it took very short time for the SiO_2 micro-beads in this area to precipitate. The experiment took a much longer time and it can be confirmed that the SiO_2 micro-beads mostly precipitated once the matrix was melt.

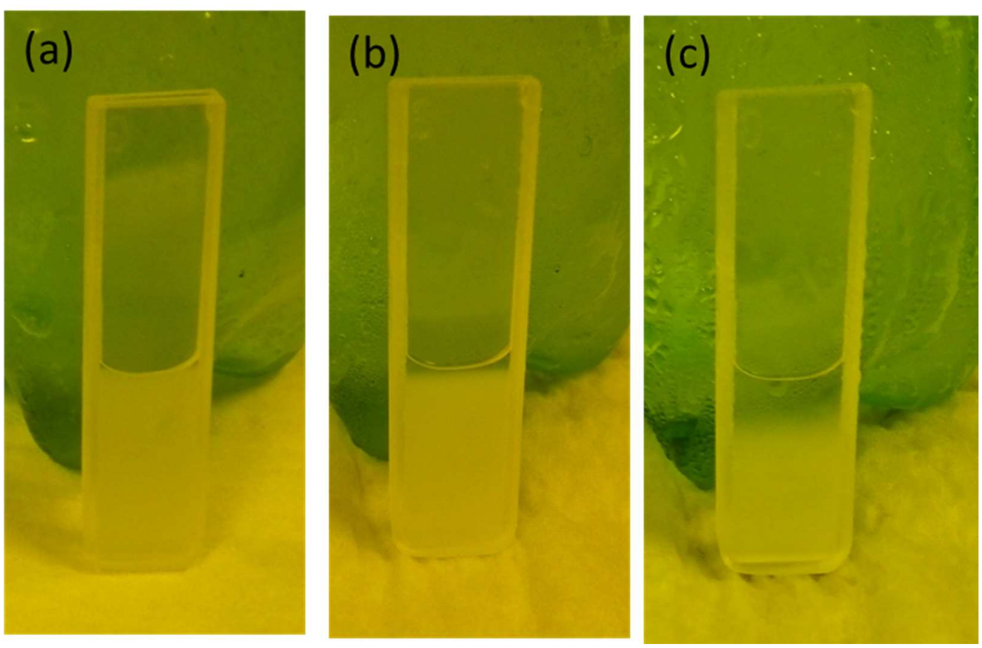

Fig. S3. Optical image for the SiO_2 micro-bead dispersion at the precipitation time of (a) 4 minutes, (b) 10 minutes, and (c) 60 minutes

SiO_2 Micro-bead Precipitation Study

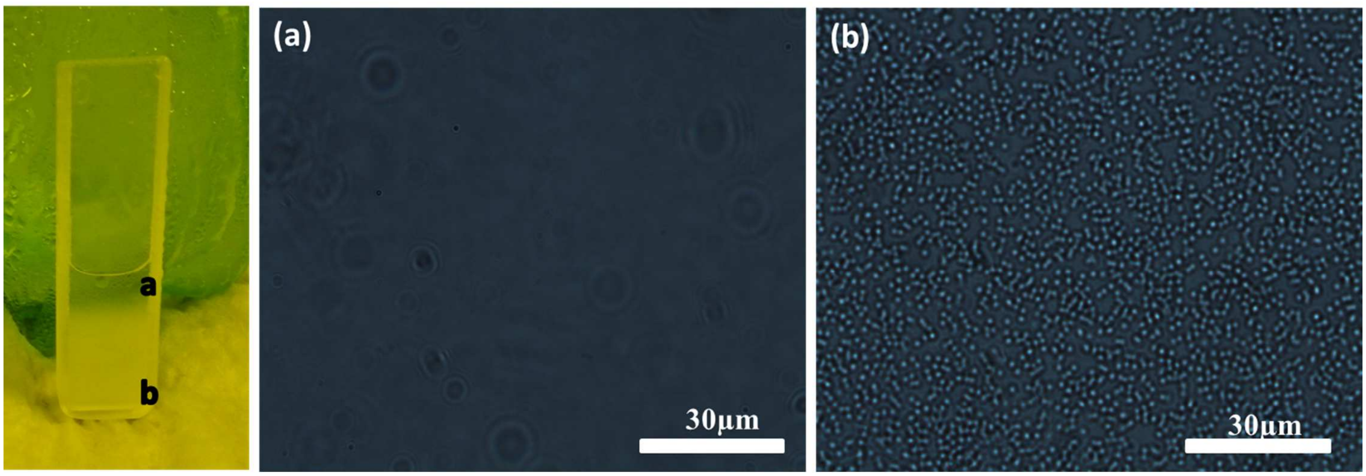

Fig. S4. Optical microscope images of the dispersion in (a) upper solution and (b) bottom solution. It can be seen from the image that after precipitation, most of the SiO_2 micro-beads resides in the bottom where the solution looks opaque. On the other hand, the upper part is free of the SiO_2 micro-beads and looks transparent.

Z-scan Measurement for Water and SiO_2 micro-beads

It shows that there is no nonlinear response for water and SiO_2 micro-beads

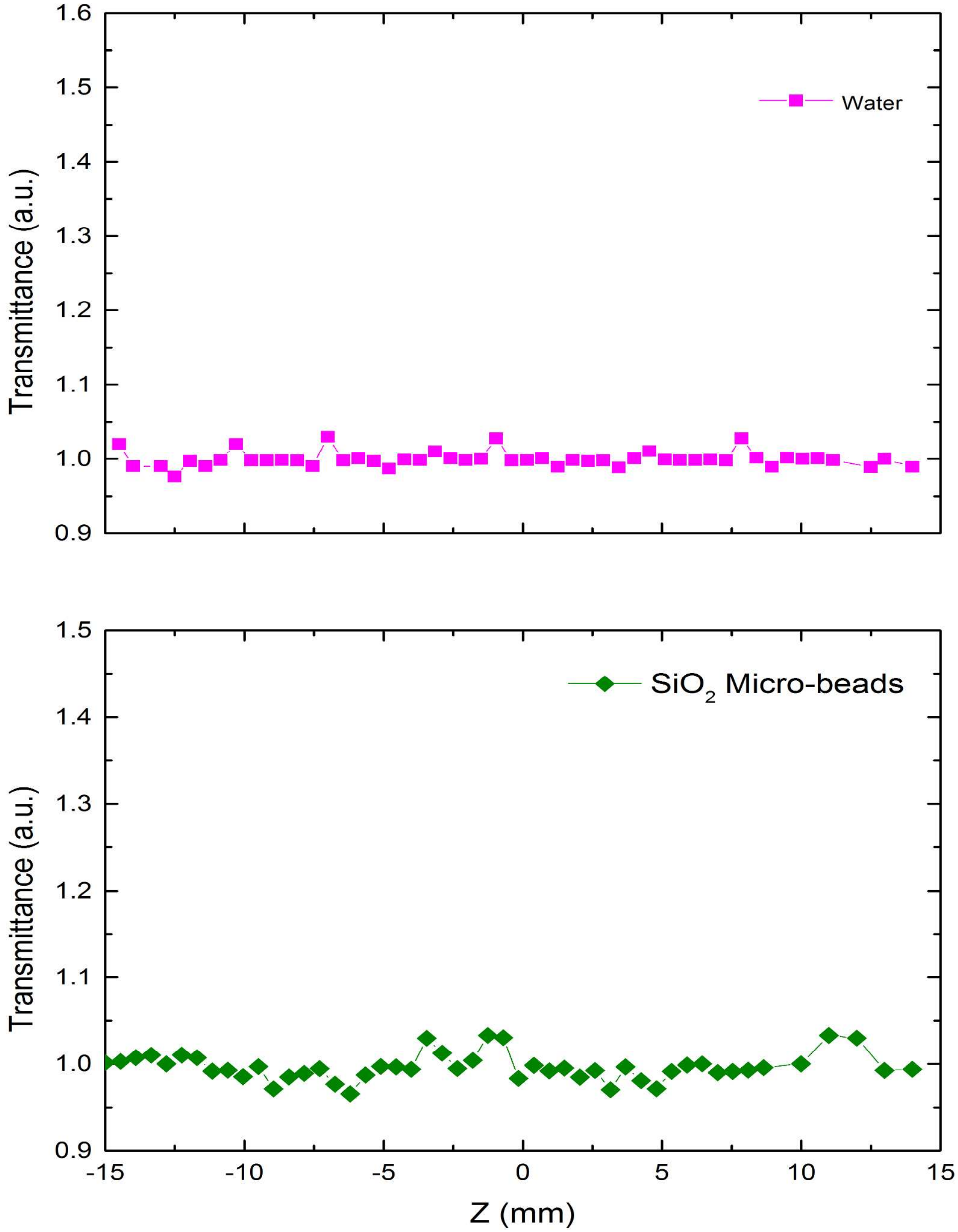

Fig. S5. Open aperture Z-scan results for the (a) water and (b) SiO_2 micro-beads